Conformational Analysis. 21. Ethane-1,2-diol. An Electron-Diffraction Investigation, Augmented by Rotational Constants and ab Initio Calculations, of the Molecular Structure, Conformational Composition, SQM Vibrational Force Field, and Anti-Gauche Energy Difference with Implications for Internal Hydrogen Bonding

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Abstract: The gas-phase molecular structure and anti−gauche composition of ethane-1,2-diol (ethylene glycol) at 376 and 733 K has been analyzed from electron-diffraction data augmented by rotational constants for eight isotopic species and with the help of results from ab initio calculations. The system model consisted of three conformers, g^-Ga, g^-Gg, and aAa, which were found to provide a good representation of the 10 possible different conformations. Scaled quantum-mechanical (SQM) force fields in internal coordinates were also evaluated for these three conformers using a set of 13 scale constants determined by a least-squares fitting of the theoretical (HF/6-31G*) force constants to observed wave numbers for the most abundant conformer, g^-Ga. The mole fraction of conformers with anti *vs* gauche OCCO torsion angles (*i.e.* aAa *vs.* $g^-Ga + g^-Gg$) was found to be 0.08 ($2\sigma = 7$) at 376 K and 0.18 ($2\sigma = 11$) at 733 K, under conditions in which the mole ratios of g^-Ga to g^-Gg were maintained at the theoretical predictions of 0.58−0.34 (376 K) and 0.40−0.42 (733 K). An estimate of the internal energy difference is $\Delta E° = 1.4$ (5) kcal/mol for the reaction G → A and may also be taken as a rough value for the energy of the O−H···O internal hydrogen bond. The value is consistent with estimates made in like fashion for other types of hydrogen bonds in 1,2-disubstituted ethanes. Average values of some of the more important parameters (r_α^0/Å; $\angle_\alpha$/deg) with estimated 2σ uncertainties at 376 K for the conformers g^-Ga, g^-Gg, and aAa, respectively, are $r(C-C) = \{1.517, 1.521, 1.517\}$ (5); $r(C-O) = \{1.424, 1.424, 1.424\}$ (1); $r(O-H) = \{0.961, 0.962, 0.960\}$ (8); $r(C-H) = \{1.118, 1.117, 1.118\}$ (6); $\angle CCO = 109.3$ (4), 111.2 (7), 110.5 (30); $\angle COH = 105.8$ (27), 108.2 (21), 109.6 (21); $\langle \angle CCH, OCH \rangle = 109.1$ (10), 108.0 (11), 110.5 (21); $\angle OCCO = 60.7$ (18), 57.5 (30), [180]. Values in curly brackets were refined as groups with differences between members frozen.

Introduction

1,2-Disubstituted ethanes exist in the gaseous state as a mixture of gauche and anti forms that result from internal rotation around the C−C bond. The gauche forms are always the more stable when the substituents tend to form strong (internal) hydrogen bonds or when both substituents are very electronegative—a phenomenon known as the "gauche effect".[1] Typical examples where both factors play a role are 2-fluoroethanol[2] and ethylenediamine,[3] each more than 80% gauche at room temperature. However, in room-temperature 1,2-difluoroethane[4] where internal hydrogen bonding cannot exist, the gauche form is still the dominant one at about 95%. With pairs of less electronegative substituents the gauche effect is largely absent and the influence of steric factors is felt more strongly; in such cases the relative stabilities of the gauche and anti forms reflect the interplay between steric repulsion which favors anti and internal hydrogen bonding which favors gauche. Thus, with

the exception of the difluoro compound, all the 1,2-dihaloethanes either with like or unlike substitutents are predominately anti.[5]

Since OH groups have both high electrogativity and strong hydrogen-bonding properties, the more stable form of the molecule ethane-1,2-diol (ethylene glycol, Figure 1, hereafter EG) is predicted to have the heavy atoms in a gauche conformation. It was shown to be so by an early electron-diffraction (GED) investigation[6] of the gas in which only this form was detected and by IR spectroscopic studies[7] of matrix-isolated molecules. The matter of internal hydrogen bonding in the gauche arrangement of the EG skeleton, of course, also involves torsions around the two C−O bonds. Because of the relatively weak scattering from the torsion-sensitive terms H_O···C, the GED study just mentioned provided no information about the positions of the H_O atoms. However, the IR work identified two different hydrogen-bonded conformers that we may charactize as g^-Ga and g^-Gg, where upper/lower case letters refer to rotations about C−C/C−O bonds and a positive sign designates counterclockwise motion of the forward group along the chain away from the cis conformation. From microwave spectroscopy there are also rotational constants for

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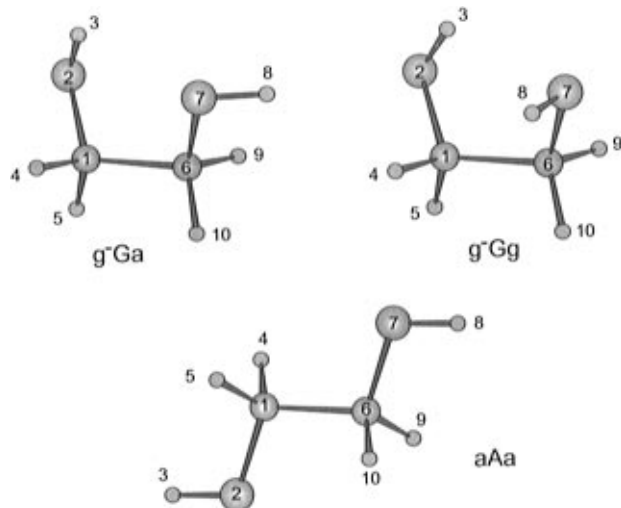
Figure 1. Diagrams with atom numbering of the three conformers comprising the model of ethane-1,2-diol.

several isotopic species of the conformers g^-Ga and g^-Gg. For g^-Ga these species are the undeuterated parent (OHOH),[8] the monodeuterated OHOD and ODOH,[9] the dideuterated ODOD,[10] and the dideuterated CH_2CD_2 and CD_2CH_2;[11] for g^-Gg they are the dideuterated species CH_2CD_2 and CD_2CH_2.[11] There are also optimized structures and energies from ab initio calculations.[7,12,13]

Rotational isomerism in simple organic molecules has been the subject of many experimental studies from this laboratory. The main interests have been the energy and entropy differences of the conformers (which may be explored by measurements of the temperature dependence of the conformational equilibria) and the implications these hold for chemical properties such as those mentioned above. EG is especially interesting because of the absence of measurable amounts at room temperature of conformers with the heavy atoms in an anti arrangement. Several years ago we attempted to generate measurable amounts of this form at higher sample temperatures,[14] but even at 460 °C only an uncertain 5−10% was indicated. We have now reanalyzed the data from the original experiments with the use of a more elaborate model and the sets of rotational constants mentioned above; the latter are of particular value in helping to determine the CCOH torsion angles and other angles involving hydrogen atoms that are difficult to measure by GED. As before, the object of the work was to obtain precise experimental values for the parameters of the several important forms of EG and an experimental measure of the relative amounts of the hydrogen-bonded and non-hydrogen-bonded forms. In pursuit of the objective we have obtained optimized structures for all conformers at the ab initio HF level and carried out normal coordinate analyses leading to quadratic vibrational

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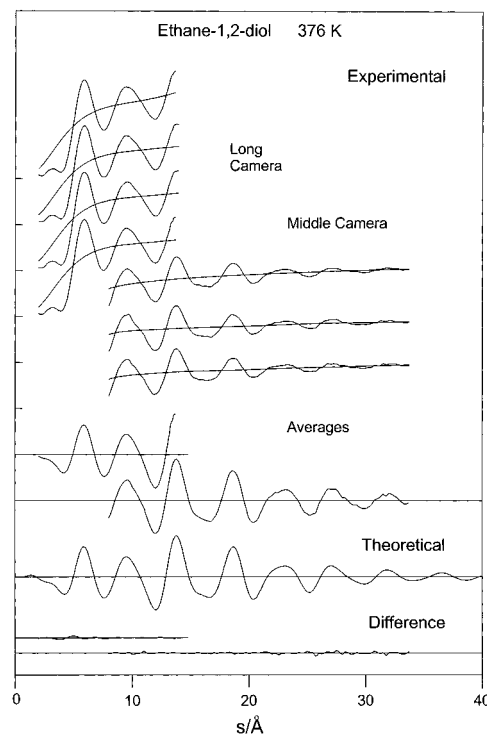
Figure 2. Intensity curves from the lower temperature experiments. The long and middle camera curves are in the form s^4I_t and are shown amplified by a factor of five relative to the backgrounds on which they are superimposed. The average curves are $s[s^4I_t - \text{bkgd}]$. The difference curves are experimental minus theoretical.
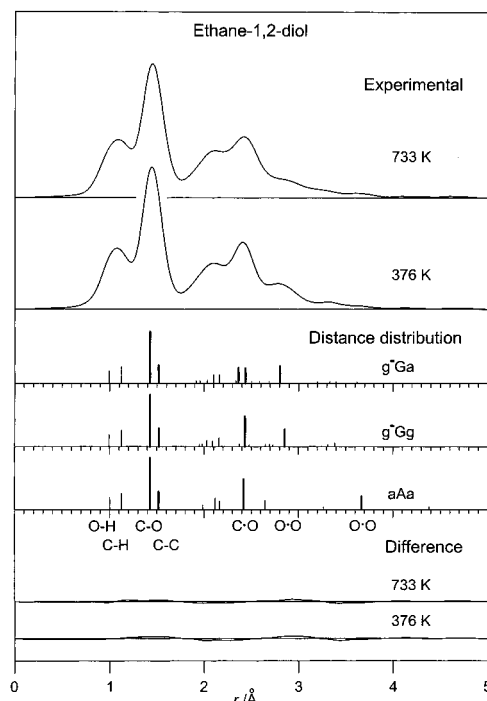
Figure 3. Radial distribution curves. The sets of bars indicate distance distribution (H···H were ignored) and weights of the terms in the three conformers of the final model; heavy-atom distances are designated by thicker bars. The difference curves are experimental minus theoretical.

force fields for the more abundant species. This article is a report of the results.

Experimental Section

The sample of EG was Baker Analyzed Reagent grade, further purified by fractional distillation under reduced pressure through a column packed with glass helices. A middle fraction was chosen for

Table 1.   Ab Initio (HF/6-31G*) Data for Conformers of Ethane-1,2-diol

no.	conf.[a]	$\tau(CCOH_3)$[b]	$\tau(OCCO)$[b]	$\tau(CCOH_8)$[b]	$(E+228.0)/E_h$	$\Delta E/kcal \cdot mol^{-1}$	X^c_{376}	X^c_{733}
			Hydrogen Bonded					
1	g^-Ga	−53.9	60.7	−170.2	−0.925 726 69	0.0	0.576	0.345
2	g^-Gg	−45.6	57.8	76.0	−0.924 664 72	0.666	0.236	0.218
3	g^-Gg^-	−81.4	57.0	−81.4	−0.923 672 52	1.289	0.103	0.142
			Not Hydrogen Bonded					
4	aAg^-	176.0	179.8	−75.3	−0.921 876 55	2.416	0.023	0.066
5	gAg^-	73.6	180.0	−73.7	−0.921 729 77	2.508	0.020	0.062
6	aAa	180.0	180.0	180.0	−0.922 423 39	2.073	0.018	0.042
7	gAg	70.8	177.9	70.8	−0.921 113 64	2.895	0.012	0.047
8	gGg	44.2	49.1	44.2	−0.920 266 50	3.426	0.006	0.033
9	aGa	−166.3	72.6	−166.3	−0.919 038 96	3.758	0.004	0.026
10	gGa	59.1	64.0	−178.2	−0.919 738 00	4.197	0.002	0.019

[a] The lower/upper case letters refer to rotations about the C−O/C−C bonds, and a minus sign means a clockwise movement of the forward group. [b] Torsion angles in degrees. [c] Mole fractions at the indicated temperatures. Small zero point vibrational energy corrections were ignored; rotational degeneracies have been taken into account.

Table 2.   Theoretical Results for Structures of Ethane-1,2-diol Conformers[a]

parameter	g^-Ga	g^-Gg	aAa[b]	parameter	g^-Ga	g^-Gg	aAa[b]
			Bond Lengths				
O_2H_3	0.949	0.949	0.946	C_6H_{10}	1.088	1.088	1.087
O_7H_8	0.946	0.948	0.946	C_1O_2	1.397	1.396	1.403
C_1H_4	1.088	1.091	1.087	C_6O_7	1.408	1.409	1.403
C_1H_5	1.083	1.083	1.087	C_1C_6	1.514	1.517	1.513
C_6H_9	1.087	1.082	1.087				
			Bond Angles				
$C_1O_2H_3$	107.7	107.9	109.7	$C_6O_7H_8$	110.2	109.7	109.7
$H_4C_1H_5$	108.1	107.5	108.0	$H_9C_6H_{10}$	108.6	108.3	108.0
$O_2C_1H_4$	111.0	110.8	111.5	$O_7C_6H_9$	110.7	106.1	111.5
$O_2C_1H_5$	107.2	107.4	111.5	$O_7C_6H_{10}$	111.0	111.2	111.5
$C_6C_1H_4$	109.1	109.6	109.2	$C_1C_6H_9$	109.5	109.7	109.2
$C_6C_1H_5$	110.0	110.3	109.2	$C_1C_6H_{10}$	110.3	110.8	109.2
$O_2C_1C_6$	111.3	111.1	107.2	$C_1C_6O_7$	106.7	110.5	107.2
			Torsion Angles				
$C_6C_1O_2H_3$	−53.9	−45.6	180.0	$O_2C_1C_6O_7$	60.7	57.8	180.0
$C_1C_6O_7H_8$	−170.2	76.0	180.0				
			Relative Energies[c]				
$E/kcal \cdot mol^{-1}$	0	0.034	1.06				
$E_0/kcal \cdot mol^{-1}$	0.020	0	0.702				

[a] HF/6-31G*. [b] C_i form. [c] E: ab initio relative energies. E_0: relative energies after correction for zero point vibration.

the experiments. Diffraction photographs were made in the Oregon State apparatus at nozzle-tip temperatures of 376 and 733 K. Conditions of the diffraction experiments were as follows: sector shape, r^3; photographic plates, Kodak projector slide medium contrast 8 × 10 in. developed in D19 diluted 1 × 1; ambient apparatus pressure during exposure, 1.8×10^{-6}–1.8×10^{-5} Torr; exposure times, 60−180 s; beam currents, 0.33−0.44 μA, nominal nozzle-to-plate distances, 750 cm ("long camera"), 30 cm ("middle camera"); nominal electron wavelengths 0.058 Å accurately determined by voltage calibration against gaseous CO_2 ($r_a(C=O) = 1.1646$ Å and $r_a(O\cdots O) = 2.3244$ Å). Four long-camera plates and three middle-camera plates from both the high- and low-temperature experiments were chosen for analysis. Data over the ranges $2.00 \le s/Å^{-1} \le 13.75$ and $2.00 \le s/Å^{-1} \le 14.00$, respectively, were obtained for the low- and high-temperature experiments from the long camera, and correspondingly the ranges $8.00 \le s/Å^{-1} \le 33.75$ and $7.00 \le s/Å^{-1} \le 33.00$ from the middle camera. The data interval was $\Delta s = 0.25$ Å^{-1}. Procedures used for obtaining the total scattered intensities (s^4I_t) and the molecular intensities ($sI_m(s)$) have been described.[15,16] Figure 2 shows the curves of the scattered intensities and the final backgrounds from the lower temperature experiment. The corresponding curves for the higher temperature experiment are found in the Supporting Information. Figure 3 shows

the experimental radial distribution of distances at both temperatures calculated with use of theoretical intensity data from the final models for the unobserved or uncertain range $s/Å^{-1} \le 2.75$. The electron scattering amplitudes and phases for these and other calculations were taken from tables.[17]

Structure Analysis. There are ten possible conformers of EG, exclusive of enantiomers, all of which have similar bond distances and bond angles. It is not possible to measure all these parameters as independent entities by GED alone, so one seeks auxiliary data from other sources that will either allow a substantial simplification of the problem or provide constraints on the GED parameters that could otherwise not be refined. One finds these simplifications and/or constraints in the results of theoretical calculations and in the other experimental results from vibrational and rotational spectroscopy.

Molecular Orbital Calculations. We carried out ab initio optimizations for all ten conformers of EG at the HF/6-31G* level with the program SPARTAN.[18] (Similar calculations at this and other levels had already been carried out,[12,13] but not all the results needed for our work were available.) These calculations yielded predictions of the conformer abundances through their relative energies and thus of the relative importance of each conformer in the make-up of the system.

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(17) Ross, A. W.; Fink, M.; Hilderbrandt, R. L. *International Tables for Crystallography*; International Union of Crystallography; Kluwer: Boston, Dordrecht, London.
(18) Wavefunction, Inc., 18401 Von Karman #370, Irvine, CA 92715.

Table 3.   Internal Coordinates for the g^-Ga and g^-Gg Conformers of Ethane-1,2-diol[a]

$S_1 = \Delta r_{78}$	OH str
$S_2 = \Delta r_{23}$	OH str
$S_3 = 1/\sqrt{2}\Delta(r_{14} - r_{15})$	CH asym str
$S_4 = 1/\sqrt{2}\Delta(r_{69} - r_{610})$	CH asym str
$S_5 = 1/\sqrt{2}\Delta(r_{14} + r_{15})$	CH sym str
$S_6 = 1/\sqrt{2}\Delta(r_{69} + r_{610})$	CH sym str
$S_7 = 1/\sqrt{40}\Delta(4\alpha_{415} - \beta_{214} - \beta_{215} - \beta_{614} - \beta_{615} + 4\alpha_{9610} - \beta_{769} - \beta_{7610} - \beta_{169} - \beta_{1610})$	CH$_2$ scis
$S_8 = 1/\sqrt{40}\Delta(4\alpha_{415} - \beta_{214} - \beta_{215} - \beta_{614} - \beta_{615} - 4\alpha_{9610} + \beta_{769} + \beta_{7610} + \beta_{169} + \beta_{1610})$	CH$_2$ scis
$S_9 = 1/\sqrt{8}\Delta(\beta_{214} + \beta_{215} - \beta_{614} - \beta_{615} + \beta_{769} + \beta_{7610} - \beta_{169} - \beta_{1610})$	CH$_2$ wag
$S_{10} = 1/\sqrt{8}\Delta(\beta_{214} + \beta_{215} - \beta_{614} - \beta_{615} - \beta_{769} - \beta_{7610} + \beta_{169} + \beta_{1610})$	CH$_2$ wag
$S_{11} = \Delta r_{12}$	CO str
$S_{12} = \Delta r_{67}$	CO str
$S_{13} = \Delta r_{16}$	CC str
$S_{14} = 1/\sqrt{2}\Delta(\alpha_{123} + \alpha_{678})$	COH sym bend
$S_{15} = 1/\sqrt{2}\Delta(\alpha_{123} - \alpha_{678})$	COH asym bend
$S_{16} = 1/\sqrt{8}\Delta(\beta_{214} - \beta_{215} - \beta_{614} + \beta_{615} + \beta_{769} - \beta_{7610} - \beta_{169} + \beta_{1610})$	CH$_2$ twist
$S_{17} = 1/\sqrt{8}\Delta(\beta_{214} - \beta_{215} - \beta_{614} + \beta_{615} - \beta_{769} + \beta_{7610} + \beta_{169} - \beta_{1610})$	CH$_2$ twist
$S_{18} = 1/\sqrt{8}\Delta(\beta_{214} - \beta_{215} + \beta_{614} - \beta_{615} + \beta_{769} - \beta_{7610} + \beta_{169} - \beta_{1610})$	CH$_2$ rock
$S_{19} = 1/\sqrt{8}\Delta(\beta_{214} - \beta_{215} + \beta_{614} - \beta_{615} - \beta_{769} + \beta_{7610} - \beta_{169} + \beta_{1610})$	CH$_2$ rock
$S_{20} = 1/\sqrt{2}\Delta(\alpha_{216} - \alpha_{167})$	CCO asym bend
$S_{21} = \Delta\tau_{6123}$	CCOH$_3$ torsion
$S_{22} = 1/\sqrt{2}\Delta(\alpha_{216} + \alpha_{167})$	CCO sym bend
$S_{23} = \Delta\tau_{1678}$	CCOH$_8$ torsion
$S_{24} = \Delta\tau_{2167}$	C-C torsion

[a] Atom numbering from Figure 1.

Table 4.   Values of Scale Factors and SQM (HF/6−31G*) Quadratic Force Constants for the g^-Ga Conformer of Ethane-1,2-diol[a,b]

scale factors		F_1 / F_{13}	F_2 / F_{14}	F_3 / F_{15}	F_4 / F_{16}	F_5 / F_{17}	F_6 / F_{18}	F_7 / F_{19}	F_8 / F_{20}	F_9 / F_{21}	F_{10} / F_{22}	F_{11} / F_{23}	F_{12} / F_{24}
0.791(2)	F_1	7.523											
	F_2	0.001	7.422										
0.820(2)	F_3	-0.001	0.014	4.683									
	F_4	0.005	0.003	-0.011	4.598								
	F_5	-0.004	-0.023	-0.095	-0.011	4.802							
	F_6	-0.001	0.001	-0.008	0.017	0.016	4.729						
0.774(4)	F_7	0.006	-0.004	-0.000	-0.003	0.060	0.070	0.561					
	F_8	-0.005	-0.001	0.005	-0.002	0.073	-0.082	0.004	0.559				
0.763(7)	F_9	-0.023	0.008	-0.016	-0.006	-0.021	-0.018	-0.020	-0.001	0.706			
	F_{10}	0.019	-0.004	0.008	-0.015	0.001	-0.002	-0.002	-0.023	-0.014	0.684		
0.774(11)	F_{11}	-0.010	0.022	0.060	0.009	0.280	0.020	-0.130	-0.125	0.264	0.325	5.203	
	F_{12}	-0.032	-0.018	0.009	-0.018	0.016	0.301	-0.126	0.118	0.268	-0.319	0.042	4.946
0.836(25)	F_{13}	-0.009	-0.021	0.010	0.002	0.092	0.074	-0.131	-0.013	-0.255	-0.004	0.240	0.222
		4.339											
0.802(10)	F_{14}	0.068	0.111	-0.013	0.002	0.019	-0.003	-0.006	-0.021	0.010	0.024	0.235	0.215
		0.012	0.735										
	F_{15}	-0.068	0.110	-0.009	0.005	0.013	-0.011	-0.011	-0.004	0.034	0.023	0.222	-0.189
		-0.036	0.033	0.706									
0.824(18)	F_{16}	-0.001	-0.023	-0.044	-0.049	-0.008	0.000	0.003	-0.002	0.048	0.002	0.042	0.035
		-0.042	-0.026	-0.039	0.742								
	F_{17}	0.013	-0.013	-0.027	0.029	-0.002	-0.010	-0.001	-0.017	-0.001	-0.029	-0.033	0.039
		0.000	-0.018	-0.040	-0.004	0.658							
0.811(15)	F_{18}	-0.006	-0.026	0.117	0.106	0.002	0.011	-0.014	-0.006	-0.025	-0.003	-0.033	-0.046
		0.013	-0.041	-0.011	0.093	0.003	0.914						
	F_{19}	-0.003	-0.033	0.085	-0.074	-0.020	0.016	-0.007	0.012	-0.005	0.036	0.052	-0.052
		0.003	-0.037	-0.028	0.006	0.145	0.037	0.809					
0.814(22)c	F_{20}	-0.055	-0.020	0.059	-0.062	-0.064	0.067	-0.002	-0.010	0.012	-0.015	0.282	-0.277
		-0.034	-0.073	0.065	0.006	-0.136	0.029	0.130	1.394				
0.580(24)	F_{21}	-0.003	-0.016	0.003	-0.009	-0.002	0.002	-0.001	-0.003	0.000	-0.005	-0.002	-0.005
		-0.002	0.004	0.005	0.004	0.001	0.012	0.017	-0.002	0.052			
0.814(22)c	F_{22}	0.042	-0.036	-0.046	-0.054	-0.050	-0.058	-0.026	-0.004	-0.110	0.026	0.095	0.232
		0.348	0.003	-0.109	0.152	-0.009	-0.093	0.017	-0.026	0.000	1.231		
0.844(42)	F_{23}	0.006	0.002	0.000	0.002	-0.001	0.007	0.003	0.001	0.003	-0.002	0.010	-0.017
		-0.007	0.008	0.008	-0.010	0.011	0.011	-0.005	0.016	0.001	-0.011	0.033	
1.076(80)	F_{24}	-0.009	-0.011	0.016	0.009	0.010	-0.001	-0.009	-0.006	-0.022	0.005	-0.069	-0.020
		0.078	-0.006	-0.010	-0.067	0.003	-0.072	-0.001	-0.014	0.038	-0.014	-0.001	0.250

[a] Diagonal values are theoretical ones multiplied by the scale constants k; off-diagonal values by $(k_ik_j)^{1/2}$. [b] Units are aJ/Å^2 for stretches, aJ/rad^2) for bends; coordinates are those of Table 3. [c] Refined together as a group.

Certain distance and angle differences were obtained from the optimized structures and used in the formulation of some of the parameters to be refined. Theoretical vibrational wavenumbers and Cartesian force constants were also calculated for the g^-Ga, g^-Gg, and aAa forms, which for reasons given later were eventually chosen to represent the the entire EG system. Table 1 lists the calculated torsion angles, relative

Table 5. Wavenumber Fits (cm^{-1}) for Isotopes of the g$^-$Ga Conformer of Ethane-1,2-diol

	OH,OH		^{18}OH,^{18}OH		OD,OD		CD$_2$,CD$_2$	
	obs	diff[a]	obs	diff[a]	obs	diff[a]	obs	diff[a]
$\tilde{\nu}_1$	3667.0	−1.5	3655.5	−0.9	2970.0	0.9	3666.0	−2.5
$\tilde{\nu}_2$	3629.0	−13.6	3618.0	−12.8	2940.0	11.3	3629.5	−13.0
$\tilde{\nu}_3$	2968.0	−0.8	2969.0	0.2	2888.0	−8.4	2246.0	43.2
$\tilde{\nu}_4$	2940.0	11.3	2939.0	10.3	2882.0	−6.2	2195.0	19.0
$\tilde{\nu}_5$	2891.0	−5.3	2889.0	−7.3	2706.0	34.1	2137.0	21.1
$\tilde{\nu}_6$	2885.0	−3.1	2885.0	−3.1	2678.0	26.7	2106.5	6.6
$\tilde{\nu}_7$	1468.0	−1.7	1468.0	−1.6	1465.5	−3.0	1313.0	−11.8
$\tilde{\nu}_8$	1459.5	0.4	1459.0	0.0	1457.5	−1.4	1302.5	−6.3
$\tilde{\nu}_9$	1415.5	−8.6	1413.5	−7.8	1399.5	−3.6	1165.0	−6.9
$\tilde{\nu}_{10}$	1383.0	−1.7	1381.0	1.2	1370.0	12.3	1123.0	−22.0
$\tilde{\nu}_{11}$	1350.0	−3.1	1347.0	−4.0			1110.0	5.1
$\tilde{\nu}_{12}$	1271.0	−2.0	1262.5	−7.0			1064.0	7.3
$\tilde{\nu}_{13}$	1246.0	−6.1	1243.0	−6.0	1144.0	−15.5	980.5	18.4
$\tilde{\nu}_{14}$	1163.0	20.9	1161.5	21.0	1096.0	2.8	963.0	21.0
$\tilde{\nu}_{15}$	1100.0	−3.9	1091.0	−5.9	1087.5	6.0	942.5	13.2
$\tilde{\nu}_{16}$	1069.0	−12.8	1058.0	−7.1	958.0	−7.5	894.0	−18.9
$\tilde{\nu}_{17}$	1041.5	2.1	1026.5	2.1	915.0	−2.8		
$\tilde{\nu}_{18}$	880.0	3.5	870.5	2.5	836.0	13.5	748.0	9.7
$\tilde{\nu}_{19}$	865.0	5.9	854.5	5.1	814.5	12.7	739.0	10.6
$\tilde{\nu}_{20}$	514.0	0.7	507.0	1.1	504.0	5.7	441.5	−2.6
$\tilde{\nu}_{21}$	361.0	2.5	355.0	2.3	342.5	7.8	351.0	1.1
$\tilde{\nu}_{22}$	309.0	−8.0	306.0	−7.9	249.0	−0.4	282.5	−5.6
$\tilde{\nu}_{23}$	268.0	0.4	267.0	1.0			264.0	−0.2
$\tilde{\nu}_{24}$	185.0	−3.8	185.0	3.1			183.0	7.1

[a] Observed minus calculated. Calculated values from the force field of Table 4.

Table 6. Rotational Constants (in MHz) for Ethane-1,2-diol

isotope	A_0; B_0; C_0	A_z; B_z; C_z	σ^a	$\Delta B_z^{376 \ b}$	$\Delta B_z^{733 \ b}$
	g$^-$Ga				
OHOH	15363.280	15368.100	17.33	18.569	31.604
	5587.098	5579.888	10.00	−5.881	−1.757
	4613.537	4611.407	10.00	0.281	−2.104
ODOD	14394.114	14404.514	17.33	−40.186	−39.178
	5276.246	5270.496	10.00	10.734	10.259
	4323.647	4322.217	10.00	5.476	0.544
OHOD	15126.955	15134.515	17.33	−4.169	26.614
	5311.085	5305.145	10.00	0.364	−4.558
	4412.157	4410.497	10.00	2.919	−2.964
ODOH	14620.287	14628.437	17.33	−19.048	−36.342
	5548.481	5541.501	10.00	4.826	13.877
	4517.854	4515.994	10.00	2.702	1.141
CD$_2$CH$_2$	13562.625	13567.705	17.33	20.417	24.136
	5356.147	5350.027	10.00	−3.707	−8.163
	4432.101	4430.241	10.00	−1.439	−12.714
CH$_2$CD$_2$	13509.256	13514.256	17.33	27.532	24.324
	5362.112	5356.132	10.00	1.603	17.135
	4428.858	4426.918	10.00	4.761	3.819
	g$^-$Gg				
CD$_2$CH$_2$	13438.063	13439.773	17.33	18.298	29.583
	5307.625	5301.455	10.00	13.882	22.461
	4410.672	4408.392	10.00	−0.863	−11.966
CH$_2$CD$_2$	13403.429	13404.849	17.33	7.846	18.124
	5312.809	5306.629	10.00	9.906	18.577
	4408.148	4405.908	10.00	−4.495	−15.291

[a] Used to establish weighting $(1/\sigma^2)$ relative to diffraction data. [b] Equal to $B_z^{obs} - B_z^{calc}$.

energies, and mole fractions for all conformers calculated with assumption of a Boltzmann distribution. Table 2 contains distance and angle values for the three conformers mentioned above.

Normal Coordinate Calculations. In its latest version, the program ASYM40[19] allows the refinement of scale factors applied to theoretical, nonredundant sets of internal force constants in order to bring the calculated wavenumbers into best agreement with experiment. We applied this program to the ab initio results for the g$^-$Ga conformer: first to generate the nonredundant internal force constants and then to refine 13 scale factors for groups of these constants to fit the experimental (IR[7]) wavenumber assignments of four isotopic species OH,OH; ^{18}O^{18}O; OD,OD; and CD$_2$CD$_2$. The set of scale factors was then applied to the theoretical sets of internal force constants for the g$^-$Gg and aAa forms to generate plausible scaled quantum mechanical (SQM) force fields for them based on the structures shown in Table 2. The nonredundants set of internal or "symmetry" coordinates for g$^-$Ga are given in Table 3, the corresponding force constants and scale factors in Table 4, and the wavenumber fits provided by this force field in Table 5. Force fields for the other two conformers are similar and are found in the Supporting Information.

As mentioned in the Introduction, there are available eight sets of ground state rotational constants for EG from microwave spectroscopy.[9−11] These data are of great importance, especially in helping to determine the several bond and torsion angles affecting the positions of hydrogen atoms. However, in order to use them properly with the GED data it was necessary to convert the B_0's to B_z and to be able to express the GED parameters in terms of $r_\alpha^0 = r_z$; *i.e.*, to take account of differences between the effects of vibrational averaging at 0 K and at the temperatures of the GED experiments.[20] The calculations for these conversions were again done with ASYM40 as well as calculations of theoretical vibrational amplitudes, some of which were used to provide estimates for vibrational amplitude parameters that cannot be measured. Table 6 contains the observed and converted rotational constants resulting from this procedure.

System Model. Any model that includes representations of all the possible EG conformers would be very complicated. However, Table

(19) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1994**, *160*, 117.
(20) For an excellent account of the interrelation of these quantities, see: Robiette, A. In *Molecular Structure by Diffraction Methods*; Specialist Periodical Reports; The Chemical Society: London, 1973; Vol. 1, Chapter 4.

1 reveals several important features of the EG system that simplifies the design of a model. First, except for the last three, all the non-hydrogen-bonded conformers have an anti arrangement of the molecular skeleton. The three exceptions are predicted to be present in negligible amounts at 376 K, and even at 733 K to constitute only about 8 mol %, which suggests they could be safely ignored as components of the model. Second, since the g$^-$Gg$^-$ form likely constitutes only a small proportion of the hydrogen-bonded type of conformer, and especially since its heavy-atom structure is similar to that of g$^-$Gg, it need not be specifically included as a part of the model. Third, the predicted mole fraction sum of the four anti forms is relatively small, and because they differ essentially only in the CCOH torsion angles that cannot be measured by GED alone (there are no rotational constants for them), the presence of these forms should be adequately represented by just one of the molecules. Adoption of these simplifications led to a model for refinement that consisted of a mixture of two gauche forms with intramolecular hydrogen bonds, g$^-$Ga and g$^-$Gg, and an anti form, aAa. Despite the reduction in the number of conformers from ten to three, however, there remained many different bond distances and bond angles of similar type, so that the parameters required for definition of the model numbered far too many to be refined independently. The problem was handled by forming averages and differences of similar distances and angles, drawing again on the ab initio results mentioned above for certain components of the differences. For example, the four parameters $\langle r(\text{O}-\text{H})\rangle$, $\langle r(\text{C}-\text{H})\rangle$, $\langle r(\text{C}-\text{O})\rangle$, and $r(\text{C}-\text{C})$, were chosen to represent the lengths of the different types of bonds for the system. The individual bond values that comprise each of these averages were constrained to reflect their theoretical *differences* as obtained from the ab initio optimizations. The remaining parameters of the system occur in three sets, one pertaining to each conformer. For g$^-$Ga and g$^-$Gg the sets were the same: $\langle \angle\text{CCO}\rangle = [\angle(\text{C}_6\text{C}_1\text{O}_2) + \angle(\text{C}_1\text{C}_6\text{O}_7)]/2$; $\Delta\angle(\text{CCO}) = \angle(\text{C}_6\text{C}_1\text{O}_2) - \angle(\text{C}_1\text{C}_6\text{O}_7)$; $\langle \angle\text{COH}\rangle = [\angle(\text{C}_1\text{O}_2\text{H}_3) + \angle(\text{C}_6\text{O}_7\text{H}_8)]/2$; $\langle \angle(\text{RC}_{1,6}\text{H})\rangle = [\langle \angle(\text{RC}_1\text{H})\rangle + \langle \angle(\text{RC}_6\text{H})\rangle]/2$ (here each of the last two terms is the average of the two CCH and two OCH angles at the carbon atoms); $\Delta\langle \angle(\text{RC}_{1,6}\text{H})\rangle = \langle \angle(\text{RC}_1\text{H})\rangle - \langle \angle(\text{RC}_6\text{H})\rangle$; and three torsion angles $\angle\text{CCOH}_3$, $\angle(\text{OCCO})$, and $\angle\text{CCOH}_8$. For the aAa form the remaining parameters were $\angle(\text{CCO})$, $\angle(\text{COH})$, and $\langle \angle\text{RC}_{1,6}\text{H})\rangle = [\angle(\text{RC}_1\text{H}) + \angle(\text{RC}_6\text{H})]/2$. The theoretical distance and angle values used in formulating the various averages and differences in these parameter definitions may be deduced from the data of Table 2.

Table 7. Structural Parameter Values (r_α^0/Å; $\angle_\alpha$/deg) for Ethane-1,2-diol at 376 and 733 K[a]

	conformer											
	376 K						733 K					
	g⁻Ga		g⁻Gg		aAa		g⁻Ga		g⁻Gg		aAa	
⟨r(O−H)⟩	{ 0.961		0.962		0.960 } (8)		{ 0.945		0.946		0.944 } (6)	
⟨r(C−H)⟩	{ 1.118		1.117		1.118 } (6)		{ 1.128		1.128		1.129 } (6)	
⟨r(C−O)⟩	{ 1.424		1.424		1.424 } (1)		{ 1.427		1.427		1.427 } (2)	
r(C−C)	{ 1.517		1.521		1.517 } (5)		{ 1.529		1.533		1.529 } (7)	
⟨∠(CCO)⟩	109.3 (4)		111.2 (7)		110.5 (30)		109.0 (6)		110.6 (8)		110.2 (21)	
Δ∠(CCO)	5.6 (34)		0.5 (21)	*0.6*	[0.0]		11.2 (38)		0.5 (24)	*0.6*	[0.0]	
⟨∠(COH)⟩	105.8 (27)		108.2 (21)	*108.8*	109.6 (21)	*109.7*	105.1 (35)		108.2 (23)	*108.8*	109.7 (24)	*109.7*
⟨∠(RC$_{1,6}$H)⟩	109.1 (10)		108.0 (11)	*109.5*	110.5 (21)	*110.4*	107.6 (11)	*109.9*	106.7 (12)	*109.5*	110.6 (23)	*110.4*
Δ∠(RC$_{1,6}$H)	2.0 (41)		0.0 (19)	*−0.1*	[0.0]		2.6 (46)		0.0 (21)	*−0.1*	[0.0]	
∠(CCOH$_3$)	−54.0 (21)	*−53.9*	−45.6 (21)	*−45.6*	[180.0]		−53.9 (24)	*−53.9*	−45.5 (24)	*−45.6*	[180.0]	
∠(OCCO)	60.7 (18)		57.5 (30)		[180.0]		60.7 (23)		58.2 (31)		[180.0]	
∠(CCOH$_8$)	−169.7 (20)	*−170.2*	76.0 (21)	*76.0*	[180.0]		−170.3 (23)	*−170.2*	76.2 (24)	*76.0*	[180.0]	
X[b]	{ 0.58		0.34		0.08 } (7)		{ 0.40		0.42		0.18 } (11)	
R(GED)[c]	0.048						0.058					
R(B$_z$)[c]	0.001						0.002					

[a] Where used, predicate values are in italics. Quantities in square brackets were assumed, those in curly brackets were refined as groups. Estimated 2σ uncertainties are in parentheses. [b] Mole fraction. [c] Quality of fit. For GED data: $R = [\sum_i w_i \Delta_i^2/w_i(s_i I_i(\text{obsd})^2]^{1/2}$ with $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calc})$; for MW data: $R = [\sum_i w_i \Delta_i^2/w_i(B_z(\text{obsd})^2]^{1/2}$ with $\Delta_i = B_z(\text{obsd}) - B_z(\text{calc})$.

In addition to the structural parameters mentioned above, there exists a large number of vibrational amplitude parameters for which there is no hope of refinement except through the formation of groups consisting of similar types of terms. As is customary in our laboratory, the differences between member-amplitudes of each of these groups were kept at values determined by the normal coordinate calculations based on the SQM force fields. (The amplitude groupings can be found in Table 8.)

Structure Refinements. The parameters to be refined comprised the four sets of structure-defining ones (the average bond distances for all three conformers; the average bond angles, average angle differences, and torsion angles for g⁻Ga and for g⁻Gg; and ∠(CCO) and the bond angles involving hydrogen atoms for aAa), a total of 23 as well as a composition parameter X (the mole fraction of the hydrogen-bonded species) and four group-amplitude parameters. The data on which the refinements were based were those from GED and the B_z rotational constants seen in Table 6. The latter were especially valuable for helping to locate the hydrogen atoms, particular the H$_o$ atoms involved in possible hydrogen bonding. The proper choice for the relative weighting of these two types of data is uncertain; we chose them such that weighted sum of squares of the residuals was about 10 times greater for the GED data at the end of the refinements. Some of the parameters involving hydrogen atoms, particularly angle parameters, were found to be unstable. Refinement of these parameters was aided by the use of reasonable predicate values[21] by which their movement was restrained to a degree determined by the weighting of these values. The weights assigned to predicates are arbitrary and for the case at hand were chosen so as to achieve reasonable parameter stability during refinement. Each was given a weight of $1/(0.01)^2$; within limits changes in the weighting did not materially affect the converged values. Under the conditions described the refinements converged smoothly to the parameter values listed in Tables 7 and 8. Table 9 is a correlation matrix for the low-temperature structural parameters; the correlation matrix for the higher temperature parameters is similar.

Discussion

We believe our results provide the most complete description of the structure and composition of the gaseous EG system presently available. It could perhaps be argued that the quantitative aspect of the fit provided by our model to the MW data (Table 6) could be better in view of the precision of this type of measurement. However, the approximations built into

(21) Bartell, L. S. In *Molecular Structure by Diffraction Methods*; Specialist Periodical Reports, The Chemical Society: London, 1975; Vol. 5, Chapter 4.

the various corrections designed to bring about compatibility between the MW and GED data (*i.e.*, B_0 to B_z and r_a to r_z) are necessarily imprecise and lead to compomises in the fitting. We judge the *simultaneous* fit of our model to both the GED and MW data to be very good.

As is seen from Table 5, the SQM force field of Table 4 affords a good fit to the observed wavenumbers of the several isotopomers of the g⁻Ga conformer of EG. Although the main reasons for our normal coordinate analysis of EG were to obtain the distance and rotational constant corrections as well as estimates of some of the vibrational amplitudes used in the structure determination, the results themselves have some interest. The values of the 13 scale constants are seen in Table 4, and the groups of force constants to which they apply are indicated by the curly brackets. The compositions of the groups were based on the similarities among the set of nonredundant internal coordinates given by the assignments listed in Table 3. The refined scale factors have values consistent with experience—about 0.8, except for F_{21} at about 0.6 that describes the C−O torsion affecting the hydrogen bond, and F_{24} at about 1.1 that describes the C−C torsion. Normal coordinate analysis of EG has also been done by Frei et al.[7] With a few exceptions, detailed comparisons of theirs and our results are not readily made because of slight differences in the molecular geometries employed and because of the different definitions of the nonredundant coordinates. However, the coordinates for the O−H and C−C stretches and the C−C and C−O torsions are similar in the two studies, and the force-constant values are in excellent agreement. These values from our/their work are 7.422/7.393 (O−H$_{H−bond}$ str), 7.523/7.561 (O−H str), 4.339/4.237 (C−C str), 0.250/0.234 (C−C tors), 0.052/0.050 (C−O$_{H−bond}$ tors), and 0.033/0.029 (C−O tors).

Although our model for the EG system contains a number of assumptions and approximations, we believe that the results of Tables 7 and 8 provide an accurate picture of the structures of the major system components and of the amount of hydrogen bonding that takes place at the two experimental temperatures. Justification for a model consisting of only three of the total of ten possible conformers was given in an earlier section; the question it poses is the extent to which the results are biased by the absence of the remaining species. The answer to this question is suggested by comparison of the values given in Table 2. Both the theoretical bond distance and bond angle values

Table 8. Selected Interatomic Distances (r_g/Å) and Vibrational Amplitudes (*l*/Å) for Ethane-1,2-diol[a]

	conformer					
	376 K			733 K		
	g⁻Ga	g⁻Gg	aAa	g⁻Ga	g⁻Gg	aAa
$\langle r(\text{O–H})\rangle$[b]	{ 1.001	0.999	1.007 } (8)	{ 0.985	0.983	0.991 } (6)
$\langle r(\text{C-H})\rangle$[b]	{ 1.133	1.133	1.133 } (6)	{ 1.144	1.144	1.144 } (6)
$r(\text{C}_1\text{–O}_2)$	⌠1.422	1.422	1.430 ⌉ (2)	⌠1.427	1.426	1.435 ⌉ (2)
$r(\text{C}_6\text{–O}_7)$	⌡1.433	1.434	⌡	⌡1.438	1.439	⌡
$r(\text{C}_1\text{–C}_6)$	{ 1.520	1.524	1.519 } (5)	{ 1.535	1.539	1.534 } (7)
$r(\text{C}_1\cdot\text{O}_7)$	2.365 (27)	2.435 (18)	2.422 (42)	2.329 (30)	2.441 (21)	2.430 (30)
$r(\text{C}_6\cdot\text{O}_2)$	2.439 (25)	2.433 (18)		2.488 (29)	2.438 (20)	
$r(\text{O}_2\cdots\text{O}_7)$	2.813 (6)	2.859 (9)	3.669 (56)	2.813 (8)	2.862 (10)	3.677 (40)
$\langle r(\text{C·H}_\text{O})\rangle$[b]	1.942 (32)	1.970 (25)	1.991 (25)	1.925 (41)	1.960 (27)	1.982 (28)
$\langle r(\text{O·H}_\text{C})\rangle$[b]	2.088 (28)	2.064 (18)	2.122 (26)	2.081 (32)	2.058 (20)	2.134 (29)
$\langle r(\text{C·H}_\text{C})\rangle$[b]	2.165 (29)	2.163 (18)	2.170 (28)	2.165 (33)	2.165 (20)	2.191 (31)
$r(\text{O}_7\cdots\text{H}_4)$	2.596 (76)	2.703 (45)	2.663 (39)	2.510 (84)	2.662 (52)	2.676 (28)
$r(\text{O}_7\cdots\text{H}_5)$	3.335 (27)	3.385 (17)		3.305 (29)	3.388 (20)	
$r(\text{O}_2\cdots\text{H}_9)$	2.697 (69)	2.658 (43)		2.715 (78)	2.619 (49)	
$r(\text{O}_2\cdots\text{H}_{10})$	3.399 (25)	3.390 (15)		3.434 (30)	3.393 (18)	
$r(\text{C}_6\cdots\text{H}_3)$	3.520 (52)	2.492 (40)	3.270 (35)	2.563 (62)	2.489 (45)	3.265 (28)
$r(\text{C}_1\cdots\text{H}_8)$	3.203 (25)	2.742 (36)		3.161 (30)	2.738 (40)	
$r(\text{O}_7\cdots\text{H}_3)$[c]	2.365 (45)	2.372 (35)	4.383 (51)	2.374 (55)	2.406 (40)	4.380 (41)
$r(\text{O}_2\cdots\text{H}_8)$	3.632 (18)	3.331 (33)		3.628 (20)	3.329 (36)	
l(O–H)	⌠0.072	0.072	0.072 ⌉ (9)	⌠0.067	0.067	0.067 ⌉ (6)
l(C–H)	⌡0.082	0.082	0.082 ⌡	⌡0.077	0.077	0.077 ⌡
l(C$_1$–O$_2$)	⌠0.056	0.052	0.051 ⌉	⌠0.061	0.061	0.062 ⌉
l(C$_6$–O$_7$)	{ 0.057	0.053	} (3)	{ 0.062	0.063	} (4)
l(C$_1$–C$_6$)	⌡0.055	0.056	0.053 ⌡	⌡0.065	0.065	0.064 ⌡
l(C$_1$·O$_7$)	⌠0.071	0.071	0.074 ⌉ (9)	⌠0.086	0.085	0.091 ⌉ (12)
l(C$_6$·O$_2$)	⌡0.071	0.071	⌡	⌡0.084	0.085	⌡
l(O$_2$···×d7O$_7$)	{ 0.149	0.151 } (16)	[0.071]	{ 0.217	0.220 } (38)	[0.091]
$\langle l(\text{C·H}_\text{O})\rangle$[d]	⌠0.107	0.107	0.107 ⌉	⌠0.107	0.107	0.108 ⌉
$\langle l(\text{O·H}_\text{C})\rangle$[d]	{ 0.107	0.108	0.107 } (3)	{ 0.107	0.107	0.107 } (4)
l(C·H$_\text{C}$)[d]	⌡0.115	0.115	0.115 ⌡	⌡0.118	0.118	0.119 ⌡
l(O$_7$···H$_4$)	[0.168]	[0.164]	[0.207]	[0.209]	[0.202]	[0.269]
l(O$_7$···H$_5$)	[0.102]	[0.102]		[0.112]	[0.112]	
l(O$_2$···H$_9$)	[0.167]	[0.166]		[0.207]	[0.205]	
l(O$_2$···H$_{10}$)	[0.102]	[0.102]		[0.112]	[0.112]	
l(C$_6$···H$_3$)	[0.200]	[0.196]	[0.099]	[0.256]	[0.251]	[0.111]
l(C$_1$···H$_8$)	[0.100]	[0.200]		[0.114]	[0.258]	
l(O$_7$···H$_3$)	[0.267]	[0.259]	[0.113]	[0.356]	[0.345]	[0.130]
l(O$_2$···H$_8$)	[0.209]	[0.263]		[0.279]	[0.351]	

[a] Values in parentheses are estimated 2σ uncertainties; those in curly brackets were refined as a group, and those in square brackets were assumed. [b] Ab initio differences of distances were maintained in the model. [c] Hydrogen-bond distance. [d] Calculated amplitude differences within each average were maintained in the model.

Table 9. Correlation Matrix (×100) for Structural Parameters of Ethane-1,2-diol at 376 K

	parameter[a]	$100\sigma_\text{LS}$[b]	r_1	r_2	r_3	r_4	$\angle_5$	$\angle_6$	$\angle_7$	$\angle_8$	$\angle_9$	$\angle_{10}$	$\angle_{11}$	$\angle_{12}$	$\angle_{13}$	$\angle_{14}$	$\angle_{15}$	$\angle_{16}$	$\angle_{17}$	X
1	$\langle r(\text{O–H})\rangle$	0.275	100																	
2	$\langle r(\text{C–H})\rangle$	0.222	−31	100																
3	$\langle r(\text{C–O})\rangle$	0.035	10	−1	100															
4	$\langle r(\text{C–C})\rangle$	0.177	37	−18	13	100														
5	$\langle \angle(\text{CCO})\rangle$	15.7	−17	19	−9	−40	100													
6	$\Delta\angle(\text{CCO})$	121.	6	−3	1	3	−5	100												
7	$\langle \angle(\text{COH})\rangle$	97.1	−30	4	−17	−26	−21	8	100											
8	$\langle \angle(\text{RC}_{1,6}\text{H})\rangle$	33.7	11	−46	−13	−12	−23	−10	−45	100										
9	$\angle(\text{OCCO})$	62.8	5	−14	2	5	−90	9	31	34	100									
10	$\langle \angle(\text{CCO})\rangle$	25.2	−14	3	−15	−38	−17	−24	10	33	32	100								
11	$\Delta\angle(\text{CCO})$	73.4	<1	−1	−1	−1	−1	1	<1	3	2	<1	100							
12	$\langle \angle(\text{COH})\rangle$	72.7	−1	−4	−2	−3	3	5	−9	12	−1	−9	−1	100						
13	$\langle \angle(\text{RC}_{1,6}\text{H})\rangle$	37.4	−5	−26	−11	−12	28	10	19	−18	−27	−51	−4	−28	100					
14	$\angle(\text{OCCO})$	106.	7	2	10	16	28	22	−2	−35	−36	−93	4	7	64	100				
15	$\angle(\text{CCO})$	104.	−10	2	−12	−27	−15	−21	17	15	25	−19	−1	4	28	27	100			
16	$\angle(\text{COH})$	74.4	<1	<1	<1	<1	1	<1	<1	−1	−1	1	<1	<1	−1	−1	<1	100		
17	$\angle(\text{RC}_{1,6}\text{H})$	73.7	<1	1	1	<1	4	−4	8	−12	−5	4	<1	1	−6	−5	−2	<1	100	
18	X	2.48	−8	1	−14	1	6	−19	12	−13	−9	8	<1	<1	−5	−9	−1	1	−3	100

[a] Items 1–4 are common to all conformers; 5–9 refer to g⁻Ga, 10–14 to g⁻Gg, and 15–17 to aAa. [b] σ is the standard deviation from least squares.

shown for the conformers of the system model are highly characteristic of those for the omitted conformers as well. Since the model itself incorporates many of the theoretical differences between parameter values of the three components, it may be concluded that the refined values would not be significantly different were all possible conformers included.

The complexity of the distance spectrum of the model precluded refinement of more than a few of the more important

amplitudes of vibration (Table 8). For purposes of comparison, the theoretical values for the g⁻Ga conformer obtained with use of the force fields already described are $l(O-H) = 0.070$ Å (both temperatures), $l(C-H) = 0.079$ Å (both temperatures), $l(C-O) = 0.049$ Å (376 K) and 0.054 (733 K), $l(C-C) = 0.052$ Å (376 K) and 0.058 (733 K), $l(C \cdot O) = 0.073$ Å (376 K) and 0.092 Å (733 K), $l(O \cdots O) = 0.209$ Å (376 K) and 0.279 Å (733 K).

Because of the large relative uncertainties that attach to the measurements of the conformational composition, neither they nor the thermodynamic quantities derivable from them are very reliable. It is nevertheless pleasing that the theoretical and experimental values for the composition are in good agreement. The theoretical mole fraction of the non-hydrogen-bonded species based on those components comprising our model (conformers 1, 2 + 3, and 4−7 of Table 1) is 0.07 at 376 K and 0.23 at 733 K, and the corresponding experimental ones (Table 7) are 0.08 ($\sigma = 4$) and 0.18 ($\sigma = 6$). These data permit some rough estimates of the free energy differences between the hydrogen-bonded (G) and non-hydrogen-bonded (A) forms. From $\Delta G° = -Rt \ln K$ and with $K = X_A/X_G$ one obtains $\Delta G°_{376} = 1.8$ (5) kcal/mol and $\Delta G°_{733} = 2.2$ (4) kcal/mol for the reaction G → A, values that correspond to an internal energy difference, $\Delta E°$, of 1.4 (5) kcal/mol. (Here quantities in parentheses are estimated standard deviations.) The corresponding theoretical values are $\Delta G°_{376} = 1.9$ kcal/mol, $\Delta G°_{733} = 1.8$ kcal/mol, and $\Delta E° = 2.0$ kcal/mol.

The experimental internal energy difference of 1.4 (5) kcal/mol in EG may be taken as a rough estimate of the average energy of the internal O−H···O hydrogen bond. Similar identifications were made in the cases of ethane-1,2-diamine,[3] 2-aminoethanethiol,[22] and ethane-1,2-dithiol,[23] where the N−H···N, S−H···N, and S−H···S bond energies, respectively, were found to be 0.68 (41), 0.18 (22), and 0.41 (43) kcal/mol. This series of values, including the present one for the O−H···O bond, agrees with the conventional views about their relative strengths.

Supporting Information Available: Figure of the intensity curves from the 733 K experiments and tables of the symmetry coordinates for the aAa conformer, the force constants, and scale factors for the g⁻Gg and aAa conformers, the correlation matrix for the parameters of the 733 K experiment, and the average molecular intensities from the 376 and 733 K experiments (9 pages). See any current masthead page for ordering and Internet access instructions.

(22) Barkowski, S. L.; Hedberg, K. *J. Am. Chem. Soc.* **1987**, *109*, 6989.
(23) Barkowski, S. L.; Hedberg, K. *J. Am. Chem. Soc.* **1986**, *108*, 6898.