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APPLICATION OF *ab initio* MOLECULAR-ORBITAL CALCULATIONS TO THE STRUCTURAL MOIETIES OF CARBOHYDRATES*

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ABSTRACT

Ab initio RHF/4-31G molecular-orbital calculations have been performed on 1-methoxyethanol as a model for examining the anomeric effect in pyranoses, especially 2-deoxypyranoses, and on 1-methoxyethanediol as a model for the $\Delta 2$ effect. The results give a value of 2.0 kcal/mol for the anomeric energy and a difference of 1.2–2.0 kcal/mol in anomeric energies for the $\Delta 2$ effect. The calculations with 1-methoxyethanol also predict that the −synclinal orientation of a β-glycosidic hydroxyl bond is favored over the +synclinal orientation by 1 kcal/mol. This is consistent with the exo-anomeric effect and is in agreement with the available data from crystal structure analyses. Bond-length optimization for the 1-methoxyethanol model gave results in agreement with the experimental data for the hemiacetal moiety of the pyranose sugars.

INTRODUCTION

In previous papers in this series[2,3], methanediol and methoxymethanol were used as models for *ab initio* molecular-orbital studies of the hemiacetal moiety of a pyranose sugar. Similarly, dimethoxymethane was used as a model for the acetal moiety of the methyl pyranosides[4].

In this paper, we make a closer approximation to the molecules of primary interest by using 1-methoxyethanol (**1**) as a model for pyranoses and, in particular, a 2-deoxypyranose. This model, which has an asymmetric carbon atom, permits a comparison between the conformational energies of the + and −synclinal orientations of the β-glycosidic bond, which was not possible with the previous methanediol and methoxymethanol models[2,3]. It provides, therefore, a better test for compliance with the exo-anomeric effect.

In order to examine the $\Delta 2$ effect[5], which infers that the anomeric stabilization energy for a pyranose sugar is greater with an axial than with an equatorial hydroxyl group at C-2, we have used the molecule 1-methoxyethanediol (**2**).

*Part VII in this series. For Part VI, see ref. 1.

TABLE I

ENERGIES (IN HARTREES[a] AND RELATIVE KCAL/MOL) OF 1-METHOXYETHANOL (1) AND 1-METHOXYETHANEDIOL (2), CALCULATED WITH GAUSSIAN 74, USING RHF/4-31G BASIS SET

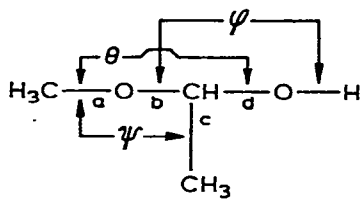
1	θ,ψ (degrees)	φ (degrees)	Energies	
			Standard geometry	*Optimized geometry*
α-D-$^4C_1$	+60, −60	−60	−267.55292	
			8.41	
		+60	−267.56537	−267.56632
			0.60	0.00
		180	−267.55766	
			5.43	
β-D-$^4C_1$	180, −60	−60	−267.56148	−267.56277
			3.04	2.23
		+60	−267.55998	
			4.00	
		180	−267.55056	
			9.89	

2		θ,ψ (degrees)	φ (degrees)	χ (degrees)	ω (degrees)	Energies *Standard geometry*
α-D-$^4C_1$	α a 1	+60, −60	+60	−60[b]	+60	−342.30479
						0.51
	α a 2				180	−342.29953
						3.81
	α a 3				−60	−342.29974
						3.68
	α e 1			180[c]	+60	−342.29651
						5.40
	α e 2				180	−342.29749
						5.10
	α e 3				−60	−342.30560
						0.0
β-D-$^4C_1$	β a 1	180, −60	−60	−60[b]	+60	−342.29449
						6.97
	β a 2				180	−342.28910
						10.35
	β a 3				−60	−342.30018
						3.40
	β e 1			180[c]	+60	−342.30282
						1.74
	β e 2				180	−342.29340
						7.66
	β e 3				−60	−342.29159
						8.79

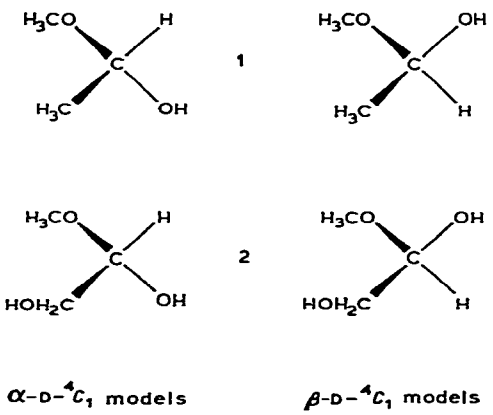
[a]One hartree = 627.544 kcal/mol. [b]C-2–OH axial. [c]C-2–OH equatorial.

TABLE II

OPTIMIZED C–O AND C–C BOND LENGTHS IN 1-METHOXYETHANOL

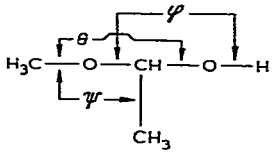


Theory	*θ (degrees)*	*ψ (degrees)*	*φ (degrees)*	*Bond lengths (pm)*			
				a	*b*	*c*	*d*
α-D-$^4C_1$ model (C-1–OH axial)	+60	−60	+60	145.2	145.4	152.1	141.7
β-D-$^4C_1$ model (C-1–OH equatorial)	180	−60	−60	144.4	145.5	152.1	139.9

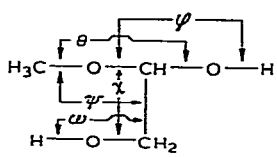


The Molecular orbital calculations. — Closed-shell, restricted Hartree–Fock theory was used with a 4-31G basis set[6] for the energy calculations shown in Table I. The calculations were made on a DEC KL-10 computer, using GAUSSIAN 74 (ref. 7). The calculations were performed with standard bond-lengths[8], (C–C = 154 pm; C–O = 143 pm; C–H = 109 pm; O–H = 96 pm), and tetrahedral valence-angles. For molecule **1**, the calculations were repeated with C–O and C–C bond length optimization by means of point-by-point energy calculations. These results are shown in Table II.

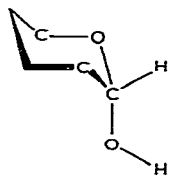
Conformations of **1** were examined in which $\theta = +60°$, $\psi = -60°$, corresponding to a model for the α-D-$^4C_1$ pyranose configuration, (**1α**), and $\theta = 180°$, $\psi = -60°$, corresponding to a model for the β-D-$^4C_1$ configuration (**1β**). The three staggered orientations of the glycosidic O–O bond are then represented by $\varphi = \pm 60$, 180°.



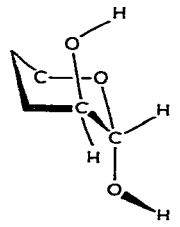
1



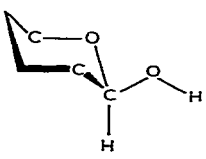
2



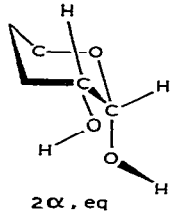
1α



2α, ax



1β



2α, eq

For molecule **2**, only standard geometry was used. Again, values of θ and ψ of $+60$, $-60°$ and 180, $-60°$ model the α- and β-D-$^4C_1$ configurations, respectively. Therefore, when $\theta = +60°$, $\psi = -60°$, $\varphi = +60°$, and $\chi = -60°$, the model corresponds to the lowest energy α-D-$^4C_1$ (+sc) glycosidic conformation, with the 2-hydroxyl group in the axial disposition (**2α**, ax). When $\chi = 180°$, the 2-hydroxyl group is equatorial (**2α**, eq). Similarly, the models having $\theta = 180°$, $\psi = -60°$, $\varphi = -60°$, and $\chi = -60°$ and 180° correspond to the lowest energy β-D-$^4C_1$ (−sc) glycosidic conformation, with the 2-hydroxyl group axial when $\chi = -60°$ and equatorial when $\chi = 180°$. No geometry optimization was calculated for this molecule. These results are shown in Table I.

RESULTS

The results for molecule **1** give a minimum-energy conformation with $\theta = +60°$, which corresponds to the α-D-$^4C_1$ configuration with a glycosidic torsion-angle of $+60°$. The energy difference between this conformation and that of the lowest energy with $\theta = 180°$, namely, the β-D-$^4C_1$ configuration, is 2.4 kcal/mol with standard geometry and 2.2 kcal/mol with optimized C–O and C–C bond lengths. This

energy difference corresponds to the anomeric energy for the isolated molecules at rest. As with the previous calculations with simpler models, these results are consistent with both the anomeric and exo-anomeric effects[9].

In the previous models (methanediol and methoxymethanol), C-2 of the pyranose ring was simulated by a hydrogen atom and no distinction could be made between the + and −synclinal orientation of a β-glycosidic hydroxyl bond (namely, $\theta = 180°$, $\varphi = \pm 60°$). With molecule **1**, this distinction is made. As shown in Table I, the −synclinal orientation ($\theta = 180°$, $\psi = -60°$, $\varphi = -60°$) is more stable than the +synclinal ($\theta = 180°$, $\psi = -60°$, $\varphi = +60°$) by 1 kcal/mol. This is the exo-anomeric energy for a β-glycosidic linkage, which has not previously been calculated in this series of investigations. This exo-anomeric effect is analogous to the Δ2 effect discussed later, as the less stable β +sc orientation is that in which the glycosidic O–H bond bisects the C-1–O-5 and C-1–C-2 ring bonds. The highest energy, that is, least stability, is obtained with both θ and $\varphi = 180°$, namely, the β-D-$^4C_1$ configuration with a *trans*-glycosidic C–O–C–O–H disposition, which has parallel lone-pair dipoles on O-5 and O-1. As with the simplest model studied in this series (methanediol[2]), this dipole interaction remains a dominant conformational factor, even when one of the hydroxyl hydrogen atoms and one of the methylene hydrogen atoms are replaced by methyl groups, to better simulate the carbohydrate molecule.

The results for molecule **2** gave the lowest energy for the conformation α e 3 ($\theta = +60°$, $\psi = -60°$, $\varphi = +60°$, $\chi = 180°$, $\omega = -60°$) in Table I. This corresponds to the α-D-$^4C_1$ configuration with the equatorial 2-O-H bond directed towards O-1. The corresponding α a 1 conformation with the axial 2-O-H bond directed towards the ring oxygen atom (O-5) is 0.5 kcal/mol higher. It is the resulting intramolecular hydrogen-bond interactions, 2-O-H···O-1, 2-O-H···O-5, which make these the most stable conformations for an isolated molecule.

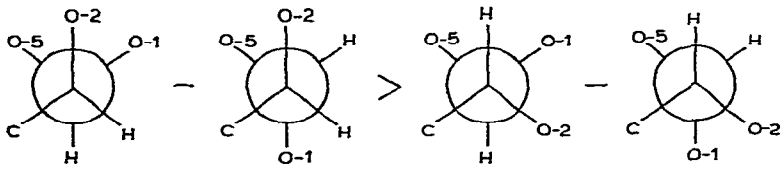
For a given configuration at C-2, the anomeric energy ΔE_{anom} (β-D-$^4C_1$) − (α-D-$^4C_1$) depends upon which of the three staggered arrangements of 2-O–H ($\omega = \pm 60°, 180°$) is considered most important. For the isolated molecules, intramolecular hydrogen-bonding from 2-O-H to O-1 or O-5 will favor the conformations α a 1 and α e 3 for α-D-$^4C_1$, and β a 3 and β e 1 for β-D-$^4C_1$. These are the orientations of 2-O-H, where the hydrogen atom is directed towards an oxygen atom in the same molecule; they are, in fact, calculated to have significantly lower energies. For these favored conformations, such as might be found in a non-polar solvent, ΔE_{anom} is 2.9 kcal/mol when O-2 is axial and 1.7 kcal/mol when O-2 is equatorial, that is, corresponding to E(β a 3) − E(α a 1) and E(β e 1) − E(α e 3). This gives a Δ2 effect of 1.2 kcal/mol.

In the crystalline state, or in aqueous solution, intermolecular hydrogen-bonding is generally favored over intramolecular bonding[10], and the favored conformations could be the other two staggered arrangements of higher energies. Taking the mean of the anomeric energies for these conformations, $\Delta E_{anom} = {}^1/_2\{E(\beta\ a\ 1) + E(\beta\ a\ 2) - E(\alpha\ a\ 2) - E(\alpha\ a\ e)\} = 5.0$ kcal/mol when O-2 is axial, versus $\Delta E_{anom} =$

$^1/_2\{E(\beta\,e\,2) + E(\beta\,e\,3) - E(\alpha\,e\,1) - E(\alpha\,e\,2)\} = 3.0$ kcal/mol when O-2 is equatorial. This corresponds to a larger $\Delta 2$ effect of 2.0 kcal/mol.

Therefore, depending upon the orientation of the 2-O-H bond, the anomeric energy is greater when 2-O-H is axial than when it is equatorial, by amounts calculated to be between 1.2 and 2.0 kcal/mol. This is in qualitative agreement with Reeves' statement of the $\Delta 2$ effect[5], which states that an extra destabilization-energy term of 1 kcal/mol must be considered when the C-2–OH-2 bond bisects the O-5–C-1, C-1–O-1 bonds in projection along C-1–C-2. Reeves' result is based on equilibrium studies of molecules in solutions, whereas our calculations refer to isolated molecules at rest, so more-quantitative comparisons are not appropriate.

Thus, the results for molecule **2** confirm the overall concept of the $\Delta 2$ effect, and show it to be due to an enhancement of the anomeric effect when C-2–O-2 is axial in a pyranose sugar. This result is represented diagrammatically below in the Newman projections down the C-2–C-1 bonds.



βa (1,2,3) αa (1,2,3) βe (1,2,3) αe (1,2,3)

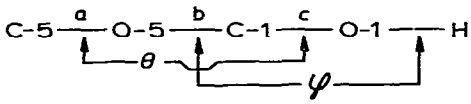
The $\Delta 2$ effect, like the anomeric and exo-anomeric effects, can be regarded as a special case of the *gauche* effect[11], which states that "molecules with polar bonds tend to adopt that structure which has the maximum number of *gauche* interactions between the adjacent electron pairs and/or polar bonds". This implies that the β a (1,2,3) conformations will have lower energies relative to α a (1,2,3) than β e (1,2,3) has relative to α e (1,2,3) by reason of its two *gauche* interactions.

Comparison with previous results and experimental data. — The results on molecule **1** are consistent with the previous calculations on methanediol and methoxymethanol[2,3] which gave anomeric energies of 4.4 and 2.7 kcal/mol, respectively. This further justifies the assumption that the use of small molecules, with hydrogen atoms replacing carbon atoms, as models for the hemiacetal moiety of a sugar, does not obscure the principal conclusions. As with the simpler models, the α-D-$^4C_1$ configuration is more stable than the β-D-$^4C_1$ (the anomeric effect), and the favored conformation of the glycosidic bond is +sc for the α anomer and —sc for the β anomer (the exo-anomeric effect). These more-sophisticated models make possible a distinction between the +sc and —sc orientation of the β-glycosidic bond and show the latter to be the more stable by 1 kcal/mol.

The anomeric energy (2.2 kcal/mol) is lower than for the previous models, confirming our view that the simpler models in which hydrogen atoms replace carbon atoms tend to overestimate these energy differences. The estimated anomeric energy

TABLE III

EXPERIMENTAL C–O HEMIACETAL BOND-LENGTHS AND TORSION ANGLES IN PYRANOSES FROM CRYSTAL STRUCTURE DATA[a]



Molecule	*Configuration O-1 axial (α-D-$^4C_1$, except where noted)*					σ^b	*Reference*[c]
	Torsion angles (degrees)		*Bond lengths (pm)*				
	θ	φ	*a*	*b*	*c*		
2-Deoxy-D-*erythro*-pentose-$^1C_4$	−75	−96	141	145	141	1.5	DRIBSE[d]
β-L-Arabinose	+86	+61	144	142	138	1.0	ABINOS[e]
β-L-Arabinose (N)	+61	+64	143.2	141.8	139.8	0.3	ABINOS01[e]
β-DL-Arabinose	+61	+75	145.0	143.5	139.4	0.4	ABINOR[f]
β-DL-Arabinose (N)	+61	+70	144.6	142.8	139.1	0.1	[g]
α-L-Xylose-$^1C_4$	−62	−94	144.9	142.8	139.3	0.6	XYLOSE[e]
α-L-Xylose-$^1C_4$ (N)	−62	−105	143.2	142.0	139.2	0.1	[h]
α-D-Galactose	+59	+45	143.2	144.6	141.0	0.7	ADGALA01[e]
	+57	+141[i]	142.6	143.3	140.0	0.4	ADGALA10[e]
α-D-Glucose (N)	+61	+75	142.8	142.7	139.1	0.2	GLUCSA[j]
α-D-Glucose · H_2O	+67	[k]	141	141	140	1.0	GLUCMH[k]
	+64	+97	145.1	142.7	141.2	0.3	GLUCMH11[l]
α-D-Mannose	+60	+69	144.0	141.2	140.4	0.4	ADMANN[e]
	+62	[k]	144.8	141.5	142.1	0.4	
α-DL-Mannose	+57	+81	144.4	144.7	139.5	0.5	ADLMAN[f]
α-D-Talose	+61	+65	144.9	143.8	140.3	0.4	ADTALO01[e]
	+61	+75	144.5	143.5	139.9	0.2	ADTALO10[e]
6-Deoxy-α-L-galactose-$^1C_4$	−61	−79	148.1	141.2	138.2	0.9	ALFUCO[e]
β-D-Fructose-$^2C_5$	−63	−70	143.6	141.3	141.2	0.4	FRUCTO11[m]
β-D-Fructose-$^2C_5$ (N)	−63	−65	143.0	141.3	140.7	0.2	FRUCTO02[n]
α-L-Rhamnose-$^1C_4$	−65	−94	144.4	142.1	140.0	0.3	RHAMAH01[f]
α-L-Rhamnose-$^1C_4$ (N)	−65	−91	143.9	141.9	140.4	0.2	RHAMAH02[o]
α-L-Sorbose-$^2C_5$	−60	−47	144.0	142.0	141.5	0.5	SORBOL[f]
α-L-Sorbose-$^2C_5$ (N)	−60	−50	143.1	142.3	139.6	0.3	[p]
α-D-Tagatose-$^5C_2$	+62	+45	143.2	142.6	140.5	0.4	TAGTOS[f]
2-Acetamido-2-deoxy-α-D-galactose	+61	+74	143.4	143.7	139.7	0.5	AGALAM10[q]
	+60	+72	143.9	144.4	139.5	0.5	AGALAM01[r]
2-Acetamido-2-deoxy-α-D-glucose	+60	+68	144.8	143.3	139.0	0.3	ACGLUA11[s]
β-L-Lyxose-$^1C_4$ (N)	−175	−78	142.8	143.1	138.6	0.3	LYXOSE01[t]
β-L-Lyxose-$^1C_4$	−175	−72	142.2	143.5	136.4	0.6	LYXOSE10[f]
2-Deoxy-2-fluoro-β-D-mannose	180	−70	143.0	142.9	139.9	0.3	XFMANP[e]
β-D-Galactose	+177	−75	143.7	141.3	139.5	0.9	BDGLOS01[e]
	+178	−77	144.0	142.2	139.6	0.4	BDGLOS10[e]
β-D-Glucose	−179	−96	143.7	143.3	138.4	0.2	GLUCSE01[f]
2-Acetamido-2-deoxy-β-D-mannose · H_2O	+170	+44	144.2	142.6	138.8	0.3	NACMAN10[u]

[a]X-ray analyses, except where (N) indicates a neutron analysis. In the ketoses, the atomic numbering is increased by +1. [b]The standard deviations, σ, are mean values for the non-hydrogen distances and angles, in picometers or degrees. They provide a measure of the accuracy of the analysis. For individual values, the original papers should be consulted. [c]The six-letter codes are the REFCODES of the Cambridge Crystallographic Data File, from which these data were retrieved. These data are frequently more reliable than the primary publications, as they have been checked and corrected for inconsistency errors. [d]See ref. 15. [e]See Tables VIII and IX of ref. 4. [f]See Table 2 of ref. 2. [g]See ref. 16. [h]See ref. 17. [i]See ref. 18. [j]See ref. 19. [k]See ref. 20. [l]See ref. 21. [m]See ref. 22. [n]See ref. 23. [o]See ref. 24. [p]See ref. 25. [q]See ref. 26. [r]See ref. 27. [s]See ref. 28. [t]See ref. 29. [u]See ref. 30.

for the most comparable pyranose molecule, 2-deoxy-D-*erythro*-pentopyranose, based on the equilibrium in solution, is 0.85 kcal/mol[12].

The crystal data given in Table III show that for the β configuration, the favored orientation of the O–H bond is −synclinal, in agreement with the theory, except for one molecule, 2-acetamido-2-deoxy-β-D-mannose. Here the 1-O-H bond, in the observed +sc orientation, is parallel to the C-2–N bond, so that the H···N separation is 200 pm, which is within weak hydrogen-bonding distance, thereby stabilizing by hydrogen-bond formation the otherwise less favorable conformation.

The optimized bond-lengths, given in Table II, indicate a shortening of the glycosidic C–O bonds which is greater in the β than in the α anomer. This is unchanged from the results with methoxymethanol as the model compound. The only significant change is in the reversal of the relative lengths of the C–O bonds to the ring-oxygen atoms. This model predicts that C-1–O-5 > C-5–O-5, although the difference is very small, being only 0.5 pm for the α anomer.

Table III gives a compilation of the experimental bond-length and torsion-angle data that is more complete than that given in the previous papers in this series[2,3], because of recent additions to the data. Only one 2-deoxypyranose has been studied and this is an early analysis with low accuracy. For this structure, the agreement with theory is within the experimental errors of the structure analysis ($\Delta_{\text{theory-exp}} < 3\ \sigma$).

The majority of the experimental results on the normal sugars report C-5–O-5 > C-1–O-5. All of the bond lengths for pyranose rings are susceptible to expansion or contraction from their equilibrium minimum-energy values because of steric effects that are not included in our acyclic model compound. Any differences in overall ring conformation, arising from intramolecular interactions between substituents or intermolecular interactions between adjacent molecules in the crystal, will result in corresponding differences in bond lengths and valence angles that are required to maintain ring closure[13]. None of the molecules listed in Table III have ideal chair conformations, and, in general, the puckering parameters vary over a significant range[14]. For this reason, we are uncertain whether the reversal of the order of the length of the ring C–O bonds predicted for a 2-deoxypyranose is significant.

The optimized value for the C–C bond length of 152.1 pm is in good agreement with the mean experimental value for C-1–C-2, which was 152.6 pm when C-1–OH is axial and 153.0 pm when C-1–OH is equatorial.

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REFERENCES

1 G. A. JEFFREY AND J. H. YATES, *Carbohydr. Res.*, 79 (1980) 155–163.
2 G. A. JEFFREY, J. A. POPLE, AND L. RADOM, *Carbohydr. Res.*, 25 (1972) 117–131.
3 G. A. JEFFREY, J. A. POPLE, AND L. RADOM, *Carbohydr. Res.*, 38 (1974) 81–95.

4 G. A. JEFFREY, J. A. POPLE, J. S. BINKLEY, AND S. VISHVESHWARA, *J. Am. Chem. Soc.*, 100 (1978) 373–379.
5 R. E. REEVES, *J. Am. Chem. Soc.*, 72 (1950) 1499–1506.
6 R. DITCHFIELD, W. J. HEHRE, AND J. A. POPLE, *J. Chem. Phys.*, 54 (1971) 724–728.
7 Quantum Chemistry Program Exchange, No. 236, Chemistry Department, Indiana University, Bloomington, Indiana.
8 J. A. POPLE AND M. GORDON, *J. Am. Chem. Soc.*, 89 (1967) 4253–4261.
9 W. A. SZAREK AND D. HORTON (Eds.), *Anomeric Effect: Origin and Consequences, ACS Symp. Ser.*, 87, American Chemical Society, Washington, DC, 1979.
10 G. A. JEFFREY, in H. S. ISBELL (Ed.), *Carbohydrates in Solution, Adv. Chem. Ser.*, 117 (1973) Chap. 10.
11 S. WOLFE, *Acc. Chem. Res.*, 5 (1972) 102–111.
12 J. F. STODDART, *Stereochemistry of Carbohydrates*, Wiley–Interscience, New York, 1971.
13 J. D. DUNITZ AND J. WASER, *J. Am. Chem. Soc.*, 94 (1972) 5645–5650.
14 G. A. JEFFREY AND R. TAYLOR, *J. Comput. Chem.*, 1 (1980) 99–109.
15 S. FURBERG, *Acta Chem. Scand.*, 14 (1960) 1357–1363.
16 S. TAKAGI, S. NORDENSON, AND G. A. JEFFREY, *Acta Crystallogr. Sect. B*, 35 (1979) 991–993.
17 S. TAKAGI AND G. A. JEFFREY, *Acta Crystallogr. Sect. B*, 35 (1979) 1482–1486.
18 G. A. JEFFREY AND R. SHIONO, *Acta Crystallogr. Sect. B*, 33 (1977) 2700–2701.
19 G. M. BROWN AND H. A. LEVY, *Acta Crystallogr. Sect. B*, 35 (1979) 656–659.
20 R. C. G. KILLEAN, W. G. FERRIER, AND D. W. YOUNG, *Acta Crystallogr.*, 15 (1962) 911–912.
21 E. HOUGH, S. NEIDLE, D. ROGERS, AND P. G. H. TROUGHTON, *Acta Crystallogr. Sect. B*, 29 (1973) 365–367.
22 J. A. KANTERS, G. ROELOFSEN, B. P. ALBLAS, AND I. MEINDERS, *Acta Crystallogr. Sect. B*, 33 (1977) 665–672.
23 S. TAKAGI AND G. A. JEFFREY, *Acta Crystallogr. Sect. B*, 33 (1977) 3510–3515; *Sect. B*, 34 (1978) 1048.
24 S. TAKAGI AND G. A. JEFFREY, *Acta Crystallogr. Sect. B*, 34 (1978) 2551–2555.
25 S. NORDENSON, S. TAKAGI, AND G. A. JEFFREY, *Acta Crystallogr. Sect. B*, 35 (1979) 1005–1007.
26 A. NEUMAN, H. GILLIER-PANDRAUD, F. LONGCHAMBON, AND D. RABINOVICH, *Acta Crystallogr. Sect. B*, 31 (1975) 474–477.
27 R. D. GILARDI AND J. L. FLIPPEN, *Acta Crystallogr. Sect. B*, 30 (1974) 2931–2933.
28 F. MO AND L. H. JENSEN, *Acta Crystallogr. Sect. B*, 31 (1975) 2867–2873.
29 S. NORDENSON, S. TAKAGI, AND G. A. JEFFREY, *Acta Crystallogr. Sect. B*, 34 (1978) 3809–3811.
30 A. NEUMAN, H. GILLIER-PANDRAUD, AND F. LONGCHAMBON, *Acta Crystallogr. Sect. B*, 31 (1975) 2628–2631.