slurry of CuCN (5 mmol) in dry Et_2O (5 mL) was cooled to −78 °C, and RLi (MeLi or PhLi, 9.85 mmol) was added. The mixture was allowed to warm to 0 °C until it became a homogeneous light tan solution. The flask was then recooled to −78 °C, and 7 (2.5 mmol) in Et_2O was introduced. The reaction mixture was stirred to −50 °C for various times (15 min for R = Me, 1 h for R = Ph). Upon completion, the reaction was quenched at −78 °C with a 10% NH_4OH/90% saturated aqueous NH_4Cl solution followed by filtration under pressure, extractions in Et_2O, and drying on Na_2SO_4. Chromatography on silica gel with Et_2O/hexane (20/80) gave 1 (88%) and 2 (85%), respectively.

Compound 1 was also prepared as described above by using CuI in the place of CuCN and quenching with a NH_4Cl saturated solution[6] (method 1a) giving the same results. 1: IR (film) ν_{max} 1700 cm^{-1}; MS, (*m/e*) for $C_{13}H_{16}OSe$ 264–270, 111. 2: IR (film) ν_{max} 1700 cm^{-1}; MS, (*m/e*) for $C_{18}H_{18}OSe$ 326–332, 173.

trans-2-(Phenylseleno)-3-phenylcyclohexanone (2t). 2-Cyclohexenone (5 mmol) in Et_2O is added at −78 °C to the $Ph_2Cu(CN)Li_2$ (10 mmol) prepared as above. After stirring for 1 h at −60 °C, PhSeBr (21.67 mmol)[5] in THF is added, and stirring is continued for 30 min. After extractions and usual workup, the ^1H NMR spectrum of the crude product shows the presence of 2t. Column chromatography on silica gel with Et_2O/hexane (20/80) gives a mixture of 2c/2t (60/40) (65%).

cis-2-(Phenylseleno)-3-[cyano(dimethylamino)phenyl-methyl]cyclohexanone (3c). *n*-BuLi (5.5 mmol) is added dropwise to a solution of dimethylaminophenylacetonitrile (5 mmol) in THF, and the mixture was cooled at −78 °C.[1] After stirring for 10–15 min. the α-enone 7 (5 mmol) in THF is added, and the reaction mixture is stirred for 40 min at −78 °C and then quenched with a saturated aqueous NH_4Cl solution. After usual workup and recrystallization from Et_2O, 3c was obtained (65–70%): mp 111–112 °C; IR ($CDCl_3$) ν_{max} 1705 cm^{-1}. Anal. Calcd for $C_{22}H_{24}N_2OSe$: C, 64.23; H, 5.88; N, 6.81; O, 3.89. Found: C, 64.04; H, 5.87; N, 6.78; O, 3.62.

trans-2-(Phenylseleno)-3-[cyano(dimethylamino)-phenylmethyl]cyclohexanone (3t). To the carbanion 12 (5 mmol) prepared as above is added the 2-cyclohexenone (5 mmol) in THF at −78 °C. After stirring for 15 min, PhSeBr (5.77 mmol)[5] in THF is added, and stirring is continued for 40 min at −60 °C. Extractions, workup, and recrystallization for 3c yielded 3t (60–65%): mp 91–92 °C; IR ($CDCl_3$) ν_{max} 1705 cm^{-1}. Anal. Calcd for $C_{22}H_{24}N_2OSe$: C, 64.23; H, 5.88; N, 6.81; O, 3.89. Found: C, 64.22; H, 5.85; N, 7.08; O, 3.77.

2-(Phenylseleno)-3-benzoylcyclohexanone (4). Compound 3 (0.28 mmol) is stirred for 40 min at room temperature with a solution of 0.5 N aqueous $AgNO_3$ (0.5 mL), THF (1 mL), and Et_2O (0.5 mL). After usual workup, 4c is obtained as a mixture of 4c, 4t, and 14 while crude 4t is purified by preparative TLC Et_2O/hexane (55/45) to yield diketone 4t (95%): IR (film) ν_{max} 1715, 1680 cm^{-1}; MS, (*m/e*) for $C_{19}H_{18}OSe$: 354–360, 201.

Ethylene ketals of 2-(phenylseleno)-3-methylcyclo-hexanone (5) and 2-(phenylseleno)-3-phenylcyclohexanone (6) were prepared according to the method described in the literature.[3] Preparative TLC with Et_2O/hexane (40/60) gave the ketal selenides (90%) 5: MS, *m/e* for $C_{15}H_{20}O_2Se$ 308–314, 155. 6: MS, *m/e* for $C_{20}H_{22}O_2Se$ 370–377, 217.

3-Methyl-2-cyclohexenone (15), 3-phenyl-2-cyclohexenone (16), 3-[cyano(dimethylamino)phenylmethyl]-2-cyclo-hexenone (13), and 3-benzoyl-2-cyclohexenone (14) were prepared after oxidation with H_2O_2 according to ref 3. 13: mp 88–89 °C; IR ($CDCl_3$) ν_{max} 1660, 1610 cm^{-1}; ^1H NMR 90 MHz ($CDCl_3$) δ 7.7–7.35 (m, 5 H), 6.7 (d, 1 H) H_2, 2.7–1.5 (m, 6 H), 2.3 (s, 6 H) $N(CH_3)_2$. Anal. Calcd for $C_{16}H_{18}NO$: C, 75.56; H, 7.14; N, 11.01; O, 6.29. Found: C, 75.59; H, 7.22; N, 11.27; O, 6.31. 14: IR (film) ν_{max} 1680–1660 cm^{-1}; ^1H NMR 90 MHz ($CDCl_3$) δ 7.65–7.15 (m, 5 H), 6.1 (m, 1 H) H_2, 2.6–1.9 (m, 6 H). 15: IR (film) ν_{max} 1660, 1615 cm^{-1}; ^1H NMR 90 MHz ($CDCl_3$) δ 5.9 (s, 1 H) H_2, 2.45–1.8 (m, 6 H), 1.95 (s, 3 H) CH_3. 16: mp 53–54 °C; IR ($CDCl_3$) ν_{max} 1660, 1610 cm^{-1}; ^1H NMR 90 MHz ($CDCl_3$) δ 7.7–7.35 (m, 5 H), 6.15 (m, 1 H) H_2, 2.95–2.2 (m, 6 H).

Supplementary Material Available: 2D J correlated (COSY et SECSY) spectra of 1c, 1t, 2c, and 2t compounds showing long range W stereospecific couplings and proton assignments (4 pages). Ordering information is given on any current masthead page.

Empirical Force Field Calculations. 27.[1] A Study on the Conformations of the Simple Vicinal Diols

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The results of molecular mechanics calculations using the MM2 force field on 1,2-ethanediol, 1,2-propanediol, and the 2,3-butanediols are reported; results on 1,3-propanediol and 1,2-dimethoxyethane are included for comparison. The preference of the 1,2-diols for gauche O–C–C–O forms is evoked by the torsional energy function in the force field and is strengthened by electrostatic interactions between the hydroxyl groups at low dielectric constant. The effects of solvation are discussed. Calculations show that the gauche O–C–C–O forms of the diols are stabilized in protic media by specific solvation. A cyclic structure composed of the diol and a hydroxyl group of the solvent molecule is proposed. Energy increments for gauche Me/Me, Me/OH, and OH/OH interactions are calculated; those involving hydroxyl groups are dependent on the dielectric constant.

Dihydroxy compounds react with boric acid and borate in aqueous medium with formation of boric acid esters, borate monoesters, and borate diesters.[2,3] These were of importance in the configurational analysis of carbohydrates[2] and are applied in various separation techniques[4] and in the sequestration of cations by mixtures of borate and sugar acids.[5,6] An experimental study of the relative

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(1) Part 25: Koningsveld, H. v.; Baas, J. M. A.; Graaf, B. v. d. *Acta Crystallogr., Sect. C: Struct. Commun.* **1984**, *C40*, 1463. Part 26: Baas, J. M. A.; Bleichrodt, F.; Graaf, B. v. d.; Hoefnagel, M. A.; Peters, J. A. *Delft Prog. Rep.* **1985**, *10*, 191.

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**Figure 1.** Effect of n higher energy minima ($E = E_i$) upon $\bar{E}$.
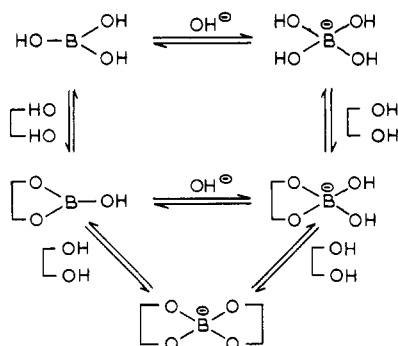
stabilities of the borate esters in a series of polyhydroxy compounds is presented in a previous paper.[7] In addition, a molecular mechanics study was carried out to elucidate the steric and electrostatic interactions in the diols and in the borate monoesters. 1,3-Dioxolanes were studied as model compounds for the borate monoesters.

In this paper we present the results of our calculations on a series of diols: 1,2-ethanediol, 1,2- and 1,3-propanediol, and meso and racemic 2,3-butanediol. We also present some results on 1,2-dimethoxyethane to illuminate the so-called gauche effect. The results of the calculations are compared with data from the literature.

Calculations

The calculations were performed by using Allinger's MM2 empirical force field[8] and DELPHI, the Delft molecular mechanics computer program.[9] As dielectric constants (ϵ) 1.5 and 80 were used. The former is the standard value used in the force field; the latter is more relevant to the aqueous medium of the studies on borate ester stabilities. The calculations for 1,2-propanediol and for meso and racemic 2,3-butanediol were carried out for the (S)-1,2-propanediol and the (R,S)- and (S,S)-2,3-butanediol configurations. The various conformers were found by starting from the corresponding staggered conformations. In some cases torsion angle driving with the Lagrange multiplier method[10] was used to locate a particular conformer. Because of symmetry it is not necessary to perform calculations for all rotational isomers around the C–C and C–O bonds.

Depending on the O–C–C–O backbone three forms are distinguished, viz., the anti (a), the right handed gauche (g^+), and the left handed gauche (g^-) forms; each form
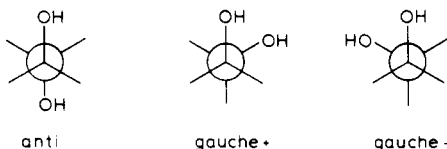
includes the various conformers resulting from all possible C–C–O–H torsion angles. Note that the designations g^+ and g^- interchange when R and S configurations are interchanged.

The steric energies and the characteristic torsion angles of all relevant conformers are compiled in Tables SI to SVI (supplementary material). The mean steric energies of the anti and gauche forms, $\bar{E}_a$ and $\bar{E}_g$, were calculated at 25 °C with the Boltzmann equation. In the same way the
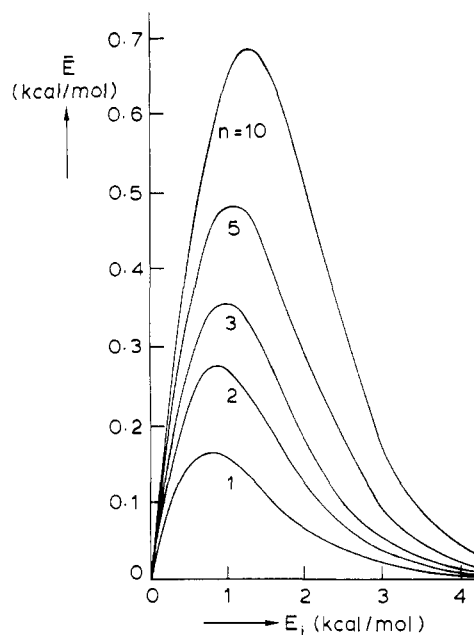
mean steric energy $\bar{E}$ was calculated for each compound. $\Delta\bar{E}$ is defined as $\bar{E}_g - \bar{E}_a$; $\Delta\bar{E}$ values are given in Table I along with the heats of formation ($\Delta H_f°$) calculated from the increments of the MM2 force field.[8] In Table III energy increments for gauche vs. anti Me/Me, Me/OH, and OH/OH interactions are presented. These were obtained from a least-squares fit on all $\Delta\bar{E}$ values at $\epsilon = 1.5$ and 80.

Discussion

Before dealing with each compound in detail we want to discuss the effect of higher energy conformers upon the mean energy ($\bar{E}$) of a set of conformers. In the case of n higher energy conformers ($E = E_i$) besides the conformer of lowest energy ($E = 0$) we obtain eq 1. Figure 1 shows

$$\bar{E} = nE_i \exp(-E_i/RT)/(n \exp(-E_i/RT) + 1) \quad (1)$$

$\bar{E}$ as a function of E_i for $n = 1$–3, 5, and 10 at 25 °C. For $n = 1$ the maximum value of $\bar{E}$ is only 0.16 kcal/mol for $E_i = 0.87$ kcal/mol. With other E_i values the contribution of higher energy conformers diminishes rapidly. For $n > 1$ the maximum value of $\bar{E}$ shifts to higher values of E_i.

1,2-Ethanediol. The gauche forms are calculated to be more stable than the anti form at $\epsilon = 1.5$ ($\Delta\bar{E} = -0.91$ kcal/mol). The conformer of lowest energy of the two gauche forms has one C–C–O–H torsion angle of nearly 180°, while the other angle is about +60° or -60°. These conformers are stabilized by large dipole–dipole interactions (-1.28 kcal/mol) between the hydroxyl groups which can be regarded as intramolecular hydrogen bonds (Table II). Energetically, hydrogen bonds can be seen as the sum of both electrostatic and charge transfer effects.[11] Only the former ones are included in the MM2 force field.
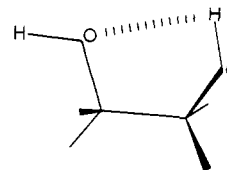
The dipole–dipole attraction term becomes very small at $\epsilon = 80$ and the intramolecular hydrogen bonds vanish.

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Table I. Energetic Data[a] Obtained with the MM2 Force Field

compd	form[b]	$\epsilon = 1.5$ $\Delta\bar{E}$	$\epsilon = 1.5$ $\Delta H_f°$	$\epsilon = 80$ $\Delta\bar{E}$
1,2-ethanediol	a	0.00		0.00
			−91.65	
	g^+,g^-	−0.91		−0.42
(S)-1,2-propanediol	a			0.00
	g^+			−0.74
	g^-			−0.40
(R,S)-2,3-butanediol	a	0.00[c]		0.00[c]
			−109.73	
	g^+,g^-	−0.79		−0.07
(S,S)-2,3-butanediol	a	0.00[c]		0.00[c]
	g^+	−2.12	−110.16	−0.94
	g^-	−1.56		−1.16
1,3-propanediol[d]	a,a			0.00
	$a/g^+, a/g^-, g^+/a, g^-/a$			0.30
	$g^+/g^+, g^-/g^-$			0.60
	$g^+/g^-, g^-/g^+$			0.86
1,2-dimethoxyethane	a			0.00
	g^+,g^-			−0.59

[a] $\Delta\bar{E}$ ($\bar{E}_g - \bar{E}_a$) and $\Delta H_f°$ are given in kcal/mol. [b] Each form includes the various C–C–O–H conformers; a and g refer to the O–C–C–O backbone. [c] $\bar{E}_a[(R,S)$-2,3-butanediol]$-\bar{E}_a$ [(S,S)-2,3-butanediol] is −0.78 (ϵ = 1.5) and −0.69 kcal/mol (ϵ = 80), respectively. [d] a and g refer to the O–C–C–C backbone.

Table II. Characteristic Dimensions (Å, deg) of the Intramolecular Hydrogen Bonds Stabilizing the Gauche Conformation of Diols at $\epsilon = 1.5$
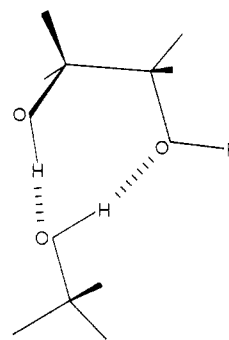
	1,2-ethanediol	(R,S)-2,3-bu-tanediol	(S,S)-2,3-bu-tanediol
O···O	2.84	2.83	2.78
O···H	2.48	2.45	2.41
O···H–O	102	104	103

However, the gauche forms remain preponderant ($\Delta\bar{E}$ = −0.42 kcal/mol) due to the stabilizing V_2 term of the O–C–C–O torsion angle energy function. The difference between the torsion energies of the most stable gauche and anti conformers at ϵ = 80 is −0.47 kcal/mol and almost equals $\Delta\bar{E}$. The V_2 term is incorporated in the MM2 force field[8] to cope with the gauche effect.[12] This will be discussed below in connection with the results for 1,2-dimethoxyethane. The gauche conformer of lowest energy at ϵ = 80 has two C–C–O–H torsion angles of about 180° thereby reducing the van der Waals interactions.

The results calculated for ϵ = 1.5 agree well with experimental data. In the gas phase[13] the gauche forms are known to be predominant, and for solutions in apolar solvents $\Delta\bar{H}$ is −0.4 to −0.6 kcal/mol.[14] The existence of intramolecular hydrogen bonds has been demonstrated for both phases.[15-17] The small difference between the calculated and the experimental[18] values of $\Delta H_f°$, −91.7 and −93.9 ± 1.5 kcal/mol, respectively, can be explained with the tendency of 1,2-ethanediol to dimerize to some extent in the gas phase.[19] $\Delta\bar{H}$ values for 1,2-ethanediol in aqueous solution and as pure liquid are almost equal, viz., −0.8 and nearly −0.7 kcal/mol.[14,20,21] The calculations are in agreement with experimental results which show that intramolecular hydrogen bonds are absent for 1,2-

ethanediol[20] and polyols[22] in polar protic environments. The shift of the calculated values of $\Delta\bar{E}$ from −0.91 at ϵ = 1.5 to −0.42 kcal/mol at ϵ = 80 is opposite to the shift of the experimental values of ΔH_{conf} from about −0.5 for apolar solvents to about −0.75 kcal/mol for polar protic solvents. This gives evidence for a solvent effect in polar protic solvents of about 0.75 kcal/mol stabilizing the gauche forms.

Part of this effect can be explained by the stabilization of the forms with the largest dipole moment, i.e., the gauche forms of 1,2-ethanediol, through intermolecular dipole–dipole interactions with polar solvents. Experimentally this effect only amounts to 0.08 kcal/mol for 1,2-dimethoxyethane when ϵ is changed from 2 to 8.[23,24] Therefore a specific solvent effect is probable. We suggest a cyclic structure containing two hydrogen bonds. Pre-

liminary calculations have demonstrated that such a structure is energetically favored.[25] Finally it should be noted that the anti form is predominant in a diluted solution of 1,2-ethanediol in Me_2SO, a solvent forming hydrogen bonds only by accepting protons.[21]

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(25) Calculations yielded energy minima for one molecule of 1,2-ethanediol with one molecule of methanol. At ϵ = 1.5 a cyclic structure with 1,2-ethanediol in a gauche conformation is favored by 0.65 kcal/mol over a 1,2-ethanediol in an anti conformation with only one hydrogen bond to methanol. The MM2 force field does not contain explicit functions for hydrogen bonding. Therefore, this energy difference must be considered to be a lower limit.

To study the effect of the negative V_2 torsional term, we have performed calculations on 1,2-dimethoxyethane. A comparison of $\Delta\bar{E}$ for 1,2-ethanediol and its dimethyl ether at ϵ = 80, -0.42 and -0.59 kcal/mol, respectively, shows that substitution of the hydroxyl groups with methyl groups has little effect upon the gauche/anti preference. The explanation is that the energetically preferred gauche and anti conformers of both compounds have C-C-O-H/C torsion angles of about 180°, thus keeping the differences in steric energy to a minimum. Experimentally, the gauche preference of 1,2-dimethoxyethane[26,27] as well as that of polyethylene glycol[28,29] is well established. For 1,2-dimethoxyethane[26] conformers decrease in stability in the series a/g/a, a/a/a, a/g/g, and a/a/g, which is in excellent agreement with our calculations (supplementary material). Thus the gauche effect can be a determining factor in the absence of other stronger effects and is justly incorporated in Allinger's force field for the present compounds.[30]

(S)-1,2-Propanediol. For this compound the g⁺ and the g⁻ forms are different. Only calculations at ϵ = 80 were carried out. Both the g⁺ and the g⁻ forms are preferred over the a form ($\Delta\bar{E}$ = -0.74 and -0.40 kcal/mol), due to the negative V_2 torsional term. The energy difference between the g⁺ and the g⁻ forms is caused by unfavorable Me/OH interactions (Table III) in the g⁻ form.

anti   gauche+   gauche -
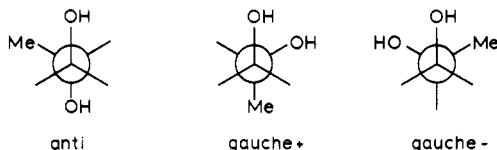
A comparison with experimental data is not possible because these concern the gas phase and apolar solvents. Intramolecular hydrogen bonds were proved to exist in both phases[31,32] stabilizing the g⁺ and g⁻ forms. As discussed for 1,2-ethanediol, the preference for the gauche forms will be enhanced in polar protic environments by specific solvation.

1,3-Propanediol. Calculations at ϵ = 80 demonstrate that the conformational energy decreases when the number of anti C-C-C-O and C-C-O-H torsion angles increases. This is reflected in the average conformational energies of the four forms, viz., 0.0, 0.30, 0.86, and 0.60 kcal/mol for a/a, a/g⁺, g⁺/g⁺, and g⁺/g⁻, respectively. The preferred conformer is that with all four torsion angles equal to 180°, i.e., a fully extended conformation. Studies on the conformation of 1,3-propanediol only concern solutions in CCl₄ and show the presence of intramolecular hydrogen bonds.[31,33]

(R,S)-2,3-Butanediol. Calculations at ϵ = 1.5 show the gauche forms to be favored ($\Delta\bar{E}$ = -0.79 kcal/mol). The somewhat smaller stabilization of the gauche forms relative to 1,2-ethanediol is due to unfavorable steric interactions caused by methyl substitution (Table III). The two gauche conformers of lowest energy are stabilized with intramolecular hydrogen bonds (Table II). At ϵ = 80 the strong

a/a   a/g⁺

g⁺/g⁺   g⁺/g⁻
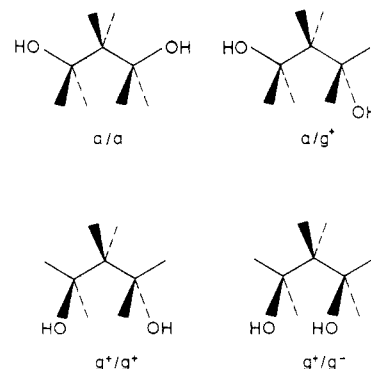
dipole-dipole interactions disappear, and steric interactions are the determining factors. Due to the negative V_2 torsional term the gauche forms remain slightly favored ($\Delta\bar{E}$ = -0.07 kcal/mol).

anti   gauche+   gauche-
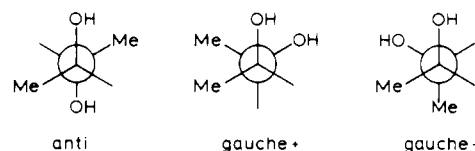
Quantitative data on conformational equilibria of this compound are not available. In diluted CCl₄ solutions the presence of both free and intramolecularly hydrogen-bonded hydroxyl groups is demonstrated.[17,31] The latter give evidence for the presence of gauche forms. Levy et al.[34] interpreted the change in the ^{13}C chemical shift of the methyl groups, going from apolar solvents (CCl₄, CHCl₃) to nonprotic polar solvents (Me₂SO, HMPO, DMF, pyridine), as a shift of the conformational equilibrium from gauche to anti. This is comparable with the results for 1,2-ethanediol.[20] For water as solvent such a change is not observed.[34] We conclude that an appreciable amount of gauche forms will be present in aqueous solution. Just as in the case of 1,2-ethanediol we rationalize this by specific solvation. Finally, Grenier-Loustalot et al.[35] also published a paper on the changes of the ^{13}C chemical shifts. We object to their analysis of the data and conclude that the conformational equilibria for this compound in both CDCl₃ and D₂O are comparable because the ^{13}C chemical shifts do not differ significantly.

(S,S)-2,3-Butanediol. Calculations at ϵ = 1.5 show a stabilization of the g⁺ and g⁻ forms due to intramolecular hydrogen bonding (Table II), $\Delta\bar{E}$ = -2.11 and -1.56 kcal/mol, respectively. Apparently the gauche Me/Me interaction is less than twice the gauche Me/OH interaction (Table III). $\Delta H_f°$ is smaller than that of the R,S compound (-110.2 vs. -109.7 kcal/mol) due to decreased steric interactions. At ϵ = 80, all intramolecular hydrogen bonds disappear, and the three forms have conformers of lowest energy with C-C-O-H torsion angles of about 180°. The g⁺ and g⁻ forms remain preponderant ($\Delta\bar{E}$ = -0.94 and -1.16 kcal/mol).

anti   gauche+   gauche-
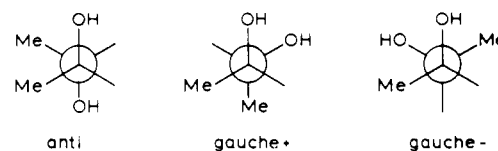
These results agree with experimental data in apolar solvents so far that an appreciable amount of intramo-

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ϵ	Me/Me	Me/OH	OH/OH
1.5	0.69	0.61	−0.88
80	0.68	0.25	−0.50

lecularly hydrogen-bonded species is present.[17,31] According to Levy et al.[34] the change from apolar to polar nonprotic solvents has a shielding effect upon the ^{13}C chemical shifts of the methyl groups, which was interpreted as a change in the equilibrium from g⁻ to a. For an aqueous solution the shielding effect is larger, and we explain this with a conformational change from g⁻ to g⁺. These two equilibrium shifts both agree with the different intermolecular hydrogen bonding in both nonprotic and protic polar solvents.

Steric Interactions in the Series of Vicinal Diols. $\Delta \bar{E}$ values in the present series of diols can be seen as the sum of gauche interactions between the substituents on the ethane backbone (Table III). For example, $\Delta \bar{E}$ for 1,2-ethanediol is explained by a gauche OH/OH interaction. As can be expected the Me/Me interaction is independent of ϵ and is close to the experimental Me/Me interaction in *n*-butane.[36] The Me/OH interaction decreases upon increase of ϵ because the C–C–O–H torsion angles in the conformations of lowest energy change from +60° or –60° to 180°. Finally the OH/OH interaction becomes less favorable when ϵ is increased due to breaking of the intramolecular hydrogen bonds; this interaction remains stabilizing due to the gauche effect. The data in Table III can be used to predict $\Delta \bar{E}$ values for other alcohols in the gas phase and in apolar solvents (ϵ = 1.5) or polar noninteractive solvents (ϵ = 80).

Conclusions

Summarizing the experimental data for the vicinal diols we can distinguish several types of environments, each with

characteristic influences upon the conformational preferences. Diols in the gas phase or dissolved in apolar solvents are able to form intramolecular hydrogen bonds. These hydrogen bonds stabilize the gauche forms relative to the anti form. Intermolecular hydrogen bonds exist in polar solvents. In polar nonprotic solvents this results in stabilization of the anti form, in polar protic environments in stabilization of the gauche forms.

Our calculations at ϵ = 1.5 for 1,2-ethanediol and the 2,3-butanediols show stabilization of gauche forms due to large dipole–dipole interactions and a negative V_2 torsional term. The results are generally in good agreement with the experimental data. Increasing ϵ diminishes the dipole–dipole interactions. Going from apolar to polar solvents not only does ϵ increase but intermolecular hydrogen bonds can be formed. These are not incorporated in the MM2 force field. Therefore, our calculations at ϵ = 80 cannot result in a good description of compounds dissolved in polar interactive solvents. The difference between the calculated results and the available experimental data points to a specific solvation of gauche forms in polar protic environments.

Energy increments for gauche Me/Me, Me/OH, and OH/OH interactions rationalize the $\Delta \bar{E}$ values in the series of the vicinal diols and may be used to predict $\Delta \bar{E}$ for other alcohols.

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Halogenated Epoxides. 9.[1] Reaction of *trans*-2,3-Dichlorooxirane with Dimethyl Sulfide

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Received September 15, 1985

Reaction of *trans*-2,3-dichlorooxirane (1) with dimethyl sulfide afforded in high yield dimethyl(1-chloro-2-hydroxyethenyl)sulfonium chloride (2a). The latter was converted into 1-chloro-2-methoxy-1-(methylthio)ethene (3b) and into 2-acetoxy-1-chloro-1-(methylthio)ethene (3c) by reaction with diazomethane and with ketene, respectively. Pyrolysis of 2a gave chloro(methylthio)acetaldehyde (4a) and dichloroacetaldehyde (6), along with a series of minor byproducts.

Introduction

In previous work we have examined oxidation reactions of unsubstituted and of alkyl-substituted 1,2-dichloroethylenes with oxygen in the liquid phase.[2] As one of

several means to detect products containing hydroperoxide groups, we have treated the crude reaction mixtures with dimethyl sulfide (Me_2S) and determined the amount of dimethyl sulfoxide formed. When this method was applied to the crude reaction product obtained from the oxidation

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