Structure and Conformations of 1,4-Butanediol: Electron-Diffraction Evidence for Internal Hydrogen Bonding

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Abstract: Evidence for internal hydrogen bonding has been sought for in a study of 1,4-butanediol (BDIOL), a molecule in which the "gauche" effect is expected to have minimal influence on the conformational preferences. This has been achieved by studying the molecular structure and the conformational equilibrium of the BDIOL molecule, using gas-phase electron diffraction (GED). Experimental data have been recorded at 60 keV at two different temperatures, 144 and 260 °C. The GED study has been supplemented by molecular mechanics calculations, carried out on the ten conformers that are in principle individually distinguishable by the GED method. Refinement of models of mixtures in which the amounts of internal hydrogen-bonded conformers were allowed to adjust led to large increase over those predicted from molecular mechanics in which hydrogen-bonding stabilization was ignored. These results are interpreted as strong evidence for the existence of internal hydrogen bonding. On the basis of the experimental results for the mixture composition, a rough estimate of the energy of the O–H···O–H internal hydrogen bond is 10–11 kJ/mol. Values for the structural parameters and conformational composition are presented.

Introduction

The existence of hydrogen bonding involving hydroxyl groups and the dramatic influence of such bonding on the physical properties and chemical reactivity of organic compounds are well-known to every chemist. Examples of the effect of intermolecular hydrogen bonding are the high boiling point of ethanol and the large differences in reactivity of heterolytic reactions in protic and aprotic solvents. If two or more hydroxyl groups are part of the same molecule and the geometry of the molecule allows for it, intramolecular hydrogen bonding is expected to compete with intermolecular hydrogen bonding. The extent of the latter kind of interaction is dependent on the concentration of the compound, while the former is concentration independent.

Carbohydrates are polyhydroxy ketones or aldehydes, and polyhydroxy compounds are abundant among naturally occurring organic compounds. The stereochemistry of carbohydrates appears, however, to be determined primarily by the formation of hemiacetal/hemiketal rings and to a lesser degree by internal hydrogen bonding. Another class of polyhydroxy compounds, the so-called sugar alcohols, have been shown by X-ray diffraction[1–3] as well as by ^{1}H and ^{13}C NMR studies[4,5] to exist predominantly in an extended planar zigzag conformation with an *anti* arrangement at all C–C bonds. Studies of such molecules as galactitol[1] or *d*-mannitol[2,3] in the crystal reveal only intermolecular (no intramolecular) hydrogen bonding. Exceptions to this general conformational preference of sugar alcohols are observed in compounds where an *all-anti* conformation would have placed two OH groups in 1,3 parallel positions.[4] In such cases, as for example in *meso*-ribitol, *d*-glucitol and riboflavin, a "bent" or "sickle" conformation is observed in the crystalline state,[6–8] with a *gauche* torsional angle placed so that 1,3 parallel oxygen atoms are avoided.

Two hydroxy groups substituted in 1,3 parallel positions are nearly ideally suited to form an intramolecular hydrogen bond. The conformational preferences of the sugar alcohols in the crystal appear to indicate that such an interaction is energetically unfavorable. A gas-phase electron-diffraction (GED) study of 1,3-propanediol[9] shows, however, that the molecules exist exclusively in a *+gauche,–gauche* (G^+G^-) conformation, with 1,3 parallel OH groups. Molecular mechanics calculations of the geometries and energies of the possible 1,3-propanediol conformers, where eventual hydrogen bonding is not taken into account,[10] indicate that the G^+G^- conformation would contribute less than 1% to the mixture composition. The observed conformation of the gas molecule must therefore be due to internal hydrogen bonding.

In the case of 1,2-ethanediol[11] (ethylene glycol), GED results show that the *gauche* conformer is considerably more stable than the *anti*: *gauche* is the only conformer detected with certainty, even at high temperature (460 °C). The stability of the *gauche* form of 1,2-ethanediol and other 1,2-disubstituted compounds with electronegative substituents might, however, also be influenced by the so-called "gauche effect".[12] The question as to how important internal hydrogen bonding is for the conformational stability of 1,2-ethanediol remains therefore unanswered.

We undertook the present study to investigate further the importance of intramolecular O–H···O–H hydrogen bonding for the determination of conformational preferences of dihydroxy-substituted molecules. 1,4-Butanediol is an especially interesting case. Of the many arrangements of the backbone atoms arising from torsion around C–C bonds, only one or two (together with

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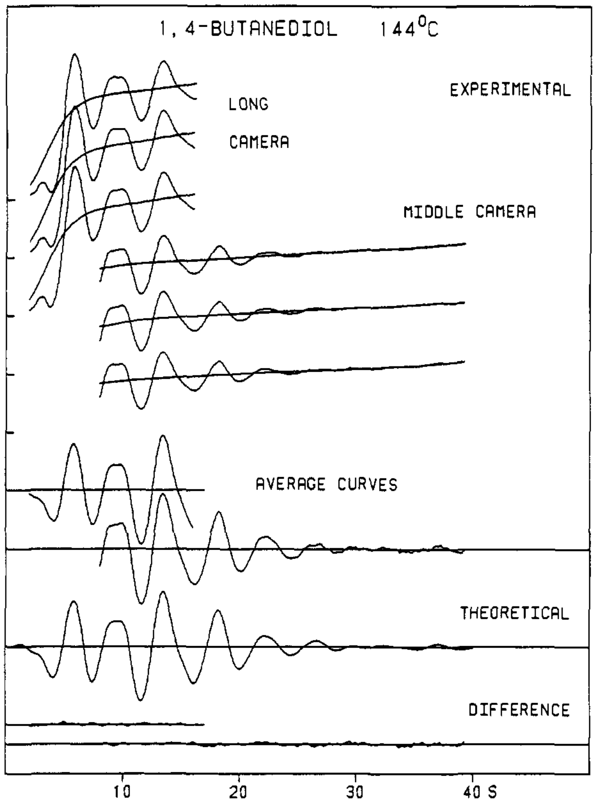

Figure 1. Experimental intensity curves ($s^4I_t(s)$) at 144 °C from each plate are shown magnified 5× with respect to the final backgrounds on which they are superimposed. The average curves are $sI_m(s) = s(s^4I_t - \text{bkgd})$. The theoretical curve is for the model of Tables 4 and 5.

their enantiomorphs) are favorable for O–H···O–H bonding. Since a *gauche* effect cannot operate in this molecule, evidence for the formation of an internal hydrogen bond would be the existence of this/these forms in amounts greater than those expected from calculations in which the stabilizing effect of the hydrogen bond was excluded. No previous diffraction work on the molecule is known to us, but studies of other flexible molecules, with other types of internal hydrogen bonding, like 4-chloro-1-butanol,[13] 4-penten-1-ol,[14] and 4-pentyn-1-ol,[15] have been reported.

Experimental Section

A commercial sample of 1,4-butanediol (BDIOL) (Aldrich, purity 99%) was used in the present study. The diffraction experiments were made with the Oregon State apparatus using a r^3 sector and Kodak projector slide plates (medium contrast) developed for 10 min in D19 developer diluted 2:1. The experiments were done at a lower temperature (LT) of 144–146 °C and a higher temperature (HT) of 258–260 °C at the nozzle tip. The accelerating voltage was ca. 60 kV (nominal electron wavelength 0.049 Å) calibrated against CO_2 in separate experiments (r_a(C=O) = 1.1646 Å; r_a(OO) = 2.3244 Å). Nominal nozzle-to-plate distances of 750 (long camera, LC) and 300 mm (middle camera, MC) were used for the studies at both temperatures. The numbers of plates selected for analysis were three from each camera distance from the LT experiments and three LC and five MC from the HT experiments. The analytical procedures have been described.[16,17] The complex scattering factors by Ross, Fink, and Hilderbrandt[18] were used. Ranges of the average modified molecular intensities ($sI_m(s)$) were $2.00 \le s/\text{Å}^{-1} \le 16.00$ (LC) and $8.00 \le s/\text{Å}^{-1} \le 39.25$ (MC), with $\Delta s/\text{Å} = 0.25$. The intensity curves for the LT and HT studies are shown in Figures 1 and 2 and the corresponding radial distribution (RD) curves in Figure 3.

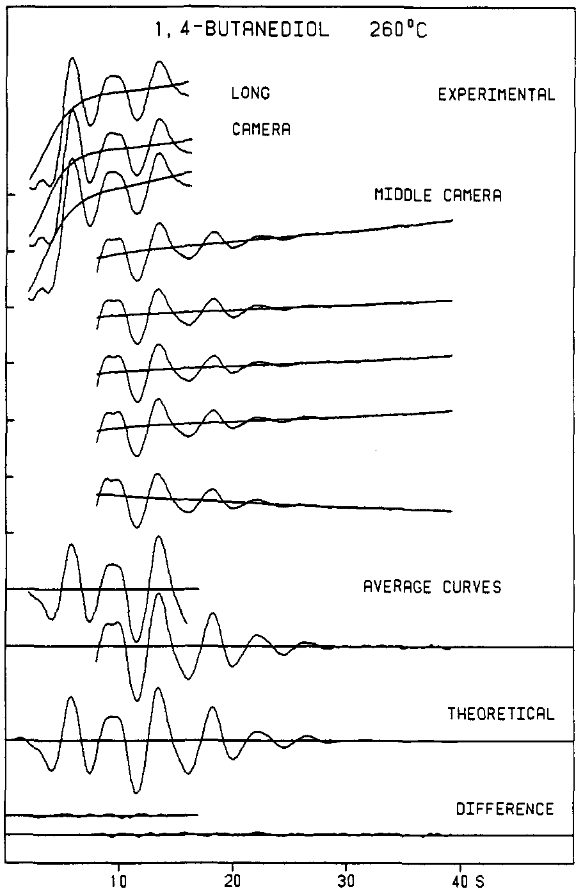

Figure 2. Intensity curves at 260 °C. See legend to Figure 1.

Structure Analysis

Consider the heavy-atom skeleton of a 1,4-disubstituted *n*-butane such as BDIOL (Figure 4). If we assume a 3-fold rotational barrier at each of the three C–C bonds, the molecule may in principle exist in 3 × 3 × 3 = 27 different conformations.[19] However, among these are several pairs of enantiomorphs which are indistinguishable by the GED method. If the two substituents are different, there are 13 pairs of such enantiomorphs in addition to the unique *all-anti* conformation. The number of potentially observable conformers is thereby reduced from 27 to 14. On the other hand, when the two substituents are identical as in 1,4-butanediol, the increased symmetry of the molecule reduces the number of potentially distinguishable conformers still further to 10. These are the following: (1) AAA; (2) AAG (AAG$^+$; AAG$^-$; G$^+$AA; G$^-$AA); (3) G$^-$AG$^+$ (G$^-$AG$^+$; G$^+$ AG$^-$); (4) GAG (G$^+$AG$^+$; G$^-$AG$^-$); (5) AGA (AG$^+$A; AG$^-$A); (6) AGG (AG$^+$G$^+$; AG$^-$G$^-$; G$^+$G$^+$A; G$^-$G$^-$A); (7) AG$^+$G$^-$ (AG$^+$G$^-$; AG$^-$G$^+$; G$^+$G$^-$A; G$^-$G$^+$A); (8) GGG (G$^+$G$^+$G$^+$; G$^-$G$^-$G$^-$); (9) G$^+$G$^-$G$^-$ (G$^+$G$^+$G$^-$; G$^-$G$^-$G$^+$; G$^-$G$^+$G$^+$; G$^+$G$^-$G$^-$); (10) G$^+$G$^-$G$^+$ (G$^+$G$^-$G$^+$; G$^-$G$^+$G$^-$). The symbols refer to *anti* (A) and *gauche* (G$^+$ or G$^-$) dihedral angles at the C_1–C_2, C_2–C_3, and C_3–C_4 bonds; for example, G$^-$AG$^+$ represents a conformer with torsion angles O–C_1–C_2–C_3, C_1–C_2–C_3–C_4, and C_2–C_3–C_4–O approximately equal to −60°, 180°, and 60°, respectively.

It is of course not possible to determine the composition of a conformational mixture of ten different conformers—each being defined by a large number of geometrical parameters—by the GED method without introducing some constraints or assumptions. As has been found for 1,3-propanediol[10] and 4-chlorobutanol,[13] molecular mechanics calculations give valuable guidance

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[19] There are, of course, still more conformers generated by torsion around the C–O bonds; these cannot be distinguished by GED.

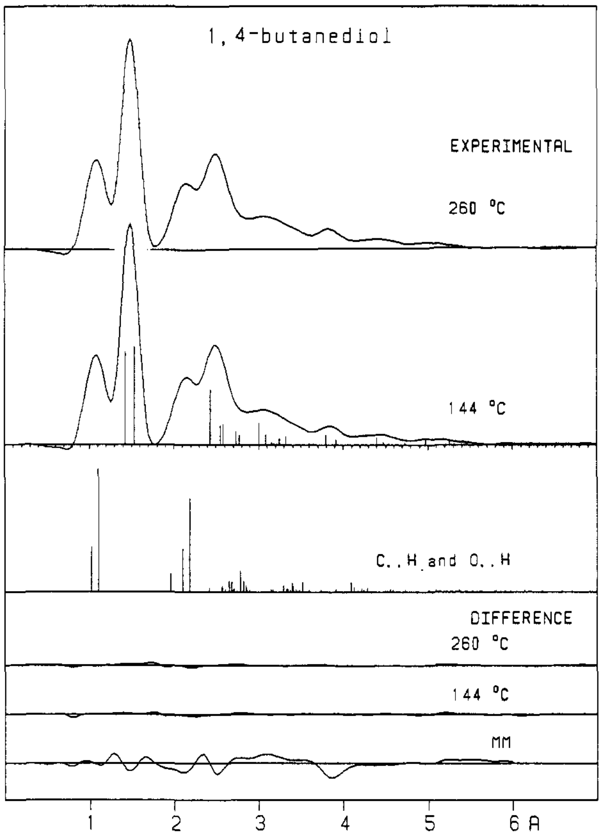

Figure 3. Radial distribution curves. The experimental curves were calculated from the intensity curves of Figures 1 and 2 according to $rD(r) = \Sigma_i s_i I_m(s_i)(Z_C s^{-2} F_C^{-1})^2 \exp(-0.0025 s^2)$; data for the unobserved regions $s/\text{Å}^{-1} < 2.00$ were taken from the final theoretical curve. The vertical bars under the 144 °C curve indicate the distances and relative weights of the C··C and O··O terms for the final model; the relative weights of the bars indicating the C··H and O··H terms have been doubled for clarity.

for making sound assumptions about structural parameters in an GED study. Furthermore, when conformational problems are involved, it is useful to know the calculated strain energies of the different conformers from which may be obtained the tentative conformational composition. In the case of BDIOL, only conformers 9 and 10 (Figure 4) have the hydroxyl groups near enough to permit internal hydrogen bonding. If molecular mechanics calculations are carried out for all conformers of BDIOL omitting terms that reflect possible hydrogen bonding, the results should lead to an appropriate estimate of the relative abundance of all conformers except those in which hydrogen bonding actually operates. Experimental evidence for internal hydrogen bonding would then lie in the detection of conformers 9 and 10 in greater abundance than predicted from the calculations.

We used Allinger's MM2 program[20] to calculate values for the structural parameters and the steric energy of each of the ten unique heavy-atom conformations of BDIOL, eliminating terms that could contribute to the formation of hydrogen bonds in conformers 9 and 10. Table 1 shows the calculated steric energies, as well as the mole ratios at 144 and 260 °C deduced from them assuming Bolzmann distributions. According to the calculated results in Table 2, the total contribution from conformers 9 and 10, *i.e.* those with backbone configurations suitable for formation of internal hydrogen bonds, is expected to be very small at both temperatures (3.5 and 4.6%), in the *absence* of internal O–H···O–H hydrogen bonding.

The conformational composition of BDIOL was treated formally as a two-conformer problem, one part consisting of conformers 1–8 and the other of the possibly hydrogen-bonded conformers 9 and 10. The relative abundances of conformers 1–8 were fixed according to their calculated mole ratios (Table I), with their total abundance treated as an independent parameter. The hydrogen-bonded conformers presented a complicated problem inasmuch as the two members of the group could exist in any mole ratio depending on the relative strengths of their hydrogen bonds. It was decided to test them individually (*i.e.*, to ignore the possible presence of one of the two forms) against the group of non-hydrogen-bonded conformers. The geometry of each of the possibly hydrogen-bonded conformers (9 and 10) was fully described by 13 bond distance, bond angle, and torsion angle parameters: r(C–C), r(C–O), r(C–H), r(O–H), ∠CCC, ∠CCO, ∠HCH, ∠COH, $\tau(OC_1C_2C_3)$, $\tau(C_1C_2C_3C_4)$, $\tau(C_2C_3C_4O)$, $\tau(C_3C_4OH)$, and $\tau(HOC_1C_2)$. From this list it is apparent that for these two conformers all bond distances and bond angles of the same type, *e.g.* r(C–C) or ∠HCH, were assumed to be the same. To reduce to a managable size the large number of

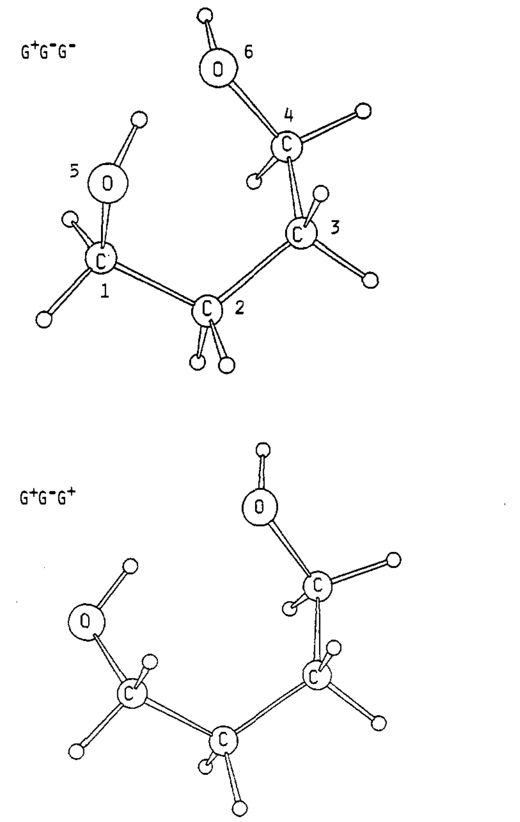

Figure 4. Diagrams of the two hydrogen-bonded forms of 1,4-butanediol. Atom numbering applies to all conformers.

Table 1. Estimated Conformational Composition of 1,4-Butanediol from Theory (MM2) and Experiment (GED)

			conformational composition, %			
			theory		expt	
conformer[a]	n[b]	E_{steric}[c]	144 °C	266 °C	144 °C[d]	266 °C[d]
1. AAA	1	16.127	14.0	10.8	8.7	7.6
2. AAG	4	18.227	29.8	27.1	18.4	19.0
3. G^+AG^-	2	18.659	13.1	12.2	8.1	8.6
4. G^+AG^+	2	20.112	8.5	8.8	5.3	6.1
5. AGA	2	20.309	8.0	8.4	5.0	5.9
6. AGG	4	21.987	9.6	11.5	5.9	8.1
7. AG^+G^-	4	22.529	8.2	10.2	5.1	7.1
8. GGG	2	21.546	5.5	6.4	3.3	4.5
9. $G^+G^-G^-$	4	26.065	2.8[e]	3.3[e]	40.2 (43)	33.1 (39)
10. $G^+G^-G^+$	2	28.457	0.7[e]	1.3[e]	[f]	[f]

[a] G, as in AAG or AGA, symbolizes G^+ or G^-, while GG (GGG) symbolizes G^+G^+ or G^-G^- ($G^+G^+G^+$ or $G^-G^-G^-$). [b] Number of indistinguishable conformers, for example conformer 3: G^+AG^- and G^-AG^+, $n = 2$. [c] Steric energy from MM2, kJ/mol. [d] Except for $G^+G^-G^-$, the conformational composition was fixed in the ratio determined from the MM2 calculations. [e] τ(CCOH) set *anti* to preclude effects of internal hydrogen bonding. [f] See text.

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Table 2. Angle Values for 1,4-Butanediol Conformers from Molecular Mechanics Calculations[a]

	conformer[b]									
	1	2	3	4	5	6	7	8	9	10
					Valence Angles					
OC_1C_2	109.3	109.3	109.9	109.9	109.2	109.3	109.2	109.9	110.9	110.2
$C_1C_2C_3$	111.7	111.7	112.6	112.6	113.3	113.4	114.3	114.5	115.1	115.1
$C_2C_3C_4$	111.7	112.6	112.6	112.7	113.4	114.5	114.9	114.5	115.4	115.1
C_3C_4O	109.3	109.8	109.9	109.9	109.2	109.9	110.6	109.9	110.0	110.2
					Torsion Angles					
$OC_1C_2C_3$	179.8	−179.7	63.3	62.9	175.3	174.2	172.3	57.1	74.3	83.6
$C_1C_2C_3C_4$	179.8	179.2	179.2	176.7	66.6	63.1	67.0	60.0	−68.9	−58.2
$C_2C_3C_4O$	179.8	64.1	−64.2	63.0	177.0	58.2	−76.0	56.8	−58.2	83.2

[a] Angles in degrees. [b] See Table 1 and text.

Table 3. Calculated Average Root-Mean-Square Amplitudes (l/Å) at 144 (260) °C for Some Important Distances in Conformers of 1,4-Butanediol[a]

	conformer[b]								
	1	2	3	4	5	6	7	8	9
					Torsion-Sensitive Distances				
$C_2\cdots O_6$	0.082 (0.090)	0.188 (0.212)	0.186 (0.210)	0.186 (0.210)	0.083 (0.090)	1.82 (0.206)	0.084 (0.092)	0.181 (0.204)	0.181 (0.204)
$C_3\cdots O_5$	0.082 (0.090)	0.082 (0.090)	0.186 (0.210)	0.186 (0.210)	0.083 (0.090)	0.083 (0.091)	0.183 (0.206)	0.181 (0.206)	0.181 (0.204)
$C_1\cdots C_4$	0.086 (0.094)	0.086 (0.094)	0.086 (0.094)	0.086 (0.094)	0.192 (0.216)	0.189 (0.213)	0.188 (0.212)	0.187 (0.211)	0.188 (0.212)
$C_1\cdots O_6$	0.106 (0.118)	0.190 (0.214)	0.189 (0.213)	0.189 (0.213)	0.185 (0.209)	0.357 (0.398)	0.177 (0.199)	0.356 (0.403)	0.316 (0.357)
$C_4\cdots O_5$	0.106 (0.118)	0.107 (0.119)	0.189 (0.213)	0.189 (0.213)	0.185 (0.209)	0.180 (0.203)	0.313 (0.354)	0.356 (0.403)	0.316 (0.357)
$O\cdots O$	0.101 (0.112)	0.256 (0.290)	0.174 (0.196)	0.174 (0.196)	0.168 (0.189)	0.378 (0.428)	0.333 (0.377)	0.414 (0.469)	0.505 (0.573)

[a] Bond-distance amplitudes (Å) for all conformers: l(C–O) = 0.050; l(C–C) = 0.054; l(C–H) = 0.079; l(O–H) = 0.070. Average geminal distance amplitudes (Å): l(C·O) = 0.083 (all except 5 at 0.084); l(C·C) = 0.091 (1–4) and 0.090 (5–9); l(C·H) = 0.112 (all); l(O·H) = 0.109 (all). [b] See Table 1.

geometrical parameters for the remaining eight conformers a number of assumptions had to be introduced. The four heavy-atom valence angles of each conformer were, for example, defined from two independent parameters, $\angle CCC_{AAA}$ and $\angle OCC_{AAA}$, according to $\angle C_iC_jC_k = \angle CCC_{AAA} + \Delta C_iC_jC_k$ and $\angle OC_iC_j = \angle OCC_{AAA} + \Delta OC_iC_j$. The reference angles $\angle CCC_{AAA}$ and $\angle OCC_{AAA}$ refer to the *all-anti* conformer where these angles are expected to have the smallest values. Values of the four Δ's for each conformer were taken from appropriate valence angle differences implicit in the data of Table 2. Other assumptions about the geometries of conformers 1–8 were the following: (a) The bond lengths, the HCH angles, and the COH angles were set equal to those for the hydrogen-bonded conformer(s). (b) The $OC_1C_2C_3$, $C_1C_2C_3C_4$, and $C_2C_3C_4O$ torsion angles were fixed at the values in Table 2. (c) The CCOH torsion angles ere fixed at 180°. The last assumption is based on results from MM2 calculations carried out for all combinations of *anti* and *gauche* CCOH torsion angles: for all conformers in the non-hydrogen-bond group 1–8, minimum steric energy was obtained for these angles at the *anti* value. The structural and conformational properties of BDIOL were thus described by 16 variables: the 13 geometric parameters specifying the hydrogen-bonded conformer(s), the minimum CCC and CCO angles for the non-hydrogen-bonded conformers ($\angle CCC_{AAA}$ and $\angle CCO_{AAA}$), and the mole fraction of the hydrogen-bonded conformer(s).

Refinements of the structural and conformational parameters of BDIOL were carried out by least-squares adjustments of the intensity curves.[21] The geometry of each of the BDIOL conformers was calculated on the basis of r_α parameters, which include corrections for shrinkage effects.[22] All together 295 interatomic distances were necessary to describe the conformers, even though most H···H terms were omitted. The vibrational amplitudes and shrinkage corrections for these distances were calculated from normal coordinate analyses carried out with the program ASYM20[23] for the various conformers. The simple force field for the calculations comprised internal force constants (stretches, bends, torsions, stretch/stretch, and stretch/bend interactions) which were given typical values estimated from similar molecules. The calculated vibrational amplitudes for the bond distances and the most important nonbond distances are presented in Table 3. The vibrational amplitudes of the bond distances and the nonbond *geminal* distances are insensitive to molecular conformation, but those for the torsion-sensitive C···O, C···C, and O···O distances vary as much as 5-fold from one conformer to another—evidence of the importance of carrying out normal coordinate analyses for all contributing species in GED studies of conformational equilibria. In the least-squares refinements, amplitudes of the same order of magnitude (Table 3) associated with distances of similar length were grouped together as a single parameter, with differences held at those determined by the calculated values. With this procedure most vibrational amplitudes of any importance were included in the refinements.

From the beginning of the study it was evident that one or more hydrogen-bonded conformers were present in large amount at both temperatures. It was not easy, however, to establish the nature of this conformer. It was possible to obtain good fits to experiment with models in which the hydrogen-bonded part was represented by the $G^+G^-G^-$ conformer as well as by the $G^+G^-G^+$ conformer. This was hardly surprising since, except for the distance between the hydroxyl groups, most of the nonbond distances in the two conformers are similar. Several items pointed finally toward rejection of the $G^+G^-G^+$ conformer. The most important of these was that the distance between the hydroxyl groups obtained from refinements of this conformer is too small (*i.e.*, $r(O\cdots O) \simeq 2.35$ Å) for an energetically favorable interation. Other items were the much larger uncertainties obtained for the

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Table 4. Some Distances (r/Å) and Root-Mean-Square Amplitudes (l/Å) for 1,4-Butanediol[a]

	144 °C			260 °C		
term[b]	$r_{a,obs}$	l_{obs}[c]	l_{calc}[d]	$r_{a,obs}$	l_{obs}[c]	l_{calc}[d]
C–O	1.426 (2)	0.061 (4)	0.048	1.429 (3)	0.070 (4)	0.050
C–C	1.528 (2)	0.063 (4)	0.052	1.527 (3)	0.072 (4)	0.054
O–H	1.014 (35)	0.094 } (10)	0.070	0.987 (15)	0.086 } (7)	0.070
C–H	1.106 (12)	0.103 }	0.079	1.110 (4)	0.095 }	0.079
O·C	2.42–2.44	0.082 (7)	0.076	2.42–2.46	0.093 (8)	0.083
C·C	2.54–2.59	0.080 (8)	0.082	2.54–2.59	0.097 (12)	0.090
C·H	2.16–2.18	0.119 (7)	0.111	2.16–2.18	0.124 (7)	0.112
O·C(G)	2.75–3.01	0.119 } (37)	0.181	2.79–3.18	0.134 } (54)	0.204
C·C(G)	3.15–3.22	0.125 }	0.188	3.16–3.25	0.141 }	0.212
O·C(A)	3.79–3.81	0.091 } (23)	0.082	3.79–3.81	0.098 } (19)	0.090
C·C(A)	3.90–3.92	0.095 }	0.088	3.90–3.92	0.102 }	0.094
O·C(AG)	4.48–4.55	[0.18–0.19]		4.48–4.55	[0.20–0.21]	
O·C(AA)	4.96–4.97	[0.11]		4.96–4.98	[0.12]	
O·C(GA)	4.41	[0.19]		4.41	[0.21]	
O·C(G^+G^-)	2.99–3.30	[0.31–0.32]		3.09–3.69	[0.36–0.40]	
O·C(G^+G^+)	3.64–3.69	[0.35–0.36]		3.64–3.69	[0.40]	
O·O($G^+G^-G^-$)	2.75 (46)	[0.50]		2.91	[0.57]	
O·O(AAA)	6.17 (3)	[0.10]		6.18	[0.11]	

[a] Observed values are averages or ranges for the conformational mixture. Quantities in parentheses are estimated 2σ uncertainties; those in curly brackets were refined as a group. [b] A or G appended to terms indicate the torsion angles separating the atoms. Example: O·C(GA) refers O and C_4 in the chain $O–C_1–C_2–C_3–C_4$ with torsion angles $O–C_1–C_2–C_3$ and $C_1–C_2–C_3–C_4$ respectively gauche and anti. [c] Assumed values in square brackets are theoretical (see text and ref 23). [d] See text and ref 23.

parameters of this conformer, especially for the torsion angles ($\tau(OC_1C_2C_3)$ = 68.9 (367)°, $\tau(C_1C_2C_3C_4)$ = –56.6 (286)°, $\tau(C_2C_3C_4O)$ = 69.7 (475)°) and the somewhat larger R factors, all indicating a poorer fit. The final model for the system is therefore based on conformers 1–8 plus the hydrogen-bonded $G^+G^-G^-$ conformer.

During the course of the refinements it was found, not unexpectedly, that two additional constraints involving hydrogen parameters of the hydrogen-bonded conformer were necessary; those introduced were $\angle COH$ = 104.5° and $\tau(CCOH)$ = 60°. Also, it was advantageous to introduce the restriction $\angle CCC_{AAA} - \angle CCO_{AAA}$ = 2.4° in the non-hydrogen-bonded group 1–8. In many of the refinements, both of these reference angles were varied together with the other parameters. The difference between the refined values for $\angle CCC_{AAA}$ and $\angle CCO_{AAA}$ was always found to be close to 2.4°, *i.e.* near the calculated difference between these two angles (Table 2). The restriction was introduced in order to reduce the number of independent parameters and to obtain a more secure convergence of the least-squares fits. This restriction did not affect the structural results noticably.

Results. Tables 4 and 5 show the geometrical and vibrational parameter values and the conformational composition obtained for BDIOL at the two experimental temperatures. The excellent fit provided by the models is evident in the difference curves of Figures 1–3. A similar refinement of a model in which the composition was held at that calculated from MM2 (Table 1) gave a very poor fit (Figure 3) and is strong evidence for a high proportion of hydrogen-bonded conformers in gaseous BDIOL. The correlation matrix for results at the lower temperature is shown in Table 6; the matrix for the higher temperature results is similar.

Table 5. Angles (deg) in Conformers of 1,4-Butanediol[a]

	144 °C	260 °C
	All Conformers	
HCH	102.3 (49)	105.2 (27)
COH	[104.5]	[104.5]
	Conformers **1–8**[b,c]	
OCC_{AAA}	110.1 } (8)	110.2 } (6)
CCC_{AAA}[d]	112.5 }	113.6 }
	Hydrogen-bonded Conformer $G^+G^-G^-$	
OCC	110.9 (16)	112.2 (25)
CCC	114.6 (19)	114.7 (33)
$OC_1C_2C_3$	67.0 (54)	69.1 (60)
$C_1C_2C_3C_4$	–69.9 (90)	–73.5 (113)
$C_2C_3C_4O$	–27.2 (156)	[–28.1]
HOC_1C_2	[60.0]	[60.0]
C_3C_4OH	[60.0]	[60.0]
	Composition and Agreement Factors	
% $G^+G^-G^+$	40.6 (124)	31.0 (120)
R_{LC}[e]	0.029	0.033
R_{MC}[e]	0.058	0.051

[a] Quantities in parentheses are estimated 2σ uncertainties; those in square brackets were assumed. [b] The valence angles for conformers **2–8** were defined as $\angle OCC = \angle OCC_{AAA} + \Delta OCC$; $\angle CCC = \angle CCC_{AAA} + \Delta CCC$, where the increments ΔOCC and ΔCCC were set equal to the angle differences obtained from the data of Table 2. [c] The heavy atom torsion angles for this group were fixed at the values of Table 2. [d] Assumed to be 2.4° larger than $\angle OCC_{AAA}$, in accordance with the MM2 results. [e] $R = [\sum w_i\Delta_i^2/w_i(s_iI_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$. The subscripts refer to the two camera distances.

Discussion

Internal O–H···O–H Bonding. The most interesting results in Table 4 are the values for the percentage of the hydrogen-bonded $G^+G^-G^+$ conformer in the mixtures and the strong evidence they hold for the existence of internal O–H···O–H hydrogen bonding in gaseous BDIOL molecules. As mentioned earlier, of the many possible conformations of BDIOL only two, $G^+G^-G^-$ and $G^+G^-G^+$, have hydroxyl groups positioned favorably for internal hydrogen bonding. According to our MM2 calculations (carried out excluding terms that would lead to hydroxyl group attraction), these conformers should be present in amounts of less than 5%. The results from our GED studies at two temperatures show the conformer $G^+G^-G^-$ and/or $G^+G^-G^+$ (although the latter was not specifically represented in the final refinements, our data do not rule it out) present in the amount of about 40% at 144 °C and 33% at 260 °C. We attribute this result to the stabilizing effect of internal hydrogen bonding. The extent to which the amount of hydrogen-bonded conformers depends on the reliability of the molecular mechanics calculations is not known. We judge, however, that reasonable variations in the relative amounts of conformers 1–8 would not affect substantially our measurements of the overall amounts of the hydrogen-bonded species.[24]

Conformational effects and hydrogen bonding in various 1,4-diols have been reported by Kuhn *et al.*[25] on the basis of IR

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[24] After our analysis based on the assumptions drawn from molecular mechanics calculations was compete, it became possible to carry out ab initio calculations in our laboratory. Results from optimizations of the structures of each conformer at the HF/6-31G* level for both relative energies and parameter values were similar to those obtained from MM2. Accordingly, it did not seem worthwhile to repeat the ED analysis with use of the ab initio data.

Table 6. Correlation Matrix (×100) for Parameters of 1,4-Butanediol at 144 °C

	$100\sigma_{LS}{}^c$	r_1	r_2	r_3	r_4	$\angle_5$	$\angle_6$	$\angle_7$	τ_8	τ_9	τ_{10}	$\angle_{11}$	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}	l_{18}	l_{19}	l_{20}
1. r(O–C)	0.06	100																			
2. r(C–C)	0.06	3	100																		
3. r(C–H)	0.42	19	14	100																	
4. r(O–H)	1.61	18	12	97	100																
5. $\angle OCC^a$	57	–18	–14	–24	–25	100															
6. $\angle CCC^a$	68	–3	–24	–10	–11	70	100														
7. $\angle HCH^a$	175	28	30	83	83	–51	–42	100													
8. $\tau(-C_1-C_2-)^a$	162	6	16	1	<1	–52	–52	23	100												
9. $\tau(-C_2-C_3-)^a$	317	4	–12	–27	–28	11	16	–25	–10	100											
10. $\tau(-C_3-C_4-)^a$	550	–11	–16	–29	–29	64	48	–38	–66	38	100										
11. $\angle OCC^b$	27	–8	–19	3	3	–49	–27	–7	38	–13	–64	100									
12. l(C–C)	0.10	53	–20	54	54	–16	5	48	1	–14	–21	4	100								
13. l(C–O)	0.10	36	–37	53	54	–12	8	43	–5	–13	–18	9	90	100							
14. l(C–H)	0.32	–10	–3	–92	–96	22	9	–77	2	26	25	–4	–49	–51	100						
15. l(O·C)	0.20	16	13	23	24	–34	–67	50	41	–14	–33	8	25	23	–20	100					
16. l(C·C)	0.28	8	10	17	18	–25	–63	34	32	2	–22	23	16	15	–15	81	100				
17. $l(O(C)\cdots C)_G$	1.29	<1	2	2	3	–46	–51	18	32	59	–9	23	–3	–3	–4	–38	–51	100			
18. l(C·H)	0.20	–1	–14	–42	–45	53	51	–60	–22	8	20	17	42	–5	45	–23	–21	–32	100		
19. $l(O(C)\cdots C)_A$	0.80	–2	–6	–6	–6	22	26	12	1	–14	16	8	<1	<1	5	–2	–1	–18	17	100	
20. $\alpha(G^+G^-G^-)$	4.40	6	6	12	13	–40	–43	23	–5	–11	–30	–4	8	7	–11	9	5	27	–27	–74	100

[a] Hydrogen-bonded conformer $G^+G^-G^-$. [b] Non-hydrogen-bonded conformers, local *anti* conformation (see text). [c] Standard deviations from least squares.

measurements. Their estimate of the ratio of the amounts of free/hydrogen-bonded molecules in BDIOL is 2.6/1, in remarkably good agreement with our experimental results.

Our measurements of the conformational equilibrium at two different temperatures permit us to make rough estimates of the magnitudes of the energy and entropy terms associated with internal hydrogen bonding in BDIOL. The temperature dependence of the equilibrium between the hydrogen-bonded and other conformers is given by the usual formula

$$\alpha/(1.0 - a) = e^{-\Delta E^\circ/RT}\, e^{\Delta S^\circ/R}$$

where α represents the mole fraction of the hydrogen-bonded conformer and $\Delta E^\circ = E_{1-8}{}^\circ - E_{HB}{}^\circ$. The results with estimated standard deviations are $\Delta E^\circ = -5.0\ (29)$ kJ/mol and $\Delta S^\circ = 15.1\ (63)$ J·mol^{-1}·deg^{-1}. Since, as Table 1 shows, the theoretical strain energies of conformers 9 and 10 are 5–6 kJ/mol greater than those for the remainder of the group (all calculated for COH arrangements that preclude the possibility of internal hydrogen bonding), the energy of the internal hydrogen bond must be greater than ΔE° by about this amount. The result, 10–11 kJ/mol, is in good agreement with that determined from IR vapor spectra by Fishman and Chen[26] (–12.55 (83) kJ/mol).

The hydrogen-bond parameter O···O of the $G^+G^-G^-$ conformer was observed to be 2.73 Å. This is about what is expected for a moderately strong O–H···O–H hydrogen bond.[27] Because the GED experiment does not locate the position of the H_O atom, the H···O distance and the O–H···O angle are indeterminate.

Bond Lengths and Associated Vibrational Amplitudes. The bond lengths of each type (C–C, O–C, O–H, C–H), which are to be interpreted as averages both among and within all conformers, are normal. The (average) C–O and C–C bond lengths were found to have the same values at 144 and 260 °C. The precision of the O–H and C–H bond-length measurements from the high-temperature study appears to be greater than that from the lower-temperature one, and the values themselves are in better agreement with results for similar molecules.[28] The experimental vibrational amplitudes of the bond distances are found to be 0.01–0.02 Å larger than the corresponding calculated quantities. This result is not unreasonable: since small differences in bond lengths surely exist among members of the groups C–O, C–C, O–H, and C–H, our neglect of the differences would tend to be manifested in larger amplitudes.

Bond Angles and Torsion Angles. The valence and torsion angles obtained for the hydrogen-bonded conformer $G^+G^-G^-$ are normal except for $\angle C_2C_3C_4O$. At a value of ~28°, this angle is probably to a large degree the result of an accommodation forced by formation of a hydrogen bond. Construction of molecular models shows this to be a reasonable way to achieve the goal.

Vibrational Amplitudes of Nonbond Distances. Most of the vibrational amplitudes of nonbond distances were found to be in good agreement with the corresponding calculated quantities. Exceptions are the experimental amplitudes for the 1,4 C···O and C···C *gauche* distances, which were observed to be appreciably smaller than the corresponding calculated values. The differences are probably related to some of the restrictions introduced in the analysis.

The mole fraction of the hydrogen-bonded conformer, $\alpha(G^+G^-G^-)$, is modestly correlated ($\rho = 0.36$) with the vibrational amplitudes discussed above. If instead of being treated as refinable parameters, the vibrational amplitudes of the 1,4 C···C and C···O *gauche* distances are fixed at the calculated values, the contribution from the hydrogen-bonded conformer is increased by about 3%. The other parameter values are nearly insensitive to this modification.

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Supplementary Material Available: Tables of total scattered intensities and final backgrounds from each plate at each temperature and average molecular intensities for each camera distances at each temperature (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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