J. Am. Chem. Soc. **1994,** *116,* 5279–5284

Conformational Analysis. 16. Ethylenediamine. An Electron-Diffraction and ab Initio Investigation of the Molecular Structure, Conformational Composition, Anti–Gauche Energy and Entropy Differences, and Implications for Internal Hydrogen Bonding

M. Rahim Kazerouni, Lise Hedberg, and Kenneth Hedberg*

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

Received December 13, 1993. Revised Manuscript Received April 1, 1994[●]

Abstract: The vapor-phase structures of the rotamers of ethylenediamine and the composition of the gaseous system at sample temperatures of 343, 463, and 713 K have been analyzed from electron-diffraction data augmented by rotational-constant data taken from the literature and by ab initio calculations. The molecules are predominately in either of two gauche conformations (A and B), each consistent with the formation of an internal hydrogen bond. The mole fractions of the combined gauche forms at 343, 463, and 713 K are 0.882(69), 0.786(96), and 0.812(92). The tendency of the composition to shift toward the anti form as the temperature increases is indicative of a lower internal energy for the gauche form. Analysis of the temperature dependence of the composition gives the energy and entropy differences as $\Delta E° = E_A° - E_G° = 0.68$ ($\sigma = 0.41$) kcal/mol and $\Delta S° = S_A° - (S_G° + R \ln 2) = -0.29$ ($\sigma = 0.90$) cal·mol^{-1}·K^{-1}. The following are values for some of the more important distances (r/Å) and angles ($\angle$/deg) for the gauche A, gauche B, and anti forms at 343 K; uncertainties estimated at 2σ are given in parentheses: r(N–H) = 0.995(6) (all forms); $\langle r(\text{C–H})\rangle$ 1.125(6), 1.124(6), 1.124(6); r(C–C) = 1.520(14), 1.526(14), 1.520(14); $r(\text{C–N}_{\text{H·acceptor}})$ = 1.473(5), 1.471(5), 1.469(5); $r(\text{C–N}_{\text{H donor}})$ = 1.466(5), 1.464(5); $\angle\text{CCN}_{\text{H·acceptor}}$ = 110.2(4), 110.3(4), 110.3 (4); $\angle\text{CCN}_{\text{H-donor}}$ = 110.1(4), 115.3(4); $\langle\angle\text{CCH}\rangle$ = 108.7(20), 108.8(20), 108.7(20); $\angle$NCCN = 63.3(9), 59.5(10), 180.0 (assumed).

Introduction

The equilibria that exist in gaseous mixtures of rotational conformers have been the subject of series of electron-diffraction (GED) investigations from this laboratory. Many of these studies have dealt with substituted ethanes, which can exist in anti and gauche forms, and were motivated by an interest in rationalizing conformational stabilities in terms of the simple chemical ideas that have contributed so much to our understanding of molecular structure. Among these are studies of several systems in which internal hydrogen bonding can play a role (2-chloroethanol,[1] 2-fluoroethanol,[2] and ethane-1,2-dithiol[3]) as well as several in which the "gauche effect"[4] might operate when internal hydrogen bonding cannot occur (1,2-difluoroethane,[5] the three mixed 1-X-2Y-haloethanes (X, Y = Br, Cl, F),[6] 1,2-dibromo- and 1,2-diiodotetrafluoroethane,[7] and 1,2-dichlorotetrafluoroethane[8]). Since internal hydrogen bonding is possible only in the gauche forms of such substituted ethanes (where the donor and acceptor groups are appropriately positioned), the formation of hydrogen bonds tends to stabilize these forms relative to the anti. The more stable form also tends to be gauche in the 1,2-di- (but not poly-) substituted ethanes when the gauche effect operates strongly, *i.e.*, when the substituents are extremely electronegative as in 1,2-difluoroethane. The fact that gauche forms may be stabilized relative to anti by either the gauche effect or internal hydrogen bond formation raises the interesting question of their relative importance when both can operate together. It is not easy to find the answer because hydrogen bond forming groups tend to be electronegative, and the strength of the bonds is greater as the electronegativity increases. The studies mentioned above, and others to come, are intended to provide experimental information from which it may be possible to answer this question.

Ethylenediamine (Figure 1, hereafter EDA) is a further example of a molecule in which both internal hydrogen bond formation and the gauche effect may operate to significant effect. An early IR study of the gaseous molecule[9] led to the conclusion that the more stable N–C–C–N conformation was either cis or gauche and not anti. Later, it became clear from a GED study[10] that the heavy-atom conformation was dominantly gauche (>95%) in the temperature range 55–118 °C. No definite conclusion was reached regarding the preferred orientation of the NH$_2$ groups from this GED work, but definitive results were obtained from a microwave investigation[11] which showed that in the dominant gauche form one of the NH$_2$ groups may assume either of two positions depending on which of the hydrogen atoms is involved in hydrogen bonding. The stability of the hydrogen-bonded gauche form(s) relative to anti is predicted by both semiempirical[10,12,13] and ab initio[13–15] quantum mechanical calculations to

---

[●] Abstract published in *Advance ACS Abstracts,* May 15, 1994.

(1) (a) Almenningen, A.; Fernholt, L.; Kveseth, K. *Acta Chem. Scand. A* **1977**, *31*, 297. (b) Almenningen, A.; Bastiansen, O.; Fernholt, L.; Hedberg, K. *Acta Chem. Scand.* **1971**, *25*, 1946.

(2) (a) Huang, J.; Hedberg, K. *J. Am. Chem. Soc.* **1989**, *111*, 6900. (b) Hagen, K.; Hedberg, K. *J. Am. Chem. Soc.* **1973**, *95*, 8263.

(3) Barkowski, S. L.; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1986**, *108*, 6898.

(4) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.

(5) (a) Friesen, D.; Hedberg, K. *J. Am. Chem. Soc.* **1980**, *102*, 3987. (b) Fernholt, L.; Kveseth, K. *Acta Chem. Scand. A* **1980**, *34*, 163. (c) Van Schaick, E. J. M.; Geise, H. J.; Mijlhoff, F. C; Renes, G. *J. Mol. Struct.* **1973**, *16*, 23.

(6) Huang, J.; Hedberg, K. *J. Am. Chem. Soc.* **1990**, *112*, 2070.

(7) Thomassen, H.; Samdal, S.; Hedberg, K. *J. Am. Chem. Soc.* **1992**, *114*, 2810.

(8) Thomassen, H.; Hedberg, K. *J. Phys. Chem.* **1992**, *96*, 7983.

(9) Sabatini, A.; Califano, S. *Spectrochim. Acta* **1960**, *16*, 677.

(10) Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2926.

(11) Marstokk, K. M.; Møllendal, H., *J. Mol. Struct.* **1978**, *48*, 221.

(12) Hadjiliadis, N.; Diot, A.; Theophanides, T. *Can. J. Chem.* **1972**, *50*, 1005.

(13) Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 693.

(14) Rasmussen, K.; Tosi, C. *Acta Chem. Scand. A* **1983**, *37*, 79.

0002-7863/94/1516-5279$04.50/0

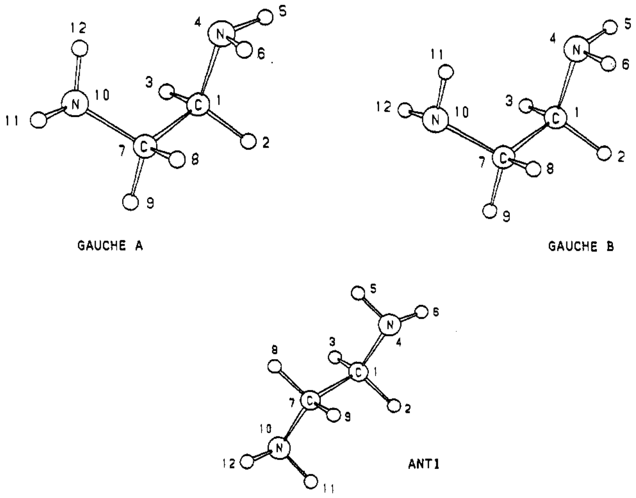

Figure 1. Diagrams with atom numbering of the three important forms of ethylenediamine.

be about 1.1–1.2 kcal/mol. Although these many studies contain a wealth of information about the structure of EDA, there is nothing from the experimental side on the energy and entropy differences of the species with different conformations of the heavy-atom backbone. We felt it worthwhile to obtain this information as a part of our program of investigation of the roles played by internal hydrogen bonding and the gauche effect in conformational stabilization. As in the previous GED study,[10] we would be unable to obtain direct information about the orientation of the NH_2 groups from the electron-diffraction data alone, but it seemed likely that we would be able to improve somewhat the precision of the parameters involving the heavy atoms by making use of the rotational constants[11] and the dipole-moment components[11] as structural constraints in our least-squares-fitting procedure.

Experimental Section

The EDA sample (Baker Analyzed Reagent 98.8%) was further purified by distillation under reduced pressure (120 Torr). The objective of the study required ED experiments at several temperatures over as large a range as possible. In order to establish the high end of the range, the temperature stability of the compound was established under the conditions of our experiment by observing the mass spectrum of the compound as it was passed through the heated nozzle of the GED apparatus. Thermal decomposition occurred at about 780 K; the spectra over the range 343–750 K were essentially the same.

Diffraction photographs were made in the OSU apparatus fitted with an r^3 sector at nozzle-tip temperatures of 343, 463, and 713 K. The sample bath was kept at 310–320 K. Experimental conditions are summarized in Table 1. Procedures for obtaining the total scattered intensity distribution, $s^4I_t(s)$, and for removing the backgrounds to yield molecular intensities in the form $sI_m(s)$ have been described.[16,17] Data were obtained at intervals ($\Delta s/\text{Å}^{-1} = 0.25$) over the ranges $2.00 \le s/\text{Å}^{-1} \le 13.50$ for the longer camera distance and $8.00 \le s/\text{Å}^{-1} \le 32.50$ for the shorter. The total intensities from the experiments at 343 K are shown in Figure 2, and the radial distribution curves for all temperatures, calculated by fourier transformation of the function $sI_m(s)Z_CZ_N(s^4F_CF_N)^{-1}\exp(-0.0025s^2)$ where F is the absolute value of the complex electron-scattering amplitude, are seen in Figure 3. These scattering amplitudes and their corresponding phases used in other calculations were obtained from tables.[18] The intensity data and figures of the intensity curves for the two higher temperatures are given in the supplementary material.

Structure Analysis

As is seen in Figure 3, the radial distribution curves for the three experimental temperatures are scarcely distinguishable. Two points are of special interest: the relative areas of the peaks in the regions of the $N{\cdot\cdot}N_A$ and $N{\cdot\cdot}N_G$ terms clearly indicate that the gauche form predominates at all temperatures, and the very small increase in the area of the $N{\cdot\cdot}N_A$ peak with change in temperature is evidence that the gauche form is the more stable and that the internal energy difference of the conformers is not large.

Construction of a suitable model for the EDA system consisting of three species, two gauche forms and an anti one all of C_1 symmetry,[19] presents a formidable problem. This problem concerns the very large number of parameters, the majority of which have values that differ only very slightly from conformer to conformer. Although it has frequently been our practice to simplify similar problems with the assumption that the structures of rotational conformers differ only in their torsion angles, we elected to define a more elaborate EDA model from the results of ab initio calculations to predict differences between values of similar parameters in the conformers and to develop force fields to be used in calculations of vibrational corrections to distances and rotational constants. Geometrical- as well as amplitude-parameter definitions would then include average values to which the calculated differences would be applied to generate the individual values.[20]

Theoretical Calculations. Although results from previous ab initio calculations were available,[13–15] our intended uses required that they be repeated. Geometry optimizations for most of the conformers of EDA were carried out at the HF/6-31G* level with use of the program GAUSSIAN 90.[21] The conformers of lowest energy are the two hydrogen-bonded gauche forms and an anti form of C_i symmetry; structural results for them are given in Table 2.

Ab initio quadratic Cartesian force fields and the corresponding wavenumbers for the optimized structures of the three forms of interest were also calculated with use of the analytical second derivative package of GAUSSIAN 90. These Cartesian force fields were converted to corresponding ones in symmetry coordinates and the force constants were scaled.[22] The scaled force constants were then used in the program ASYM20[23] to calculate all quantities intrinsic to the models intended for refinement.[24]

---

(15) Van Alsenoy, C.; Siam, K.; Ewbank, J. D.; Schäfer, L. *J. Mol. Struct.* **1986**, *136*, 77.

(16) Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.

(17) Hedberg, L. Abstracts, Fifth Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, March 1974; No. T9.

(18) Ross, A. W.; Fink, M.; Hilderbrandt, R. L. *International Tables for Crystallography*; International Union of Crystallography; Kluwer: Boston, Dordrecht, London.

(19) There are in principle nine anti forms of symmetries (multiplicities): C_{2h} (1), C_2 (2), C_i (2), and C_1 (4). There are also nine gauche forms: the two different hydrogen-bonded ones of symmetry (multiplicity) C_1 (2), three different C_2 (1) forms, and a C_1 (2) form. The energies (HF/6-31G*) of the C_{2h}, C_2, C_i, and C_1 anti forms relative to the most stable gauche form are 1.27, 1.20, 1.06, and 1.30 kcal/mol. According to ab initio calculations the gauche forms without hydrogen bonding are of much greater energy (X–Y kcal/mol) and therefore are present in negligible amounts. The two hydrogen-bonded conformers are of roughly equal energy. Because the anti form is clearly present in a relatively small amount, it was satisfactory to include only the C_i form in the model.

(20) For a review and evaluation of this approach see Schäfer, L.; Ewbank, J. D.; Siam, K.; Chiu, N.-S.; Sellers, H. L. In Stereochemical Applications of Gas-Phase Electron Diffraction; Hargittai, I., Hargittai, M., Eds.; VCH Publishers, Inc.: New York, 1988; Part A, p 301.

(21) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kalm, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1990.

(22) The scale constants were the following: 0.80 (NH and CH stretches; NCC bends; CCNH and NCCN torsions), 0.90 (CN and CC stretches), 0.78 (all bends involving H atoms). For lack of a better approximation, these are similar to those used in connection with smaller basis sets. See: Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037.

(23) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

(24) Although the vibrational spectrum of EDA has been measured (Sabatini, A.; Califano, S. *Spectrochim. Acta* **1960**, *16*, 677), the assignments were made with the assumption of molecular symmetry C_{2v} and are not complete.

Table 1. Experimental Conditions of Electron-Diffraction Experiments

	343 K		463 K		713 K	
	L.C.[a]	S.C.[b]	L.C.[a]	S.C.[b]	L.C.[a]	S.C.[b]
camera distances/mm	744.9	301.1	745.5	301.1	744.6	301.0
electron wavelength (nominal)/Å	0.058	0.058	0.058	0.058	0.060	0.060
exposure time/s	45	120–150	45–90	120–180	60–75	120–150
beam current/μA	0.40	0.48–0.51	0.37	0.38–0.53	0.42–0.46	0.55–0.56
no. of plates used	3	3	5	4	3	3
s range of data/Å^{-1}	2.0–13.0	7.0–32.5	2.0–13.0	7.0–33.5	2.0–13.5	8.0–32.5
data interval, Δs/Å^{-1}	0.25	0.25	0.25	0.25	0.25	0.25
ambient apparatus pressure/Torr × 10^5	1.2	1.0	0.5	0.7	0.9	1.0

[a] Longer camera distance. [b] Shorter camera distance.

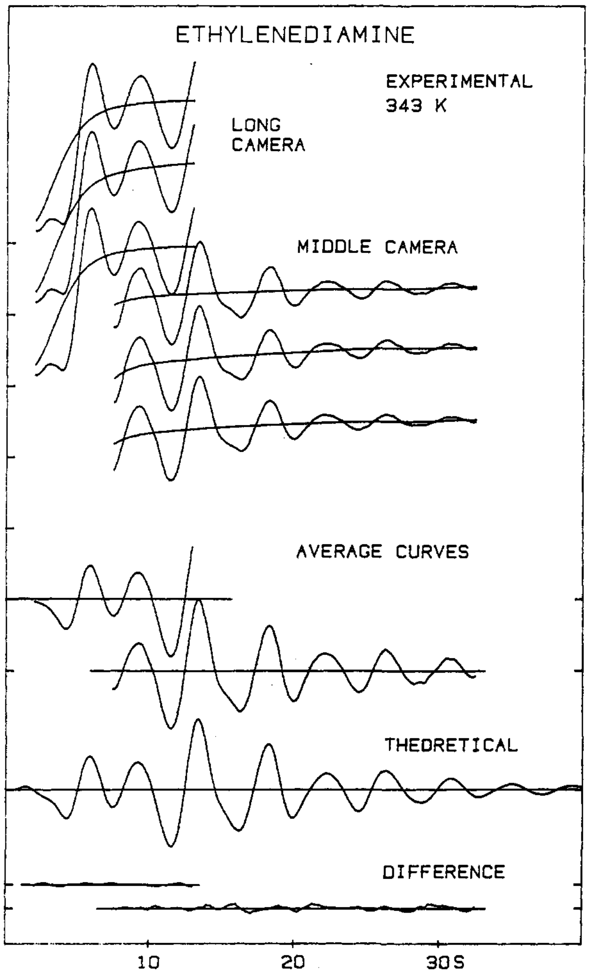

Figure 2. Intensity curves for the lowest temperature. The s^4I_t experimental curves are shown magnified seven times with respect to the backgrounds on which they are superimposed. The average curves are $s[s^4I_t - \text{backgrounds}]$. The theoretical curve corresponds to the model of Tables 3 and 4.

Models. A model of the conformational mixture was defined in terms of a gauche part consisting of equal amounts of gauche A and gauche B and the anti form of C_i symmetry. The very large number of geometrical parameters required for definition of this system required adoption of numerous assumptions. These were for the most part taken from the results of the ab initio and normal coordinate calculations. A typical example is the set of differences calculated for the four C–H bonds: these bonds should in principle all be different in each of the two gauche forms and different from the two symmetry related pairs in the anti. The calculated differences were maintained during the refinements. On the other hand, the calculated differences between the N–H bonds were judged small enough to be ignored. Many of the more important assumed differences may be deduced from the data of Table 2.

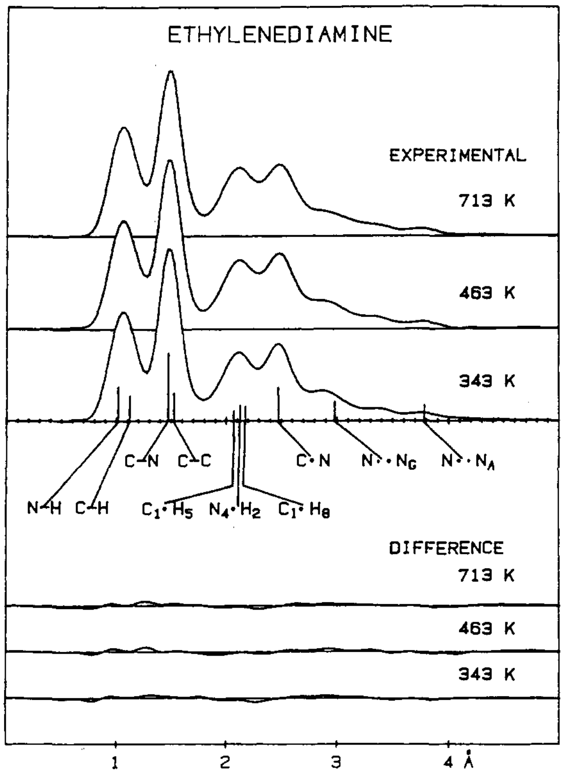

Figure 3. Radial distribution curves. The experimental curves were calculated from composites of the average intensities with use of theoretical data for the region $0 \leq s/\text{Å} \leq 1.75$ and $B = 0.0025$ Å^2. The vertical lines indicate some of the more important distances; their lengths are proportional to the weights of the distances.

The parameters themselves included averages of bond lengths, bond angles, and torsion angles, as well as differences between items in these catagories. They were chosen for convenience in the specification of the model, and since many have little structural interest otherwise, more precise descriptions are not worthwhile here. Vibrational amplitude parameters were also defined, often consisting of a group of several amplitudes with differences held at calculated values. Lastly, a composition parameter was defined that consisted of the mole fraction of the gauche form(s) held at a 1:1 ratio in the mixture. The models were specified in terms of $r_\alpha{}^\circ$ space in order to make appropriate use of rotational constants that have been measured for both gauche forms.[25] The perpendicular amplitude corrections (K), centrifugal distortions (δr), and root-mean-square amplitudes (l) used to convert $r_\alpha{}^\circ$ distances to the r_a type required for fitting the diffraction data and the quantities α^{har} needed to convert the measured rotational constants B_0 to the B_z consistent with a model in $r_\alpha{}^\circ$ space, were calculated for the three temperatures of interest from the force field described above.[26]

---

[25] Marstokk, K. M.; Møllendal, H. *J. Mol. Struct.* **1978**, *48*, 221.

Table 2. Theoretical Results for Structures of Ethylenediamine Conformers[a]

parameter	gauche A	gauche B	anti[b]	parameter	gauche A	gauche B	anti[b]
			Bond Lengths				
C–C	1.522	1.528	1.522	C_7–H_9	1.086	1.086	1.087
C_1–N_4	1.458	1.457	1.455	N_4–H_5	1.001	1.001	1.001
C_7–N_{10}	1.451	1.451	1.455	N_4–H_6	1.002	1.003	1.002
C_1–H_2	1.091	1.092	1.090	N_{10}–H_{11}	1.001	1.002	1.001
C_1–H_3	1.084	1.086	1.087	N_{10}–H_{12}	1.002	1.003	1.002
C_7–H_8	1.095	1.088	1.090				
			Bond Angles				
C–C–N_4	110.2	110.2	110.3	C–N–H_5	111.1	111.1	110.7
C–C–N_{10}	110.0	115.3	110.3	C–N–H_6	110.6	110.5	110.5
C–C–H_2	109.4	109.3	108.6	C–N–H_{11}	111.1	109.1	110.7
C–C–H_3	108.4	109.2	109.0	C–N–H_{12}	109.3	110.2	110.5
C–C–H_8	108.7	108.9	108.6	H–C_1–H	107.6	106.9	106.9
C–C–H_9	109.0	109.3	109.0	H–C_7–H	106.8	106.4	106.9
N–C–H_2	113.1	113.3	114.0	H–N_4–H	107.0	106.9	106.7
N–C–H_3	108.1	107.8	107.8	H–N_{10}–H	107.8	106.5	106.7
N–C–H_8	113.5	108.0	114.0				
N–C–H_9	108.8	108.6	107.8				
			Torsion Angles				
N–C–C–N	64.7	60.2	180.0	N–C–C–H_2	−170.4	−174.7	−54.4
C–C–N–H_{12}	−54.7	66.0	−69.9	N–C–C–H_3	−53.3	−58.0	61.8
C–C–N–H_{11}	−173.5	−50.6	172.1	N–C–C–H_8	−60.1	−61.4	54.4
C–C–N–H_6	75.0	71.4	69.9	N–C–C–H_9	−176.1	−177.2	−61.8
C–C–N–H_5	−166.4	−170.1	−172.1				
			Relative Energies[c]				
E_h/kcal·mol^{-1}	0	0.034	1.06				
E_0/kcal·mol^{-1}	0.020	0	0.702				

[a] HF/6-31G*. See ref 20. [b] C_i form. [c] E_h: ab initio relative energies. E_0: relative energies after correction for zero-point vibration.

Table 3. Selected Structural Results (r_α°/Å; $\angle_\alpha$/deg) for Ethylenediamine[a]

	343 K			463 K			713 K		
	gauche A	gauche B	anti	gauche A	gauche B	anti	gauche A	gauche B	anti
r(N–H)[b]	{0.995	0.995	0.995 }(4)	{0.997	0.997	0.997 }(5)	{0.998	0.998	0.998 }(5)
⟨r(C–H)⟩	{1.125	1.124	1.125 }(6)	{1.129	1.128	1.128 }(8)	{1.123	1.122	1.122 }(8)
r(C–C)	{1.520	1.526	1.520 }(14)	{1.513	1.520	1.514 }(25)	{1.517	1.524	1.518 }(22)
r(C–N_4)	{1.472	1.471	1.469 }(5)	{1.478	1.476	1.475 }(9)	{1.476	1.474	1.473 }(8)
r(C–N_{10})	1.465	1.464		1.470	1.470		1.468	1.468	
$\angle CCN_4$	{110.2	110.3	110.3 }(4)	{110.5	110.5	110.6 }(6)	{110.3	110.4	110.4 }(6)
$\angle CCN_{10}$	110.1	115.3		110.3	115.6		110.2	115.4	
⟨$\angle C_1N_4H$⟩	{103.5	103.5	103.3 }(22)	{103.7	103.7	108.4 }(35)	{103.1	103.1	102.8 }(26)
⟨$\angle C_7N_{10}H$⟩	117.8(44)	111.4(27)		112.6(70)	108.0(45)		114.5(57)	109.8(40)	
⟨$\angle CCH$⟩	{108.7	108.8	108.7 }(20)	{108.4	108.8	108.4 }(31)	{106.0	106.3	106.0 }(23)
$\angle NCCN$[c]	63.3(9)	59.5(10)	[180.0]	63.6(15)	59.5(15)	[180.0]	64.3(11)	60.4(12)	[180.0]
$\angle CCNX_{5,6}$[c,d]	111.4(185)	124.5(135)	[128.8]	108.2(271)	122.0(204)	[128.8]	108.6(227)	119.7(160)	[128.8]
$\angle CCNX_{11,12}$[c,d]	−103.5(91)	2.2(95)		−104.1(141)	3.5(145)		−105.3(125)	5.0(120)	
mol fraction[e]	{0.441	[0.441]	0.118 }(69)	{0.393	[0.393]	0.214 }(96)	{0.406	[0.406]	0.188 }(92)
R[f]		0.0392			0.0557		0.0446		

[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] N–H bond lengths were assumed equal. [c] Positive angles reflect a clockwise rotation of the forward bond into the eclipsed position. [d] X is the midpoint of the line joining the hydrogen atoms. [e] Mole fractions of gauche A and B were assumed equal. [f] $R = [\sum w_i\Delta_i^2/w_i(s_iI_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$.

Refinement Results. The data on which the least-squares refinements[27] of the model were based consisted of the ED intensities in the form $sI_m(s)$, the B_z values of the rotational constants, and the dipole moment components measured for both gauche forms of EDA.[25] (Our method for making use of dipole moment components in ED least-squares refinements has been described.[3]) The weights assigned to the three types of data were such as to give approximately the ratios $\sum_i w_i(s_iI_{m,i}(s))^2$:$\sum_i w_iB_{z,i}^2$:$\sum_i w_i\mu_i2$ = 1:500:0.03; these weights are arbitrary, but experience has shown that they give reasonable simultaneous fits to these types of data. The refinements were done by simultaneous fitting of theoretical scattered intensities to the two averaged experimental intensities (one from each camera distance) from the experiments at each temperature and of the corresponding rotational constants (B_z) and dipole moment components to their experimental counterparts. Final results for selected bond distance, bond angle, and amplitude parameters are shown in Tables 3 and 4. Table 5 contains the correlation matrices for the more important parameters of these tables. Table 6 shows the fit to the three types of data. The fit to the ED data is also seen in the difference curves of Figures 2 and 3.

Discussion

Molecular Structure. The results for the EDA system include measurement of 15 geometrical and 7 amplitude parameters as well as a composition parameter. The total is much larger than is ordinarily possible for structure analyses based on electron-diffraction data alone; the success for EDA is due to the constraints imposed by use of the rotational constants and dipole-moment

---

(26) The conversion formulas are $r_a^T = r_\alpha^\circ + (3a/2)[(l^2)^T - (l^2)^\circ] + \delta r^T + K^\circ - (l^2)^T/r$ and $B_z = B_0 + \sum_i \alpha_i^T d_i/2$, where a is a Morse anharmonicity constant assumed equal to 2.0 Å^{-1} and d is the degeneracy of the mode.

(27) Hedberg, K.; Iwasaki, M. *Acta Crystallogr.* **1964**, *17*, 529.

Table 4. Selected Distances (r_g/Å) and Vibrational Amplitudes (l_α/Å) for Ethylenediamine[a]

	343 K			463 K			713 K		
	gauche A	gauche B	anti	gauche A	gauche B	anti	gauche A	gauche B	anti
r(N–H)[b]	{1.023	1.023	1.023 }(4)	{1.025	1.025	1.025 }(5)	{1.027	1.027	1.027 }(5)
⟨r(C–H)⟩[c]	{1.140	1.140	1.140 }(6)	{1.144	1.144	1.144 }(8)	{1.138	1.138	1.138 }(8)
r(C–C)	{1.523	1.529	1.523 }(14)	{1.516	1.523	1.514 }(25)	{1.522	1.529	1.528 }(22)
r(C–N$_4$)	{1.475	1.474	1.474 }(5)	{1.481	1.480	1.480 }(9)	{1.481	1.480	1.479 }(8)
r(C–N$_{10}$)	1.468	1.468		1.474	1.474		1.474	1.473	
⟨r(C$_1$·H$_\mathrm{N}$)⟩[c]	{1.975	1.973	1.971 }(27)	{1.984	1.982	1.979 }(43)	{1.975	1.973	1.971 }(32)
⟨r(C$_7$·H$_\mathrm{N}$)⟩[c]	2.134(48)	2.063(31)		2.084(82)	2.029(56)		2.104(66)	2.051(47)	
⟨r(C·H$_\mathrm{C}$)⟩[c]	{2.171	2.180	2.169 }(31)	{2.164	2.173	2.162 }(40)	{2.131	2.140	2.130 {(31)
⟨r(N·H$_\mathrm{C}$)⟩[c]	{2.154	2.135	2.155 }(25)	{2.164	2.145	2.165 }(40)	{2.186	2.168	2.187 }(24)
r(C·N$_4$)	{2.457	2.462	2.457 }(5)	{2.460	2.465	2.460 }(9)	{2.461	2.466	2.461 }(8)
r(C·N$_{10}$)	2.448	2.530		2.451	2.533		2.452	2.534	
r(N··N)	2.920(13)	2.986(10)	3.750 (8)	2.933(22)	2.997(14)	3.761 (13)	2.939(19)	3.004(13)	3.758 (12)
r(N···H$_\mathrm{HB}$)[d]	2.586(70)	2.671(82)		2.529(94)	2.610(120)		2.568(83)	2.642(97)	
l(N–H)	{0.064	0.064	0.064 }(6)	{0.067	0.067	0.067 }(8)	{0.065	0.065	0.065 }(7)
l(C–H)	0.071	0.071	0.071	0.074	0.074	0.074	0.072	0.072	0.072
l(C–C)	{0.064	0.064	0.064 }(5)	{0.067	0.068	0.067 }(6)	{0.070	0.071	0.070 }(5)
l(C–N$_4$)	0.062	0.062	0.062	0.065	0.065	0.065	0.068	0.067	0.067
l(C–N$_{10}$)	0.062	0.062		0.064	0.064		0.067	0.067	
⟨l(C$_1$·H$_\mathrm{N}$)⟩[e]	{0.101	0.101	0.101 }(8)	{0.098	0.098	0.098 }(12)	{0.097	0.097	0.097 }(13)
⟨l(C$_7$·H$_\mathrm{N}$)⟩[e]	0.101	0.101		0.098	0.098		0.096	0.096	
⟨l(C·H$_\mathrm{C}$)⟩[e]	0.106	0.106	0.106	0.104	0.104	0.103	0.103	0.103	0.102
⟨l(N·H$_\mathrm{C}$)⟩[e]	0.100	0.101	0.101	0.097	0.098	0.097	0.094	0.095	0.094
l(C·N$_4$)	{0.076	0.077	0.079 }(5)	{0.088	0.088	0.090 }(8)	{0.094	0.095	0.097 }(8)
l(C·N$_{10}$)	0.076	0.075		0.087	0.086		0.093	0.091	
l(N··N)	{0.121	0.121}(25)	[0.071]	{0.125	0.124}(39)	[0.078]	{0.135	0.135}(32)	[0.091]
l(N···H$_\mathrm{HB}$)	{0.184	0.193}(37)		{0.201	0.210}(51)		{0.209	0.220}(42)	

[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] Because ab initio differences of N–H bonds were very small they were ignored. [c] Ab initio differences of distances were maintained in the model. [d] Hydrogen bond distance. [e] Calculated amplitude differences were maintained in the model.

Table 5. Correlation Matrices (×100) for Parameters of Ethylenediamine at 343 K[a]

parameter[b]	σ_LS × 100[c]	correlation coefficients																σ_LS × 100[c]	parameter[b]
r(N–H)	0.119	100		*100*	*−53*	*26*	*−24*	*15*	*−19*	*−23*	*−20*	*−1*	*−5*	*71*	*−23*	*6*	*10*	*0.119*	r(N–H)
⟨r(C–H)⟩	0.208	−53	100		*100*	*−28*	*31*	*−2*	*11*	*16*	*35*	*−25*	*−5*	*−70*	*32*	*4*	*−5*	*0.208*	r(C–H)
r(C–C)	0.503	26	−28	100		*100*	*−96*	*60*	*−65*	*−77*	*−76*	*−36*	*−41*	*32*	*−91*	*4*	*28*	*0.503*	r(C–C)
r(C–N)	0.167	−24	31	−96	100		*100*	*−54*	*59*	*69*	*79*	*27*	*34*	*−27*	*90*	*−3*	*−24*	*0.167*	r(C–N)
∠CCN	15.3	−22	31	−83	76	100		*100*	*−9*	*−32*	*5*	*−9*	*−10*	*17*	*−48*	*25*	*39*	*0.159*	r(C·N)
⟨∠C$_1$N$_4$H⟩	78.6	−4	−16	28	−30	−35	100		*100*	*75*	*71*	*69*	*12*	*−21*	*56*	*2*	*−29*	*0.457*	r(N··N)gA
⟨∠C$_7$N$_{10}$H(gA)⟩	157	5	−29	−26	17	42	−10	100		*100*	*67*	*40*	*51*	*−24*	*69*	*8*	*−45*	*0.353*	r(N··N)gB
⟨∠C$_7$N$_{10}$H(gB)⟩	95.2	7	−21	7	−11	−36	−12	−24	100		*100*	*33*	*40*	*−25*	*76*	*15*	*−2*	*0.268*	r(N··N)A
⟨∠CCH⟩	71.1	2	22	8	3	14	3	5	−20	100		*100*	*16*	*5*	*27*	*−21*	*−9*	*2.47*	r(N···H$_\mathrm{HB}$)gA
∠NCCN(gA)	33.0	−8	−18	−26	21	1	32	32	−4	−67	100		*100*	*−2*	*41*	*1*	*−8*	*2.88*	r(N···H$_\mathrm{HB}$)gB
∠NCCN(gB)	36.2	−8	−17	−19	14	−24	13	−19	47	−73	59	100		*100*	*−23*	*10*	*12*	*0.186*	l(N–H)
∠CCNX$_{5,6}$(gA)	653	<1	5	9	−7	−36	−26	−79	55	−18	−36	34	100		*100*	*6*	*−22*	*0.138*	l(C–C)
∠CCNX$_{5,6}$(gB)	476	−2	−3	−23	20	30	−24	33	−69	−11	14	−26	−22	100		*100*	*13*	*0.139*	l(C·N)
∠CCNX$_{11,12}$(gA)	321	−1	2	−34	30	72	−25	61	−42	49	−16	−62	−58	26	100		*100*	*0.878*	l(N··N)
∠CCNX$_{11,12}$(gB)	337	6	−7	38	−34	−70	36	−44	24	−50	39	36	32	−6	−80	100			
mol fraction	2.43	−4	2	−7	7	−3	−7	−1	2	−7	6	7	9	13	−10	11	100		

[a] The lower and upper triangular matrices are respectively for parameters of Tables 3 and 4. [b] The extensions gA, gB, and A refer to gauche A, gauche B, and anti forms. [c] Standard deviations from least-squares fitting. Distances (r) and amplitudes (l) in ångströms; angles (∠) in degrees.

Table 6. Fit of Final Model to Rotational Constants and Dipole Moment Components

	343 K		463 K		713 K	
	gauche A	gauche B	gauche A	gauche B	gauche A	gauche B
ΔA_z/MHz[a]	0.59	0.54	0.82	0.24	0.72	0.27
ΔB_z/MHz[a]	0.30	0.19	0.64	0.06	0.71	0.20
ΔC_z/MHz[a]	0.07	0.17	−0.07	0.28	−0.32	0.12
$\Delta\mu_a$/D[b]	0.37	0.22	0.30	0.12	0.36	0.24
$\Delta\mu_b$/D[b]	−0.09	−0.22	−0.12	−0.31	−0.14	−0.31
$\Delta\mu_c$/D[b]	−0.17	0.28	−0.50	0.29	−0.39	0.30

[a] Differences are B_z(obsd) − B_z(calcd). For gauche A in megahertz A_0 = 14472.0, A_z = 14483.0, B_0 = 5229.2, B_z = 5224.8, C_0 = 4405.5, C_z = 4404.6; for gauche *B* A_0 = 14355.5, A_z = 14366.6, B_0 = 5125.3, B_z = 5121.2, C_0 = 4356.3, C_z = 4355.4 (B_0 values from ref 24). [b] Differences are μ(obsd) − μ(calcd). Observed values in debye (ref 24) for gauche A are μ_a = 1.059, μ_b = 0.787, μ_c = 1.179 and for gauche B μ_a = 1.952, μ_b = 0.867, μ_c = 0.538.

components for the two gauche forms and the use of results in the form of certain parameter-value differences from the ab initio calculations. The latter amounts to adoption of an assumption that these differences are reflected in the real system. Although we regard this assumption to be better than the alternative of setting all conformational differences apart from torsional angles to zero, the uncertainties it introduces suggest caution in the interpretation of tabulated details such as parameter uncertainties. The inclusion of dipole-moment data in the refinements was found to be important even though they were not assigned great weight.

If the dipole-moment data were omitted, the fitting procedures sometimes failed, or could be completed only with fewer adjustable parameters.

The heavy-atom bond lengths and the C–C–N bond angle are similar to those in ethylamine[28] and show no discernable trend with change in temperature. The N–C–C–N torsion angle is similar to those in other ethane derivatives with internal hydrogen bonds[1,2] but a little smaller than those in molecules such as 1,2-halogenated ethanes where no hydrogen bonds exist.[6–8] At 2.59 Å and 2.67 Å in gauche A and B, respectively, the hydrogen-bond distances are somewhat shorter than the sum of van der Waals radii (2.77 Å) and are consistent with an attractive interaction. The average bond angle ⟨C–N–H⟩ for the group donating the hydrogen atom appears to be significantly larger than for the other group.

Energy and Entropy Differences of Conformers. Our model of the EDA system consists of only three of the many possible conformers. Most of those ignored have calculated energies much higher than the chosen three, but there is a gauche form of C_2 symmetry without hydrogen bonding (the nitrogen electron pairs point in opposite directions) that, according to ab initio calculation, has an energy only about 0.5 kcal/mol higher than the hydrogen-bonded forms. Neglect of the presence of this form in our model has little effect on our structural results. It is present in amounts of about 19–26% relative to the hydrogen-bonded forms, and apart from the torsional orientation of the NH_2 groups it has a similar structure. Thus, since our electron-diffraction data are insensitive to torsion around the C–N bond, the average measured parameter values for the forms listed in the tables will be negligibly affected.

For the temperature dependence of the equilibrium between gauche and anti forms (G → A) the formula

$$N_a/N_g = \exp(-\Delta E°/RT)\,\exp(\Delta S°/R)$$

applies; here N_a and N_g are the numbers of anti and gauche molecules in the sample. Unfortunately, as the van't Hoff plot in Figure 4 shows, the compositional data from the three experimental temperatures are consistent with the expected steady increase in the equilibrium constant only if one takes the indicated uncertainties (σ) into account. The results from a least-squares fit to the three points are $\Delta E° = E_a° - E_g° = 0.68$ ($\sigma = 0.41$) kcal·mol^{-1} and $\Delta S° = S°_a - S°_g - R \ln 2 = -0.29$ ($\sigma = 0.90$) cal·mol^{-1}·K^{-1}; here the statistical degeneracy of the enantiomorphic gauche form(s) has been removed from the entropy difference. Rather fortuitously in view of the uncertainty, our experimental value for $\Delta E°$ is in excellent agreement with the theoretical one corrected for zero-point vibration (see the $E°$ values in Table 2). The agreement is slightly degraded, however, if one corrects the experimental composition for the presence of the non-hydrogen-bonded form mentioned in the preceding paragraph. With this correction the internal energy difference between the hydrogen-bonded gauche forms and the anti becomes 0.87 ($\sigma = 0.41$) kcal/mol—still in very good agreement with theory.

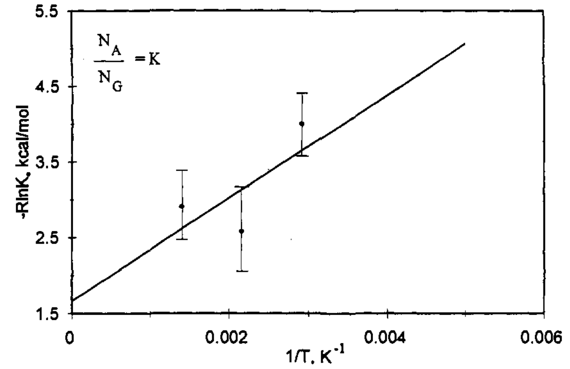

Figure 4. Van't Hoff plot for the anti–gauche equilibrium of ethylenediamine conformers.

One is tempted to identify the energy difference between the more stable hydrogen-bonded conformers and the less stable anti one as mainly the energy of the hydrogen bond itself. The picture is complicated, however, by the unknown magnitude of any gauche effect and by the likely presence of the non-hydrogen-bonded gauche conformer of lower energy than the anti. One may suppose that a measure of the gauche effect is the difference between the energies of this non-hydrogen-bonded form and the anti, *i.e.*, about 0.20 kcal/mol. Correspondingly, a measure of the hydrogen-bond energy is the energy difference between the gauche species with and without this bond; a rough estimate is somewhere in the range 0.5–0.8 kcal/mol. The estimated value for the magnitude of the gauche effect suggests, since the group electronegativities of NH_2 and F are respectively about 3.3 and 4.0, that the gauche effect operates significantly only between vicinally situated groups with electronegativities greater than about 3.5. The estimated energy of the internal H–N···H bond is plausible—larger, for example, than in ethanedithiol[3] and smaller than in glycol.[29]

Acknowledgment. This work was supported by the National Science Foundation under Grants CHE 84-11165 and CHE 91-21621. We are grateful to Oregon State University for the computer time used in the ab initio calculations.

Supplementary Material Available: Figures of the intensity curves from the 463 and 713 K experiments and tables of the average molecular intensities from the 343, 463, and 713 K experiments (6 pages). This material is contained in many libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(28) Hamada, Y.; Tsuboi, M.; Yamanouchi, K.; Kuchitsu, K. *J. Mol Struct.* **1986**, *146*, 253.

(29) Kazerouni, R. M. Ph.D. Thesis, Oregon State University, Corvallis, OR, 1987.