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Intramolecular Hydrogen Bonding, Gauche Interactions, and Thermodynamic Functions of 1,2-Ethanediamine, 1,2-Ethanediol, and 2-Aminoethanol: A Global Conformational Analysis

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The global conformational potentials of 1,2-ethanediol, 1,2-ethanediamine, and 2-aminoethanol ($X-CH_2-CH_2-Y$; X, Y = OH or NH_2) were obtained at the MP2/6-311+G(2d,p) level by scanning through the dihedral angles of the two functional groups and the carbon−carbon bond with the remaining nuclear coordinates being energy-minimized. It was found that the potentials could be represented by the direct-bond potentials between the adjacent molecular fragments and by the through-space electrostatic potentials between the vicinal and geminal fragments. Here, the through-direct-bond potentials are represented by the conventional three Fourier terms of the internal rotation angles, and the through-space potentials, which include the intramolecular hydrogen bonding between X and Y, are represented by the general functional forms of the electric dipole−dipole, dipole−quadrupole, and quadrupole−quadrupole interaction terms. The fitted electrostatic interaction strengths between the X and Y fragments are in good agreement with the predictions of the theoretical molecular fragment dipole and quadrupole moments calculated by the Hirshfeld charge population analysis. Under the present energy decomposition scheme, the intrinsic gauche interactions, which are free of the contribution of the intramolecular H-bonding, could be obtained and correlated with the group electronegativities of X and Y. The potentials were also calculated by the MM3 molecular mechanics method and compared with the present results. With the global conformation potentials, the thermodynamic functions of the molecules and also their individual conformers are calculated and compared with the gas-phase experimental thermodynamic data in the literature.

1. Introduction

It has been well-accepted that for the molecules of 1,2-ethanediol (EDO), 1,2-ethanediamine (EDA), and 2-aminoethanol (AE), the intramolecular hydrogen bond plays an important role in their conformational stabilities.[1−22] It is also well-recognized that the gauche effect may also operate in these systems, especially in the diol molecule, which could further stabilize the gauche conformer relative to the trans conformer.[10,11,16,23−26] Since the most stable conformers of these compounds are all in the gauche form, as suggested by both theoretical and experimental studies, under this conformation, the above two stabilization factors are possibly contributing to the conformation stability simultaneously. A question one would naturally pose is what would be the relative importance of these two stabilization factors. To date, a quantitative decomposition of the conformation energy into these two types of interaction energy are not available yet.

For those simple and well-studied H-bonded dimers, it is generally accepted that their major intermolecular stabilization energy could be attributed to the contribution of electrostatic interactions between molecular multipole moments.[27−30] Although there are many methods available for the partitioning of the electron density into fragment multipole moments, including the Hirshfeld partitioning scheme,[31,32] it has been shown that consistent electrostatic interaction strengths could be obtained by these various partitioning methods for some typical H-bonded dimers.[30] For the molecules with intramolecular H-bonds, in a recent global conformational potential study of 1,2-ethanediol, it was found that the general functional form of the electrostatic interactions is quite suitable for representing the intramolecular H-bonding between the two hydroxyl groups.[18] Nevertheless, owing to the complexity of the molecule, a lower order approximate form of the electrostatic interactions was employed. An unambiguous separation of the electrostatic interactions into each individual multipole component was not available in that report. In a more recent study on simpler molecular systems—methanediol, methanediamine, and aminomethanol—the problem had been clarified.[33] The study suggested that the energy contribution of the intramolecular H-bond to the global conformation potentials could be calculated by the electrostatic multipole interactions between the two functional groups according to the Hirshfeld partition method of electron density.[33] These studies demonstrated that the global conformational potentials of molecules with intramolecular H-bonds could be decomposed into the through-space electrostatic potentials and the through-direct-bond potentials. Here, the former potentials are represented by the functional forms of the electrostatic multipole interactions and the latter by the forms of the Fourier series as a function of the torsional angles.

1,2-Ethanediol, 1,2-ethanediamine, and 2-aminoethanol are prototype molecules in the class of 1,2-disubstituted ethanes with an intramolecular H-bond. Most of the theoretical studies have been focusing on the energies and structures of the locally stable conformers. To date, their global conformational potentials and the nature of the intramolecular interactions that would determine the relative conformational stabilities were only

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scarcely addressed.[17−21] In this paper, the global internal rotation potentials and the locally stable conformers of EDO, EDA, and AE were calculated. The conformational energies were then decomposed by the functional forms of the through-direct-bond and through-space interactions as developed and established in previous publications.[18,33] From the through-direct-bond interaction potentials, the intrinsic gauche energies of these systems, which are free from the contribution of the intramolecular H-bonding, were obtained. The correlation between the functional group electronegativities and the intrinsic gauche energies was explored. Based on the analytic potentials, the thermodynamic properties of the molecules and their specific conformers were also calculated and compared with the experimental results in the literature. The potentials were also calculated by the MM3 molecular mechanics method and compared with the present results.

2. Computational Procedures

2.A. Ab Initio Conformational Potentials, Atomic Charges, Atomic Dipoles, and Atomic Quadrupoles. Ab initio molecular orbital calculations were carried out by the Gaussian 92 program package.[34] For EDO, the earlier ab initio results are adapted directly for the present analysis.[17] The geometrical parameters of EDA and AE were obtained at the MP2(fu)/6-31G* and MP2(fu)/6-31G(2d,p) levels, respectively. The energies were all calculated up to the MP2(fu)/6-311+G(2d,p) level. For comparisons, representative minimum energy paths were also calculated by the molecular mechanics package MM3(94).[35−37] All standard force field parameters were used as supplied.

The conformational notations of these three molecules follow the convention in the literature.[5] The conformation of the amino group is assigned according to the dihedral angle of the lone-pair electrons (L). All the possible locally stable conformers were calculated, and their corresponding geometric parameters, harmonic vibrational frequencies, and energies were obtained. The minimum energy paths along the dihedral angle XC−CY, in which X and Y are in the general gauche and/or trans position, were calculated. These fully optimized minimum energy paths served as the standards for comparison among the ab initio, the fitted, and the MM3 potentials.

The global conformation potential was obtained by scanning through the three torsional angles with the remaining geometric coordinates being energy minimized. Starting from the $(0^0,0^0,0^0)$ conformation in which the first and the last values indicate the dihedral angles of HOCC for the hydroxyl group and LNCC for the amino group, respectively, and the second value indicates the dihedral angle of XC−CY, the torsional angle of X and Y was varied at an interval of 30° and that of the C−C bond was varied at an interval of 60°. By inclusion of the energy points of local minima and the minimum energy paths, a total of 138 potential points were calculated for EDO,[18] 106 points for EDA, and 155 points for AE. The theoretical atomic charges, atomic dipoles, and atomic quadrupoles were calculated by the local density functional method (Dmol)[38] with the Hirshfeld partition[31,32] at the double numerical basis functions with polarization functions. Since the molecular fragments, such as $-NH_2$, $-OH$, $-CH_2-$, instead of the individual atoms were considered in this study, the theoretical dipole and quadrupole moments of the molecular fragments were calculated from the atomic multipole moments according to their formal relations.[31,32]

2.B. General Functional Form of the Conformational Potentials. The conformational potentials of these internal rotors could be approximated by the following functional forms:[18,33]

$$V(\omega_a,\omega_b,\omega_c) = V_a(\omega_a) + V_b(\omega_b) + V_c(\omega_c) + V_o + V_{dd}(\omega_a,\omega_b) + V_{dq}(\omega_a,\omega_b) + V_{qq}(\omega_a,\omega_b) + V_{CH_2}(\omega_a,\omega_b,\omega_c) \quad (1)$$

with

$$V_{CH_2}(\omega_a,\omega_b,\omega_c) = V^a_{dd}(\omega_a,\omega_c) + V^a_{dq}(\omega_a,\omega_c) + V^a_{qq}(\omega_a,\omega_c) + V^b_{dd}(\omega_c,\omega_b) + V^b_{dq}(\omega_c,\omega_b) + V^b_{qq}(\omega_c,\omega_b) \quad (2)$$

in which ω_a and ω_b are the torsional angles of the two functional groups and ω_c is the torsional angle of XC−CY defined in the convention of their dihedral angles in the range 0°−360°. V_a, V_b, and V_b are the decoupled-rotor potential forms of X, Y, and XC−CY fragment, respectively. V_o is a constant. V_{dd}, V_{dq}, and V_{qq} are the electric dipole−dipole, dipole−quadrupole, and quadrupole−quadrupole interaction terms, respectively, between the vicinal functional groups X and Y with the origin located separately at the oxygen atom or the nitrogen atom. V_{CH_2} is the electric dipole−dipole, dipole−quadrupole, and quadrupole−quadrupole interaction terms between the hydroxyl or amino group and its geminal $-CH_2-$ group. For instance, $V^a_{dd}(\omega_a,\omega_c)$ is the dipole−dipole interaction between X and its geminal $-CH_2-$ and $V^b_{qq}(\omega_c,\omega_b)$ is the quadrupole−quadrupole interaction between Y and its geminal $-CH_2-$. In this report the summation of $V_a(\omega_a)$, $V_b(\omega_b)$, $V_c(\omega_c)$, and V_o is referred to as the decoupled-rotor potential.

Following the conventional approximation for the simple hindered torsional potentials, V_a, V_b, and V_c can be explicitly expressed as

$$V_a = \frac{1}{2}\{v_1(1 + \cos\omega_a) + v_2[1 - \cos(2\omega_a)] + v_3[1 + \cos(3\omega_a)]\} \quad (3)$$

$$V_b = \frac{1}{2}\{v_4(1 + \cos\omega_b) + v_5[1 - \cos(2\omega_b)] + v_6[1 + \cos(3\omega_b)]\} \quad (4)$$

$$V_c = \frac{1}{2}\{v_7(1 + \cos\omega_c) + v_8[1 - \cos(2\omega_c)] + v_9[1 + \cos(3\omega_c)]\} \quad (5)$$

in which the v_i's are parameters to be determined by a potential fitting procedure. For EDO and EDA, the parameters of V_a and V_b are identical because of the equivalence of the two functional groups. For the intramolecular electrostatic interactions, the general functional forms of the dipole−dipole, dipole−quadrupole, and quadrupole−quadrupole potentials expressed in terms of the internal rotation coordinates are detailed in the Appendix.

In the above conformational energy representation, the charge−dipole and charge−quadrupole interactions between the X and Y fragments were not explicitly considered in the present analysis for two reasons. First, their interaction strengths are only secondary to the other interactions for the present molecules. Second, the main components of these terms are dependent only on a single internal rotation angle, and therefore, their contributions are actually embedded in the decoupled-rotor potentials. Nevertheless, if the total intramolecular H-bond strengths instead of the conformational-dependence energies as considered in the present report were needed, these terms should be included for better accuracy.

2.C. Thermodynamic Functions. Conventional theoretical evaluations of the thermodynamic properties of these molecules were usually carried out under the approximation of the internal rotations by the harmonic oscillators. This approximation is not adequate under normal experimental temperatures.[18] In this report the global internal rotation potential may be regarded as a zeroth-order internal rotation potential decoupled from the rest of the vibrational motions. With the present global conformational potentials one could follow the general procedure of Kilpatrick and Pitzer for calculating the thermodynamic functions of the internal rotations[39−41] and then obtain the thermodynamic functions of the conformers.[18] From the vibrational normal-mode analysis of the locally stable conformers of these molecules, one could identify three low vibrational frequencies that correspond to the torsional motion along the three torsional axes. Replacing these three vibrational frequency modes with the full three torsional motions and treating the rest of the vibrational modes as harmonic oscillators, one could calculate the thermodynamic properties of these stable conformers more properly than the conventional harmonic oscillator approximation. The conformations considered here are defined in the classical configuration space. The complete formulas for the thermodynamic functions of the three internal rotation motion were detailed in ref 18.

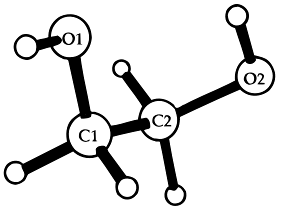
In thermodynamic function calculations of the complete molecule for the three internal rotors, the torsional frequencies were adapted directly from the ab initio harmonic vibrational frequencies of the corresponding local torsional oscillations of the most stable conformer. For the individual conformer calculations, the corresponding local torsional frequencies were adapted. The determinants of the reduced matrix of the internal rotation kinetic energy are 28.97, 23.61, and 23.94 Å^2 amu for the conformers gGg′, tGg′, and gTg of EDA, respectively, and 14.48 and 9.35 Å^2 amu for the conformers g′Gg′ and gTt of AE, respectively.[39−41] Because there is always some minor energy deviation between the ab initio potential and fitted energy for a specific local stable conformer, in practice, and also for better accuracy, the fitted potential was used solely for the calculations of the thermal corrections for the internal rotations in this report. The relative ab initio energies of the conformers were then adapted for the final complete calculations.

3. Results and Discussions

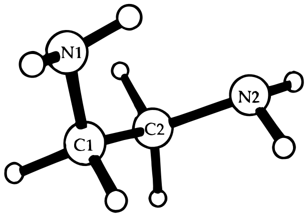
The results are discussed in the following five subsections.

3.A. Structures and Energies of the Stable Conformers. Figure 1 shows the molecular structures and the conformation notations of the most stable conformers of these three molecules: tGg′ of EDO, gGg′ of EDA, and g′Gg′ of AE. Tables 1 and 2 list the relative energies of the locally stable conformers located in this study. For AE, a locally stable g′Gg conformer was not found at the present calculation level. The energies of the stable conformers calculated by MM3 are also listed.[36,37] The zero-point energy corrections with respect to the most stable conformer are also tabulated.

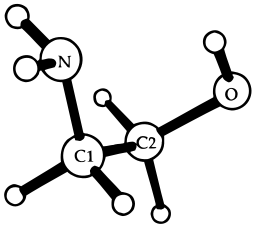
The relative ab initio conformational energies are in good agreement with the results of the more recent high-level ab initio calculations in the literature.[9,12−22] The MM3 energies of EDO and AE are generally in good agreement with the ab initio results except for a few conformation cases in which either the conformers are not locally stable or the energy deviations are larger than 0.7 kcal/mol. However, as shown in Table 1, for the case of EDA, the agreement is not satisfactory over all the conformers. This has been attributed to the overestimation of the hydrogen bonding energy of the amino groups when lone pairs are either pointing to each other or away from hydrogens.[36]



tGg'
1,2-Ethanediol



gGg'
1,2-Ethanediamine



g'Gg'
2-Aminoethanol

Figure 1. Schematic diagram and conformation notations of the most stable conformers of 1,2-ethanediol, 1,2-ethanediamine, and 2-aminoethanol.

In each of these molecules, the primary geometric parameters of the stable conformers are close to each other. For example, in the case of 2-aminoethanol, the C−C, C−O, and C−N bond distances are within 0.5%, 0.6%, and 0.5% of their average bond distances of 1.517, 1.463, and 1.422 Å, respectively; the NCC and OCC angles are both within 5° of their average bond angles of 110.7° and 110.1°, respectively. The average values of the primary geometries of the stable conformers were used as the basic geometric parameters in the following potential-fitting process.

3.B. Global Internal Rotation Potentials and the Relationship with the Theoretical Local Dipole and Quadrupole Moments of the Hirshfeld Partition. With several predetermined structural parameters, one could fit the general ab initio potential with eq 1 and obtain a set of the best-fitted parameters. Briefly, the structural parameters r, l, α, α_1, and α_2 of the molecules, whose definitions were given in the Appendix, were determined from the average primary geometries of the conformers, and the azimuthal angles of the dipole moments θ_d's of the molecular fragments were adapted from the average theoretical azimuthal angles of the corresponding dipole moments of the stable conformers. The azimuthal angles of the quadrupole moments θ_q's of the OH and NH$_2$ groups were adapted directly from the fitted values obtained in the analysis of the molecules methanediol, methanediamine, and aminomethanol.[33] Since the geminal electrostatic interaction strengths between the CH$_2$ fragment and the functional groups are expected to be weaker than the vicinal intramolecular H-bonding

TABLE 1: Relative Energies (kcal/mol) for the Conformers of 1,2-Ethanediol and 1,2-Ethanediamine

EDO[a]	tGg′	gGg′	g′Gg′	tTt	g′Tt	gTg′	tGt	gTg	gGg	tGg
HF	0.00	0.89	1.28	1.56	1.99	2.13	2.81	2.46	3.01	3.39
MP2	0.00	0.66	1.45	2.77	3.06	3.13	3.35	3.41	3.48	3.94
MM3	0.00	1.03	*b*	2.03	2.91	3.36	2.61	3.95	*b*	3.60
ZPEC[c]	0.00	0.16	−0.22	−0.39	−0.39	−0.22	−0.56	−0.24	−0.24	−0.43

EDA[d]	gGg′	tGg′	gGg	tGg	gTg′	gTg	tTt	tTg	tGt	g′Gg′
HF	0.00	0.18	0.47	0.99	0.62	0.62	0.71	0.70	1.23	3.35
MP2	0.00	0.43	0.44	1.35	1.65	1.66	1.66	1.72	1.72	3.75
MM3[e]	0.00	−0.27	−0.09	0.33	0.74	0.98	1.06	1.07	0.33	1.64
ZPEC[f]	0.00	−0.03	0.10	−0.14	−0.23	−0.27	−0.25	−0.26	−0.19	−0.57

[a] Adapted from ref 18. Energy for tGg′: HF/6-311+G(2d,p), −229.012 423 5 au; MP2/6-311+G(2d,p), −229.850 592 2 au. [b] Conformer is locally unstable. [c] Vibrational zero-point energy correction is 55.32 kcal/mol (MP2/6-31G**) for the tGg′ conformer. [d] Energy for gGg′: HF/6-311+G(2d,p), −189.337 518 4 au; MP2/6-311+G(2d,p), −190.132 636 au. [e] Adapted from ref 36. [f] Vibrational zero-point energy correction is 71.56 kcal/mol (MP2/6-31G*) for the gGg′ conformer.

TABLE 2: Relative Energies (kcal/mol) for the Conformers of 2-Aminoethanol[a]

	g′Gg′	gGt	gGg′	tGt	gGg	tGg	tGg′
HF	0.00	0.91	1.41	1.24	1.69	1.78	2.27
MP2	0.00	1.62	1.88	2.15	2.33	2.62	3.21
MM3[c]	0.00	1.49	1.30[d]	1.85	2.23	2.06	2.34
ZPEC[e]	0.00	−0.35	−0.23	−0.40	−0.27	−0.31	−0.46

	gTt	tTt	gTg	tTg	gTg′	g′Gt	g′Gg[b]
HF	1.58	1.93	1.97	2.17	2.12	4.05	
MP2	3.32	3.50	3.52	3.57	3.65	5.26	
MM3	2.57	3.17	2.87	3.44	3.25	3.69[d]	
ZPEC	−0.54	−0.56	−0.47	−0.48	−0.51	−0.70	

[a] Energies for g′Gg′: HF/6-311+G(2d,p), −209.176 681 6 au; MP2/6-311+G(2d,p), −209.993 601 5 au. [b] Conformer is locally unstable. [c] Adapted from ref 36. [d] Not reported in ref 36. [e] Vibrational zero-point energy correction is 63.53 kcal/mol (MP2/6-31G(2d,p)) for g′Gg′ conformer.

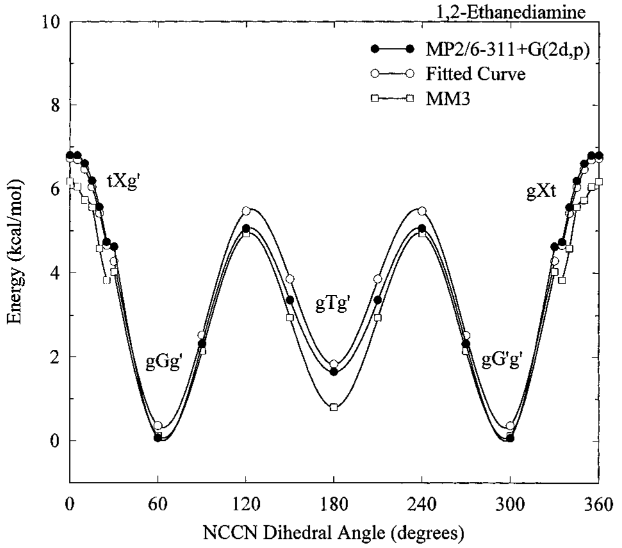


Figure 2. Minimum energy paths of 1,2-ethanediamine calculated by the ab initio method, the fitted potential, and the MM3 method.

and since also the torsional angular dependence of the vicinal charge−dipole and charge−quadrupole interactions is close to some components of these geminal interactions, the parameters of the geminal interactions turn out to be strongly dependent on each other during the fitting process. This dependency was removed by further adapting the products of the dipole moments $\mu_{CH_2}\mu_{NH_2}$ and $\mu_{CH_2}\mu_{OH}$ directly from the average theoretical values of the stable conformers. The adequacy of this substitution was supported by a previous study that has shown that the theoretical dipole moments could be employed to calculate its energy contributions to the conformational energy in the geminal electrostatic interaction cases.[32] The structural parameters and the best-fitted parameters along with their asymptotic standard errors and dependences on the parameters $\mu_{CH_2}\mu_{NH_2}$ and $\mu_{CH_2}\mu_{OH}$ set at 13.91 and 14.91 Å^3 kcal/mol, respectively, are shown in the tables in the Supporting Information section. Note that as a result of the above considerations, the fitted parameter values for the geminal electrostatic interactions are more like a set of mathematical quantities rather than the physical quantities the symbols originally intend to represent. Nevertheless, the fitted parameter values of the geminal electrostatic interactions between the two functional groups still strictly follow the physical meaning as described by the fitted potential function.

Figure 2 shows the minimum energy path of EDA with the two amino groups initially positioned in the general g and g′ conformations, respectively, and the dihedral angle of NCCN ranging from 0° to 360°. Owing to the mirror symmetry of the molecule, the potential beyond 180° is just the mirror image of that between 0° and 180°. The optimized ab initio conformations were found to switch from the initial gXg′ to tXg′, with the NCCN angles being less than 25°. The corresponding minimum energy path of the fitted and MM3 potentials was also calculated and shown in the figure. Since these two potentials have a potential barrier in the conformation transformation of gXg′ to tXg′, for comparison, their initial optimization conformations were all deliberately set to tXg′ if the NCCN angles were in the range 0°−25°. The agreement between the ab initio and fitted potentials is very good and that between the ab initio and MM3 potentials is satisfactory. The same conclusions were also observed for the global EDA potentials.

Figure 3 shows the minimum energy path of AE with both the amino and hydroxyl groups in the general g′ conformation. The ab initio optimized conformation would change from g′Xg′ to g′Xg, with the NCCO dihedral angle being less than 15° or larger than around 345°. The fitted potential also undergoes the same transformation except that the dihedral angles are around 10° and 340°. The MM3 potential possesses a potential barrier for this type of transformation, and for comparison, the conformations were artificially set to the ab initio conformations in these two regions. Similar to the EDA case, the agreement between the fitted and ab initio potentials is very good and that between the MM3 and ab initio potential is satisfactory.

For EDO, the quality of the present revised fitted potential is essentially the same as that reported in a previous publication.[18] Overall, for the present three molecules, the root-mean-square deviations of the fitted potentials are all around 0.41 kcal/mol. The absolute maximum energy deviations are around 1.2 kcal/mol for EDO in the neighborhood of (−120°, 30°, −60°), 1.3 kcal/mol for EDA in (90°, 0°, 150°), and 1.1 kcal/mol for AE in (30°, 0°, 300°).

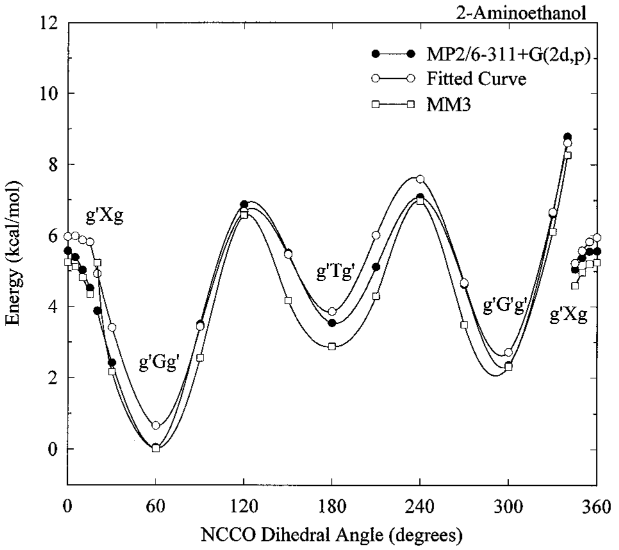


Figure 3. Minimum energy paths of 2-aminoethanol calculated by the ab initio method, the fitted potential, and the MM3 method.

Although the agreement between the ab initio and fitted energies is generally very good, there are still some minor energy-deviated points. Several possible factors could contribute to the deviations: (a) the inadequacy of the assumed cylindrical-symmetric quadrupole potential form; (b) the possible coupling terms between the electrostatic interactions and the decoupled-rotor potentials and/or between the three decoupled-rotor potentials; (c) the possible subtle variations of the conformational energy due to the minor primary structural changes in different conformations that were not properly approximated with the present potential functional forms.

As listed in the tables in the Supporting Information section, after unit conversions, the fitted dipole and quadrupole moments of the hydroxyl group of EDO are 1.35×10^{-18} esu cm and 3.21×10^{-26} esu cm^2, respectively, and those of the amino group of EDA are 1.26×10^{-18} esu cm and -2.96×10^{-26} esu cm^2, respectively. The corresponding theoretical dipole and quadrupole moments calculated by the Hirshfeld partition are 1.40×10^{-18} esu cm and 4.09×10^{-26} esu cm^2 for EDO and 1.42×10^{-18} esu cm and -3.20×10^{-26} esu cm^2 for EDA, respectively. The agreement between the theoretical and fitted dipole and quadrupole moments is excellent despite the present approximation imposed on the quadrupole moment. For the AE case, only the OH and NH_2 dipole moment product and the OH dipole and NH_2 quadrupole moment product and vice versa were obtained. Their fitted values are $\mu_{OH}\mu_{NH_2} = 2.18 \times 10^{-36}$ esu^2 cm^2, $\mu_{NH_2}q_{OH} = 5.30 \times 10^{-44}$ esu^2 cm^3, and $\mu_{OH}q_{NH_2} = -6.63 \times 10^{-44}$ esu^2 cm^3, and the corresponding theoretical values are 1.97×10^{-36} esu^2 cm^2, 6.16×10^{-44} esu^2 cm^3, and -4.32×10^{-44} esu^2 cm^3, respectively. Again, the agreement between the product values of the dipole moments is excellent and that between the dipole−quadrupole moment products is good. The transferability of the dipole and quadrupole moments of the functional groups from EDO and EDA to AE is also very good. For example, the theoretical and fitted products of the NH_2 dipole moment of EDA and the OH quadrupole moment of EDO is 5.81×10^{-44} esu^2 cm^3 and 4.04×10^{-44} esu^2 cm^3, respectively. These two values are in good agreement with the above theoretical 6.16×10^{-44} esu^2 cm^3 and the fitted 5.30×10^{-44} esu^2 cm^3 of AE. The transferability is especially good among the theoretical values. This also suggests that the discrepancies between the fitted and theoretical values may come from the uncertainties in the potential fitting procedure.

The good agreement between the theoretical and fitted dipole and quadrupole moments of the molecular fragments in the disubstituted ethanes with intramolecular H-bonds suggests that intramolecular H-bonding could be quantitatively represented by the electrostatic multipole interactions between the molecular fragments involved, and its interaction energies could be calculated directly from the atomic multipole moments obtained through the ab initio method with the Hirshfeld partition scheme. The same conclusion was also reached in a previous study on the disubstituted methanes with intramolecular H-bonds.[33]

3.C. Thermodynamic Functions of 1,2-Ethanediol, 1,2-Ethanediamine, and 2-Aminoethanol. The availability of the complete torsional potential of these three molecules enables us to calculate their thermodynamic functions with better accuracy. The three vibrational normal modes that correspond to the three torsional motions are selected and treated by the full three torsional motions defined by the torsional potential. The rest of the translational, rotational, and vibrational motions were treated by the standard statistical mechanics.[18]

Three types of the conformers were considered in these calculations: the full molecule, the xGx and xTx forms in which the conformation of the two functional groups are not fixed, and, for experimental comparisons, the specific conformers gGg′ and tGg′ of EDA. The basic geometric structures of the most stable conformers of these molecules were used for the full molecule calculations. The thermodynamic functions of EDO have been reported previously and were not repeated here.[18] Two approximation models were employed in the calculations: the conventional rigid rotor/harmonic oscillator model and the three torsional motion/rigid rotor model.

All the stable conformers have similar harmonic vibrational frequencies for the same vibrational mode except for the lowest five vibrational frequencies, which mainly correspond to the torsional motions and some low bending motions. Depending on the conformers, these four motions may intermix with each other heavily. For EDA, the three torsional motions of the conformers gGg′, tGg′, and gTg all correspond to the normal vibrational modes of υ_1, υ_2, and υ_3 . For AE, the three torsional motions of conformer g′Gg′ are identified with the υ_1, υ_2, and υ_5 normal modes. The υ_3 mode is mainly the NCCO deformation, and υ_4 is the COH bending motion. For the gTt conformer, the υ_1, υ_2, and υ_3 normal modes correspond to the three torsional motions. The presence or absence of intramolecular H-bonding affects these motions quite appreciably. One could obtain reasonably good experimental vibrational frequencies through the scaling of the harmonic vibrational frequencies by 0.95 as suggested in the literature.[42]

Table 3 shows the thermodynamic functions of the EDA molecule calculated by the conventional harmonic oscillator approximation, MM3, and the present three torsional motion models. The thermodynamic functions of the conventional and MM3 methods agree with each other to within 0.5*R* (the gas constant) over the calculated temperature 200−1000 K. On the other hand, the three torsional motion model yields a picture different from these two conventional methods. The entropy is consistently higher by about 1.5*R* in the lower temperature regime and by about 2.5*R* in the higher temperature regime, and the heat capacities of both molecules are all higher by about *R* in the low-temperature regime and are also lower by about *R* in the high-temperature regime. The enthalpies are close to those of the conventional methods, and the absolute values of the Gibbs free energies are higher by an average of 2*RT*.

Table 4 shows the thermodynamic functions of EDA in the conformations xGx and xTx calculated by the three torsional motion model. The symbol x represents a functional group that

TABLE 3: Thermodynamic Functions of 1,2-Ethanediamine[a] (cal K^{-1} mol^{-1})

T [K]	$-[g^0(T) - h^0(0)]/T$	$[h^0(T) - h^0(0)]/T$	s^0	$c_v{}^0$
		Rigid Rotor/Harmonic Oscillator Model		
200	54.25 (54.09)	10.91 (10.67)	65.16 (64.76)	13.40 (12.94)
298.15	59.03 (58.74)	13.18 (12.81)	72.21 (71.56)	18.40 (17.58)
300	59.11 (58.82)	13.22 (12.85)	72.34 (71.68)	18.51 (17.68)
400	63.26 (62.84)	15.74 (15.21)	78.99 (78.06)	24.06 (22.95)
500	67.05 (66.50)	18.32 (17.67)	85.37 (84.17)	29.16 (27.94)
600	70.62 (69.94)	20.83 (20.08)	91.44 (90.02)	33.53 (32.28)
700	74.01 (73.21)	23.19 (22.38)	97.20 (95.58)	37.23 (35.99)
800	77.26 (76.34)	25.40 (24.53)	102.65 (100.87)	40.41 (39.18)
900	80.37 (79.34)	27.44 (26.54)	107.81 (105.88)	43.16 (41.95)
1000	83.36 (82.24)	29.33 (28.40)	112.70 (110.64)	45.56 (44.38)
		MM3[b]		
200	54.51	11.71	65.68	13.73
298.15	59.39	13.46	72.85	18.65
300	59.47	13.50	72.98	18.75
400	63.69	16.00	79.69	24.18
500	67.54	18.55	86.08	29.19
600	71.14	21.02	92.16	33.51
700	74.56	23.36	97.92	37.20
800	77.82	25.55	103.37	40.38
900	80.95	27.58	108.53	43.14
1000	83.95	29.46	113.41	45.54
		Three Torsional Motion/Rigid Rotor Model		
200	57.79 (57.97)	11.69 (11.45)	69.48 (69.42)	15.17(14.71)
298.15	62.95 (63.01)	14.31 (13.94)	77.26 (76.95)	20.12 (19.30)
300	63.04 (63.09)	14.35 (13.98)	77.39 (77.08)	20.21 (19.39)
400	67.53 (67.45)	16.96 (16.44)	84.49 (83.90)	25.35 (24.26)
500	71.59 (71.39)	19.51 (18.86)	91.10 (90.24)	29.93 (28.73)
600	75.36 (75.03)	21.91 (21.16)	97.27 (96.19)	33.79 (32.55)
700	78.91 (78.45)	24.13 (23.31)	103.03 (101.77)	37.04 (35.81)
800	82.26 (81.70)	26.17 (25.30)	108.43 (107.00)	39.82 (38.60)
900	85.46 (84.79)	28.04 (27.14)	113.50 (111.93)	42.24 (41.05)
1000	88.50 (87.74)	29.77 (28.84)	118.27 (116.57)	44.36 (43.20)

[a] Ideal gaseous state. The contribution of optical isomers is included. Values in parentheses are calculated with unscaled vibrational frequencies. Reference statee is gGg′. [b] MM3(94); harmonic oscillator model. Reference state is tGg′.

TABLE 4: Thermodynamic Functions of xGx and xTx Conformers of 1,2-Ethanediamine[a] (cal K^{-1} mol^{-1})

T [K]	$-[g^0(T) - h^0(0)]/T$	$[h^0(T) - h^0(0)]/T$	s^0	$c_v{}^0$
		G Form[b]		
200	57.66 (57.83)	11.37 (11.13)	69.03 (68.96)	14.51 (14.05)
298.15	62.66 (62.72)	13.87 (13.50)	76.53 (76.22)	19.52 (18.70)
300	62.75 (62.80)	13.91 (13.54)	76.66 (76.35)	19.62 (18.80)
400	67.11 (67.03)	16.52 (15.99)	83.62 (83.03)	25.00 (23.91)
500	71.07 (70.87)	19.10 (18.45)	90.17 (89.32)	29.78 (28.57)
600	74.77 (74.44)	21.55 (20.81)	96.33 (95.25)	33.76 (32.52)
700	78.27 (77.82)	23.83 (23.01)	102.10 (100.83)	37.08 (35.84)
800	81.59 (81.02)	25.91 (25.04)	107.50 (106.07)	39.90 (38.68)
900	84.75 (84.08)	27.82 (26.92)	112.58 (111.01)	42.34 (41.15)
1000	87.78 (87.01)	29.58 (28.65)	117.36 (115.66)	44.46 (43.31)
		T Form[c]		
200	55.87 (55.93)	13.60 (13.44)	69.47 (69.37)	14.72 (14.26)
298.15	61.65 (61.61)	15.50 (15.20)	77.15 (76.82)	19.73 (18.94)
300	61.74 (61.71)	15.54 (15.24)	77.28 (76.95)	19.82 (19.03)
400	66.51 (66.37)	17.73 (17.27)	84.24 (83.64)	24.81 (23.74)
500	70.71 (70.45)	20.01 (19.42)	90.73 (89.87)	29.36 (28.18)
600	74.56 (74.18)	22.23 (21.54)	96.79 (95.71)	33.23 (32.02)
700	78.15 (77.65)	24.33 (23.56)	102.48 (101.21)	36.51 (35.29)
800	81.52 (80.92)	26.28 (25.45)	107.80 (106.38)	39.32 (38.12)
900	84.72 (84.02)	28.09 (27.22)	112.81 (111.25)	41.78 (40.60)
1000	87.77 (86.98)	29.77 (28.87)	117.54 (115.85)	43.93 (42.78)

[a] Ideal gaseous state; three-torsional-motion/rigid-rotor model. Values in parentheses are calculated with unscaled vibrational frequencies. [b] Reference state is gGg′. The contribution of optical isomer is included. [c] Reference state is gTg.

is not in a fixed conformation. The thermodynamic functions of the conformers gGg′ and tGg′ of EDA were also specifically calculated and shown in the Supporting Information section. For the same molecule, the thermodynamic functions of the G and T conformers are actually quite close to each other. The major differences between them is the Gibbs free energies and enthalpies of EDA in the low-temperature regime. Similar trends were also observed in the thermodyanmic functions of AE. They were tabulated in the Supporting Information section.

For the experimental thermodynamic measurements of EDA, in an earlier attempt by Yokozeki and Kuchitsu, the yield of the gauche conformer was found to be more than 95% in the temperature range 323−393 K by the gas electron diffraction method.[3] Later, the equilibrium constant between the gGg′ and tGg′ conformers was measured to be 1.6 ± 0.3 at 290 K through microwave spectroscopy by Marstokk and Møllendal.[5] Compared with the present theoretical equilibrium constants of 5.76×10^{-2} (G form is 94.6%) and 1.9 for the transformations of xGx ↔ xTx and tGg′ ↔ gGg′, respectively, at 298.15 K, the agreement is within the experimental uncertainties. More recently, in a gas electron diffraction experiment, the equilibrium mole fractions of the combined gauche forms at 343, 463, and 713 K were measured to be 0.882(69), 0.786(96), and 0.812(92), respectively, by Kazerouni et al.[10,15] These values are in good agreement with the present theoretical ones of 0.909, 0.852, and 0.735, respectively. With the help of the van't Hoff plot, Kazerouni et al. proceeded to deduce an experimental entropy difference of ΔS° (expt) $= S^0_{\mathrm{T}} - S^0_{\mathrm{G}} = -1.67$ ($\sigma = 0.90$) cal $\mathrm{mol^{-1}\,K^{-1}}$, in which S^0_{G} includes the contribution of its optical isomer, and an enthalpy difference of 0.68 ($\sigma = 0.41$) kcal/mol for the conformational transformation of G ↔ T. Compared with the theoretical entropy of 0.46 cal $\mathrm{mol^{-1}\,K^{-1}}$ and enthalpy of 1.80 kcal/mol at 600 K, the experimental values are all lower than the theoretical ones. A closer examination of the experimental data suggests that the obtained entropy and enthalpy appear to be in good agreement with the theoretical ones if only the above two lower temperature measurements were adopted. Owing to the sensitivities of these thermodynamic quantities to the accuracy of the equilibrium constants over the measured temperatures and also to the difficulties in this type of conformational population measurements, additional experiments are needed for the clarification of the discrepancies. As a final note, to date there are no experimental thermodynamic functions of the gaseous AE available for comparison.

With the present gas-phase analysis, a natural extension one may ask is its implication in the condensed phase. Two general consequences are discussed as follows. First, the solvation of EDO in aqueous solution and its equilibrium conformation population, a competition process between intramolecular and intermolecular H-bonding, have been studied intensively in recent years.[43−47] It has been concluded lately that there is very little effect on the gas-phase equilibrium conformation population for the dissolution of EDO in nonpolar solvents; the water molecules do not compete so strongly for the hydroxyl groups of EDO to disrupt the qualitative conformational pictures of the gas phase in water solvent.[47] Since the strength of the H-bond of AE is similar to that of EDO and since that of EDA is much weaker, it would be expected that in the condensed phase AE would behave similarly while EDA would behave differently from EDO in the condensed phase. It would be interesting to see additional detailed comparative studies among these three molecules in this direction. Second, the intramolecular force field parameters used in many condensed phase simulations were adapted directly or indirectly from those of the gas phase.[48] The present intramolecular potential would be equally adequate for the condensed phase simulations. To treat intermolecular interactions, additional terms for van der Waals interactions and possibly the mutual polarization effect would be needed. However, the present detailed treatment of the electrostatic forces would demand more computation resources than traditional point charge models.

3.D. Conformational Energy Decomposition and the Intrinsic Gauche Interactions. The general fitted function of eq 1 could be unambiguously classified into three types of conformation interactions according to their nature of interactions: (1) the intramolecular H-bonding between the vicinal X···Y groups, which is represented by the through-space dipole−dipole, dipole−quadrupole, and quadrupole−quadrupole interactions; (2) the through-space geminal interactions between the functional groups and its geminal CH_2 group whose potential forms were also represented by the electrostatic multipole moment interactions; (3) the through-direct-bond decoupled-rotor terms: V_0, V_a, V_b, and V_c. The decoupled-rotor potential is a quantitative representation of both the steric interaction and the through-direct-bond components of the gauche interactions. In other words, the gauche interactions of these molecules could be decomposed into two components: the contribution of the electrostatic interactions through space; the direct interaction through the chemical bond. In the following analysis, the through-direct-bond gauche energy is quantitatively defined as the energy difference between the G (XCCY = 60°) and T (XCCY = 180°) conformers in the decoupled-rotor potential (T − G) and is denoted as the stabilization energy due to the intrinsic gauche effect. This quantity is independent of the conformations of the X and Y groups as long as they are fixed in the above conformation energy calculations. The steric effect, which is manifested by the presence of the potential barriers in the decoupled-rotor potentials, is expected to be mainly responsible for the energy barriers of these molecules at the corresponding barrier conformations.

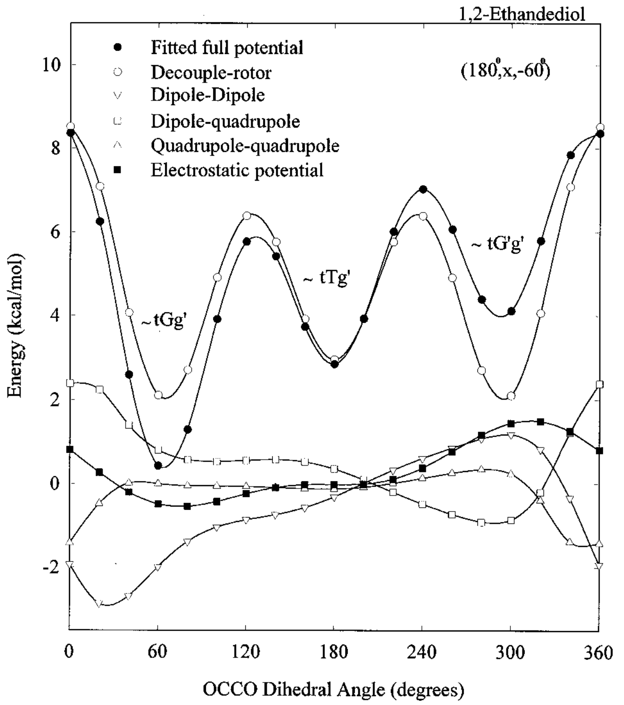


Figure 4. Energy decomposition of the fitted full potential of the energy path (180°, *x*, −60°) of 1,2-ethanediol into the decoupled-rotor potential, CH_2 electrostatic interactions, and dipole−dipole, dipole−quadrupole, and quadrupole−quadrupole potentials of OH···OH.

1,2-Ethanediol. Figure 4 shows the energy decomposition of the full fitted potential of the path (180°, *x*, −60°) of EDO into five potential components: the decoupled-rotor potential, the dipole−dipole, dipole−quadrupole, quadrupole-quadrupole potentials of OH···OH, and the electrostatic interaction potential of CH_2···OH.

As shown in the figure, the decoupled-rotor potential of 1,2-ethanediol suggests that at fixed HOCC dihedral angles the decoupled-rotor energy difference between xGx and xTx conformers is 0.84 kcal/mol. In other words, the intrinsic gauche effect of the two hydroxyl groups contributes 0.84 kcal/mol for the extra stability of the G form compared with the T form. The figure also shows that the most stable conformer tGg′ (optical isomer tG′g) is further stabilized by the dipole−dipole interaction between the OH and OH groups, while the higher energy of the tGg conformer is mainly due to the

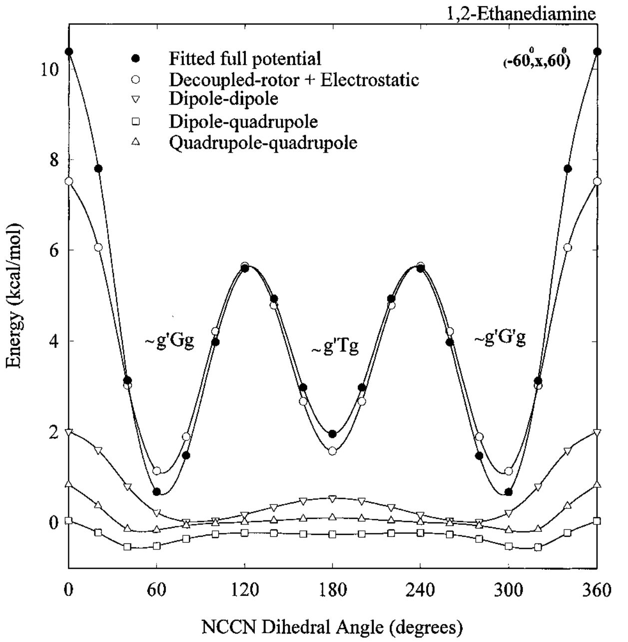


Figure 5. Energy decomposition of the fitted full potential of the energy path (−60°, *x*, 60°) of 1,2-ethanediamine into the decoupled-rotor plus CH_2 electrostatic interactions, and dipole−dipole, dipole−quadrupole, and quadrupole-quadrupole potentials of NH_2···NH_2.

repulsive OH···OH dipole−dipole and the net OH···CH_2 electrostatic interactions. For EDO, the dipole−dipole, dipole−quadrupole, and quadrupole−quadrupole potentials of OH···OH and the net electrostatic contribution of OH···CH_2 for the stable ab initio conformers in the order of the conformational energies are tGg′ (−1.60, 0.22, −0.09, −0.60), gGg′ (−0.73, −0.39, −0.33, −0.17), g′Gg′ (0.74, −0.78, 0.10, −1.56), tTt (0.72, −0.73, 0.26, 0.46), g′Tt (−0.14, 0.23, −0.11, −0.08), gTg′ (0.58, −0.34, 0.15, 0.31), tGt (−0.09, 0.96, −0.52, 0.61), gTg (−0.43, 0.19, 0.00, 0.35), gGg (−1.29, −0.38, 0.37, 0.70), and tGg (1.14, −0.84, 0.24, 1.40) kcal/mol, respectively. There are several features observed from the above decomposed energies. First, for the two most stable conformers tGg′ and gGg′, it is generally accepted that they are stabilized by intramolecular H-bonding in the dipole−dipole interaction form. The present decomposed energies suggest that tGg′ is mainly stabilized by the dipole−dipole interaction and secondarily by the OH···CH_2 electrostatic interactions, while gGg′ is stabilized by the multipole interactions as well as by the simple dipole−dipole interaction of OH···OH. Second, as expected, the contribution of the intramolecular H-bonding to the stability of the T form is generally not significant. Nevertheless, contrary to conventionally intuitive rationalization, some of the multipole interaction components, for instance, the dipole−dipole energy of gTg′, are not negligible. Finally, for the two least stable conformers gGg and tGg, the former is mainly destabilized by a higher decoupled-rotor potential and the latter is partly due to the destabilization of the OH···CH_2 electrostatic interactions.

1,2-Ethanediamine. Figure 5 shows the energy decomposition of the full fitted potential of the (−60°, *x*, 60°) path of EDA for the dipole−dipole, dipole−quadrupole, quadrupole-quadrupole interactions of NH_2···NH_2 and the sum of the decoupled-rotor and NH_2···CH_2 interaction potentials. The reason for the combination of the latter two potentials was due to the interdependency of the two potentials in the fitting procedure for the present molecule. As shown in the figure, the energy difference of the decoupled-rotor plus the NH_2···CH_2 potential between the G(60°) and T(180°) form is 0.44 kcal/mol. The corresponding NH_2···NH_2 dipole−dipole, dipole−quadrupole, quadrupole−quadrupole interactions are (0.22, −0.52, −0.17) kcal/mol for the G form and (0.53, −0.26, 0.10) kcal/mol for the T form. Through intramolecular H-bonding, the G form is stabilized with respect to the T form by 0.84 kcal/mol. It appears that for EDA, the dipole−dipole, dipole−quadrupole, quadrupole−quadrupole interactions of the two amino groups are equally important in the conformational stability of the G form.

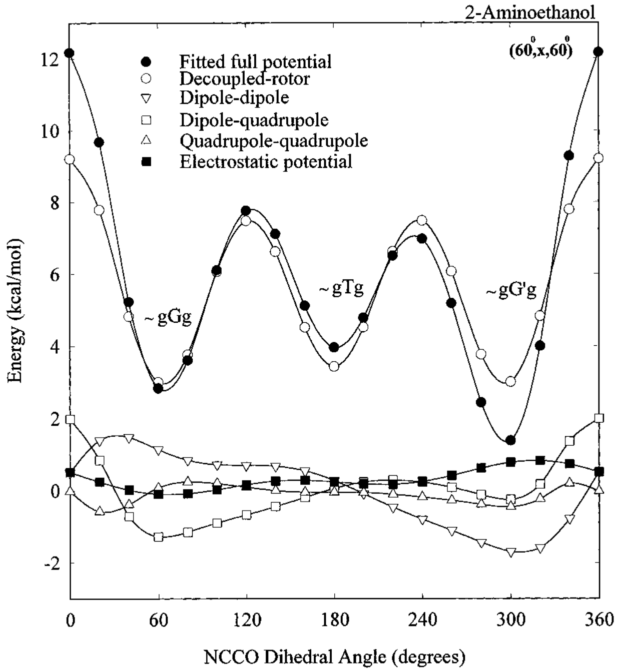


Figure 6. Energy decomposition of the fitted full potential of the energy path (60°, *x*, 60°) of 2-aminoethanol into the decoupled-rotor potential, CH_2 electrostatic interactions, and dipole−dipole, dipole−quadrupole, and quadrupole-quadrupole potentials of NH_2···OH.

The dipole−dipole, dipole−quadrupole, and quadrupole−quadrupole potentials of NH_2···NH_2 and the decoupled-rotor plus the CH_2 electrostatic interaction energy for the stable ab initio conformers arranged in the order of the conformational energies are gGg′ (−0.27, −0.49, −0.07, 1.27), tGg′ (−0.86, −0.20, 0.14, 1.54), gGg (−0.77, −0.17, 0.32, 1.46), tGg (0.50, −0.26, −0.11, 1.37), gTg′ (0.55, −0.25, 0.10, 1.47), gTg (0.07, −0.18, 0.03, 1.48), tTt (0.45, −0.39, 0.13, 1.50), tTg (−0.21, 0.10, −0.01, 1.48), tGt (0.36, 0.14, −0.28, 1.42), and g′Gg′-(0.75, −1.04, −0.10, 4.33) kcal/mol, respectively. The three most stable conformers gGg′, tGg′, and gGg are all stabilized by intramolecular H-bonding with different multipole interaction weights. The most stable conformer gGg′ is mainly stabilized by the dipole−quadrupole term, while the next two stable conformers tGg′ and gGg are stabilized by the dipole−dipole term. Similar to the case of EDO, the contribution of the intramolecular H-bonding is not significant in the T conformers. The least stable conformer g′Gg′ is mainly due to the destabilization of the decoupled-rotor potential and the CH_2 electrostatic interactions.

2-Aminoethanol. Figure 6 shows the decomposed conformational energies of AE along the conformation path (60°, *x*, 60°). The decoupled-rotor potential yields an intrinsic gauche energy of 0.44 kcal/mol. In other words, the G conformer is stabilized by this quantity with respect to its corresponding T conformer. The figure shows that the most stable conformer g′Gg′, which is an optical isomer of gG′g, is further stabilized mainly by the NH_2···OH dipole−dipole interaction in the form of an O−H···N hydrogen bond. The dipole−dipole, dipole−quadrupole, and quadrupole−quadrupole potentials of NH_2···-

OH and the net electrostatic contribution of CH_2 for some representative stable conformers arranged in the order of increasing conformational energies are g′Gg′ (−2.10, −0.83, −0.74, 1.62), gGt (−1.05, 0.78, −0.50, 0.61), gGg′ (−1.30, 0.41, −0.37, 0.04), tGt (−0.14, −0.74, 0.62, 0.01), gGg (0.89, −1.51, 0.38, 0.42), tGg (−0.14, −0.74, 0.62, 0.01), gTt (0.56, −0.44, 0.09, 0.31), tTt (−0.61, 0.70, −0.28, 1.88), gTg (0.32, 0.03, −0.04, 0.39), tTg (0.25, −0.26, 0.11, 1.96), gTg′ (−0.54, 0.27, −0.14, 0.31), and g′Gt (1.36, 0.04, −0.06, 1.62) kcal/mol, respectively. The three most stable conformers g′Gg′, gGt, and gGg′ are stabilized by intramolecular H-bonding in which the first and third conformers are in the form of O−H···N and the second one is in the form of N−H···O. Owing to the strain of the conformational structure, the intramolecular H-bond of the third conformer is much weaker than that of the first one even though they both belong to the same hydrogen bond category. The H-bonding strengths of O−H···N and N−H···O are 3.67 and 0.77 kcal/mol, respectively, for the first two conformers. It is in agreement with the well-accepted energy ordering of these two types of H-bond.[11] Again, similar to the cases of EDO and EDA, the contribution of intramolecular H-bonding to the stability of the T conformers is not significant. The least stable conformer g′Gt is mainly due to the destabilization of the repulsive dipole−dipole interaction of NH_2···OH and also the net repulsive electrostatic interaction due to the CH_2 groups. For all these conformers, the contribution of both the dipole−quadrupole and quadrupole−quadrupole interactions are essential for a quantitative analysis of the conformational energies. In short, the present energy analysis suggests that the stable conformational energies of AE are determined by the following factors arranged in the order of decreasing weight: intramolecular H-bonding, CH_2 electrostatic interaction, and the gauche interaction.

3.E. Correlation of the Intrinsic Gauche Energies of 1,2-Disubstituted Ethanes with the Group Electronegativities. The gauche effect is the preference of the gauche to the trans conformation in the molecular segment X−C−C−Y, in which X and Y are groups with large electronegativities. The effect has been rationalized as the consequence of interactions between vicinal electron pairs and/or polar bonds of molecular fragments as the conformation varies,[23] of the stabilizing effect of bonding−antibonding orbital interactions between vicinal polar bonds,[49] or of the destabilizing interaction in the trans conformer due to the formation of bent bonds.[50] Each explanation has its own line of reasoning. However, none of them could provide a quantitative measure of the gauche effect in molecules with intramolecular H-bonds.

Phenomenologically, Phillips and Wray had observed a correlation between the gas-phase energy differences of gauche and trans conformers and the sum of Huggins electronegativities of the halogen atoms of 1,2-dihaloethanes.[24] More recently, Thibaudeau et al. measured the conformational preferences of the pentofuranosyl moieties in various 3′-substituted 2′,3′-dideoxythymidine derivatives by the NMR spectrometry.[26] They found that the gauche effect enthalpies are linear with the group electronegativity of the 3′-substituents.

In the present energy decomposition scheme, the intramolecular H-bonding and the decoupled-rotor potential are partitioned according to their dependence on the torsional angles. For the 1,2-dihaloethanes systems or systems with comparatively weak intramolecular interactions, their conformational energies could be identified with the decoupled-rotor potentials of the present H-bonded systems. In other words, the decoupled-rotor potentials of the present systems are on the same footing as the conformational potentials of 1,2-dihaloethanes in terms of the interaction functional forms. The gauche energies of 1,2-dihaloethanes have been defined as the energy differences between the gauche and trans conformers. The present intrinsic gauche energies, which are defined as the energy differences between the gauche and trans conformers in the decoupled-rotor potentials, are then consistent with the conventional definition of the gauche energies for the simpler 1,2-dihaloethane systems.

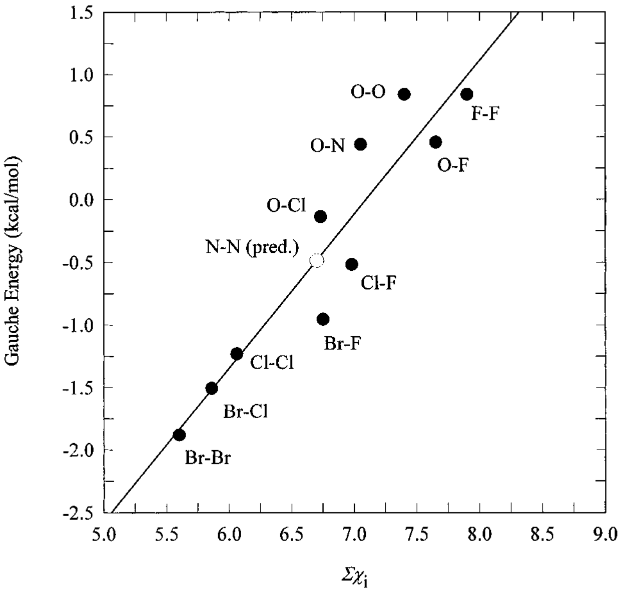


Figure 7. Linear relationship between the gauche energies of 1,2-disubstituted ethanes and the Wells'group electronegativity scale. The open circle is the predicted intrinsic gauche energy of 1,2-ethanediamine.

To complete the gauche energy study, the energy differences between gauche and trans conformers of 1,2-dihaloethanes (XCH_2-CH_2Y, where X, Y = F, Cl, Br) were also calculated at the MP2/6-311+G(2d,p)//MP2/6-31G** level. Their gauche energies are 0.84 (F, F), −0.52 (F, Cl), −0.95 (F, Br), −1.23 (Cl, Cl), −1.51 (Cl, Br), and −1.88 (Br, Br) kcal/mol. Conformational analysis of two related systems with strong intramolecular H-bonds—2-fluoroethanol and 2-chloroethanol—was also performed. Their intrinsic gauche energies were found to be 0.46 (F, O) and −0.14 (O, Cl) kcal/mol, respectively.[51] Along with the intrinsic gauche energy of EDO of 0.84 kcal/mol and that of AE of 0.44 kcal/mol, their relationship with various group electronegativity scales was examined by the following equation:[24]

$$\Delta E_{T-G} = a + b \sum x_i \tag{6}$$

in which $\sum x_i$ is the sum of the two group electronegativities. With the gauche energy in units of kcal/mol, the correlation coefficients *R*, slopes *b*, and intercepts *a* for the four electronegativity scales that cover the present functional groups are the following: (Wells' scale[52]) $R = 0.94$, $b = 1.23$, $a = -8.71$; (Inamoto's scale[53]) $R = 0.84$, $b = 1.62$, $a = -8.97$; (Huheey's scale[54]) $R = 0.82$, $b = 1.05$, $a = -7.22$; (Pauling's scale[55]) $R = 0.78$, $b = 1.13$, $a = -7.95$. The Wells' scale yields the highest correlation coefficient of 0.94, and its linear relationship with the gauche energy is shown in Figure 7. The solid dots in the figure are the molecules considered in this report and the open circle is the predicted EDA gauche energy of −0.48 kcal/mol. The linear relationships between the gauche energies and Inamoto's and Huheey's scales are only reasonably good. For the other electronegativity scales reported in the literature, such as Pauling's, Sanderson's,[56] or Marriot's,[57] they lack a good linear relationship and/or a Br electronegativity scale.

The present analysis clearly suggests that, for the molecular systems EDO, AE, and 2-fluoroethanol, the major stabilization factor for the G over T conformers is the intramolecular H-bonding. Nevertheless, the gauche effect still plays an important role in the determination of the final stabilization energy of the G conformers.

4. Conclusions

The following conclusions can be drawn from the present global conformational analysis of 1,2-ethanediol, 1,2-ethanediamine, and 2-aminoethanol.

(a) A general three-dimensional potential function was found to be adequate for representing the global conformational potential of the three molecules. The potential may be regarded as the zeroth-order potential for the three internal rotations that are decoupled from the rest of the vibrational normal mode motions. The fitted local dipole and quadrupole moments of the functional groups are in good agreement with the corresponding ab initio values calculated by the Hirshfeld charge population analysis.

(b) The MM3 conformational potential of aminoethanol is in good agreement with the ab initio results. However, it is only fair for the 1,2-ethanediamine molecule.

(c) The gaseous phase thermodynamic functions of these three molecules are calculated. The agreement with the limited available experimental results of EDO and EDA is good within the experimental uncertainties. There are nonnegligible differences between the values calculated by the conventional and the present methods, especially in the Gibbs free energies and entropies.

(d) The gauche energies defined by the decoupled-rotor potentials for molecules with intramolecular H-bonds are linear with the Wells's group electronegativity scale. The present analysis suggests that the gauche effect and the intramolecular H-bonding are equally important for a quantitative description of the stabilization of the gauche conformers for the molecules studied. The intramolecular H-bond sets the primary order of conformational energy stabilities of the gauche conformers with respect to those of the trans conformers of these molecules. The gauche effect further stabilizes the most stable gauche conformers of EDO and AE, while it destabilizes that of EDA. The present study also suggests that global conformational analysis, instead of local analysis, is usually required for a quantitative description of the interaction energies of the conformers.

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Appendix

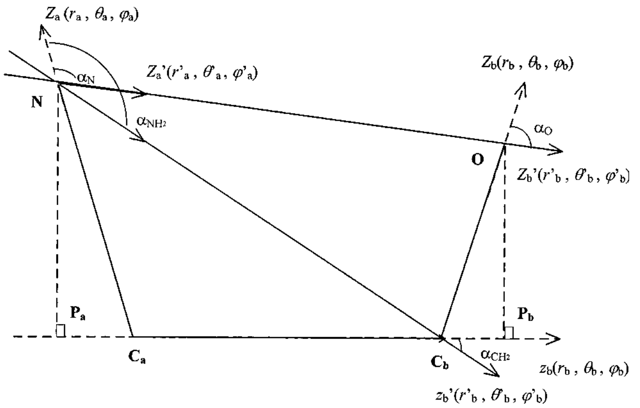

Figure 8. Schematic diagram of the internal rotation coordinates *Z* and the interdipole coordinates *Z*′ between the vicinal interaction of NH_2 and OH, and the corresponding coordinates *z* and *z*′ between the geminal interaction of NH_2 and CH_2 of 2−aminoethanol.

The general functional forms of the intramolecular electrostatic interactions expressed in terms of the internal rotation coordinates were described in this subsection. Figure 8 shows the schematic diagram of the coordinate systems used for AE. These systems are equally applicable to EDO and EDA. The interdipole coordinates for the vicinal $NH_2\cdots OH$ interaction, whose *z*-coordinate is set at the internuclear vector from N to O, are designated by $Z'(r',\theta',\varphi')$. The interdipole coordinates for the geminal $NH_2\cdots CH_2$ interaction, whose *z*-coordinate is set at the nuclear vector from N to C_b, are denoted by $z'(r',\theta',\varphi')$. The internal rotation coordinates, whose *z*-coordinate is along the internal rotation axis, are represented by $Z(r,\theta,\varphi)$ for the vicinal $NH_2\cdots OH$ interaction system and $z(r,\theta,\varphi)$ for the geminal interactions, such as the $NH_2\cdots CH_2$ interaction shown in the figure. The *x*- and *y*-coordinates, which are not shown in the figure, are defined in the same way as in previous publications.[18,33] The general functional forms of V_{dd}, V_{dq}, and V_{qq} between two molecular fragments *i* and *j* expressed in terms of the interdipole spherical coordinates (r', θ',φ') are[58]

$$V_{dd} = -\frac{\mu_i\mu_j}{r_{ij}^3}[2\cos\theta_{di}'\cos\theta_{dj}' - \sin\theta_{di}'\sin\theta_{dj}'\cos(\varphi_i' - \varphi_j')] \qquad (A1)$$

$$V_{dq} = \frac{3}{4r_{ij}^4}\{\mu_i q_j[\cos\theta_{di}'(3\cos^2\theta_{qj}' - 1) - 2\sin\theta_{di}'\sin\theta_{qj}'\cos\theta_{qj}'\cos(\varphi_i' - \varphi_j')] - \mu_j q_i[\cos\theta_{dj}'(3\cos^2\theta_{qi}' - 1) - 2\sin\theta_{dj}'\sin\theta_{qi}'\cos\theta_{qi}' \times \cos(\varphi_i' - \varphi_j')]\} \qquad (A2)$$

$$V_{qq} = \frac{3q_iq_j}{16r_{ij}^5}\{1 - 5\cos^2\theta_{qi}' - 5\cos^2\theta_{qj}' - 15\cos^2\theta_{qi}'\cos^2\theta_{qj}' + 2[\sin\theta_{qi}'\sin\theta_{qj}'\cos(\varphi_i' - \varphi_j') - 4\cos\theta_{qi}'\cos\theta_{qj}']^2\} \qquad (A3)$$

in which μ is the dipole moment, *q* is the quadrupole moment, r_{ij} is the distance between the molecular fragments *i* and *j*, and θ_d' and θ_q' are the azimuthal angles of the dipole and quadrupole moments in the interdipole coordinates, respectively. The quadrupoles of the molecular fragments are approximated by assuming them to be cylindrically symmetric. To proceed further, one needs to transform the above expressions into the internal rotation coordinates (r,θ,φ) by the following relations:[18,33]

$$\sin\theta'\cos\varphi' = \sin\theta\cos\varphi$$

$$\sin\theta'\sin\varphi' = \cos\alpha\sin\theta\sin\varphi - \sin\alpha\cos\theta$$

$$\cos\theta' = \sin\alpha\sin\theta\sin\varphi + \cos\alpha\cos\theta \qquad (A4)$$

in which α is the angle between the *z*-coordinates of the above two coordinate systems.

The vicinal interaction between X···Y and the geminal interactions, say, between X and CH_2, possesses different transformation relations between the spherical internal rotation coordinates and the geometric parameters of the molecules, which include the important dihedral angles of the molecules.[18,33] Specifically, for vicinal interaction, the relations between the dihedral angle ω and the spherical coordinate φ

are the following: for EDO, $\varphi_a = \omega_a + \beta \sin(\omega_c) + 90°$ and $\varphi_b = \omega_b + \beta \sin(\omega_c) - 90°$; for EDA, $\varphi_a = \omega_a + \beta \sin(\omega_c) - 90°$ and $\varphi_b = \omega_b + \beta \sin(\omega_c) + 90°$; for AE, $\varphi_a = \omega_a + \beta \sin(\omega_c) - 90°$ and $\varphi_b = \omega_b + \beta \sin(\omega_c) - 90°$. For all cases, $\alpha_{\mathrm{N\ or\ O}} = \alpha_1 + \alpha_2 \cos(\omega_c)$. Here α_1, α_2, and β are structural parameters and could be determined directly from the geometrical parameters. The interdipole distance r_{ij} is a function of ω_c:

$$r_{ij} = r_s(1 - l \cos \omega_c) \tag{A5}$$

in which, for instance for the AE molecule as shown in Figure 8,

$$r_s^{\,2} = r_{\mathrm{P_bO}}^{\,2} + r_{\mathrm{P_aN}}^{\,2} + r_{\mathrm{P_aP_b}}^{\,2} \tag{A6}$$

and

$$l = 2 r_{\mathrm{P_aN}} r_{\mathrm{P_bO}} / r_s^{\,2} \tag{A7}$$

For the geminal interactions of the present systems, the transformation relations are adapted directly from ref 33.

Supporting Information Available: Seven tables that include the harmonic vibrational frequencies of the conformers discussed in this paper, the fitted and structural parameters of 1,2-ethanediol, 1,2-ethanediamine, and 2-aminoethanol, and the thermodynamic functions of the conformers gGg′ and tGg′ of 1,2-ethanediamine and the confomers of 2-aminoethanol reported in this paper (8 pages). Ordering information is given on any current masthead page.

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