Molecular Orbital Theory of the Electronic Structures of Organic Compounds. 32. Conformations of Glycine and Related Systems

Saraswathi Vishveshwara and John A. Pople*

Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. Received August 13, 1976

Abstract: Ab initio molecular orbital theory (restricted Martree–Fock with the 4-31G basis set) is used to investigate the rotational potential surfaces of glycine (α-aminoacetic acid) in its un-ionized form and of α-aminoacetaldehyde. Standard values for bond lengths and angles are used. For both molecules, the lowest energy conformations (VI and VII) are found to correspond to structures in which there are bifurcated hydrogen bonds from the amine group to the carbonyl oxygen. For α-amino-acetaldehyde, a second local minimum, VIII, is found (1.4 kcal mol^{-1} above VII) with a strong interaction between the aldehyde hydrogen and the nitrogen lone pair. Glycine has a further stable structure, IX (2.2 kcal mol^{-1} above VI), with a hydrogen bond from the hydroxyl group to nitrogen. These results are compared with those of Newton and Jeffrey (preceding paper) on the corresponding hydroxy compounds.

I. Introduction

Isolated α-aminocarboxylic acids in the form NH$_2$–CHR–COOH, have amino and carbonyl groups separated by a saturated carbon atom. Consequently, direct conjugative interaction is small and a pyramidal structure for the nitrogen center is expected. This leads to three internal rotational degrees of freedom in the stereochemical description (I). In


$$\varphi_1 = \varphi_2 = \varphi_3 = 0°$$

I
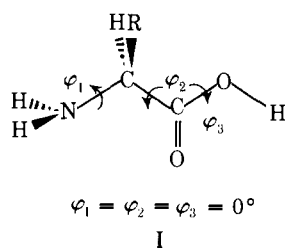
condensed media, these molecules are well known to exist in zwitterionic form II, this being stabilized by strong electrostatic and polarization interactions with the environment. These have geometries in which the N$^+$–C–COO$^-$ skeleton is usually close to planarity.[1] In addition, some of the halogen salts[2-6] of the cations III have been studied and also show near planar

II   III
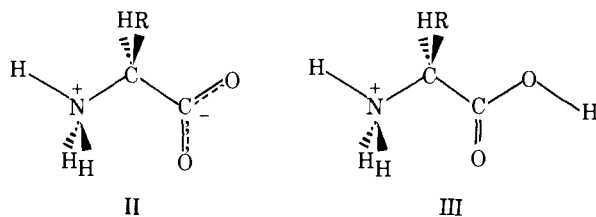
N$^+$–C–COOH structures with the ammonium nitrogen cis to the carbonyl group. To our knowledge, there is no experimental determination of the structure of the un-ionized acids I.

The objective of this paper is to make a theoretical study of the conformational potential surface of the simplest α-amino acid, glycine (R = H), in the un-ionized form I. The energy of I relative to the zwitterionic structure II will be discussed in a later study.[7] In addition we carry out a parallel study of the related molecule α-aminoacetaldehyde IV. This molecule is also uncharacterized experimentally. The stereochemistry of these systems is important as they form part of a general class of molecules V in which X and Y are either nonpolar groups (H, alkyl, . . .) or electronegative groups (NH$_2$, OH, F, . . .). In a preceding paper,[8] detailed studies of glycolaldehyde (X

= OH, Y = H, R = R' = H) and glycolic acid (X = OH, Y = OH, R = R' = H) have been presented in connection with a

$$\varphi_1 = \varphi_2 = 0°$$

IV   V
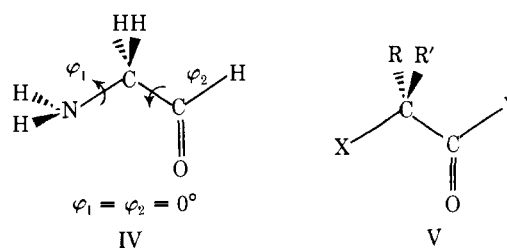
discussion of the general stereochemistry of α-hydroxycarboxylic acids and aldehydes. The corresponding α-amino structures should show some parallel features.

II. Method and Results

In order to discuss the internal rotational potential surfaces of I and IV, it is necessary to specify a convention for dihedral angles. We adopt the rotational angles indicated which are analogous to those used for the corresponding hydroxy compounds. The angle φ_1 refers to the N–C bond, the zero value corresponding to the trans arrangement for the bisector of the two NH bonds and the C–C bond. This corresponds to eclipsing of the NH$_2$ and CH$_2$ groups. The dihedral angle φ_2, referring to the C–C bond, is zero with a cis arrangement of NCC=O. Finally φ_3 is the dihedral angle for the C–O bond of the carbonyl group, zero corresponding to a cis structure for O=COH. The convention for sign followed for φ_1, φ_2, and φ_3 rotation is the same as those given in the preceding paper.

Quantum mechanical energy calculations were carried out using standard restricted Hartree–Fock molecular orbital theory with the 4-31G basis (RHF/4-31G).[9] For some geometrical arrangements, direct energy descent techniques had to be used to achieve convergence.[10] Standard values[11] were used for bond lengths and angles for structures I and IV.

The energy results are summarized in Table I. Figure 1 shows energy contour maps with φ_3 fixed at zero for glycine, in accordance with the formic acid structure[12] and the cationic amino acid[4,5] structures III. Figure 2 is the corresponding contour map for α-aminoacetaldehyde. A systematic series of sections of these potential surfaces is shown in Figures 3 and 4.
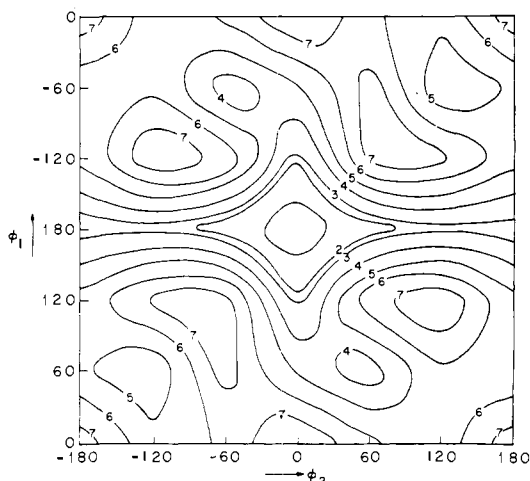
III. Discussion

The molecular orbital calculations indicate that both glycine and α-aminoacetaldehyde are most stable in the conformation

Table I. Relative Conformational Energies of Glycine and α-Aminoacetaldehyde

| Conformational angle, deg[a]		Energy, kcal/mol[b]	
φ_1	φ_2	Glycine[c]	α-Aminoacetaldehyde[d]
0	0	8.1	7.9
60		4.8	3.8
120		2.7	1.8
180		0.0	0.0
0	60	6.2	6.7
60		3.6	2.7
120		6.6	5.9
180		2.2	2.8
−120		7.6	7.6
−60		7.4	7.2
0	120	5.3	3.0
60		5.9	2.0
120		8.0	6.4
180		2.9	3.1
−120		7.3	6.9
−60		4.1	4.4
0	180	7.5	1.4
60		5.1	1.9
120		5.4	5.9
180		2.6	2.9
0	180	2.2[e]	

[a] Angles are defined in section II (see structure I). $\varphi_3 = 0°$ unless otherwise specified. [b] Relative to minimum energy conformation ($\varphi_1 = 180, \varphi_2 = 0°$). [c] Total energy for $\varphi_1 = 180, \varphi_2 = 0°$ is −282.40077 au. [d] Total energy for $\varphi_1 = 180, \varphi_2 = 0°$ is −207.61945 au. [e] φ_3 is taken to be 180°.

Figure 1. Conformational potential energy map for glycine (based on $\varphi_3 = 0°$). Contour labels refer to energy (kcal/mol) relative to $\varphi_1 = 180, \varphi_2 = 0°$.

with $\varphi_1 = 180, \varphi_2 = 0°$ (structures VI and VII). This will be used as a reference in the subsequent discussion of the potential

VI   VII
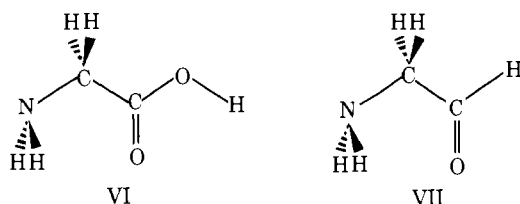
surface. The energies for glycine are relative to VI and those for α-aminoacetaldehyde are relative to VII unless otherwise mentioned. For convenience, we shall denote individual points (with $\varphi_3 = 0°$ for glycine) by a symbol (φ_1, φ_2).
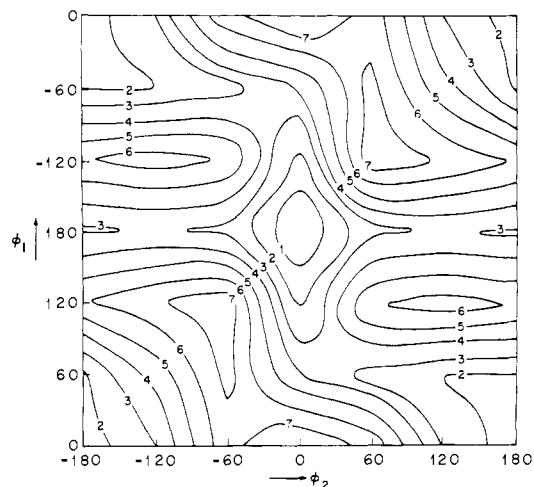
Figure 2. Conformational potential energy map for α-aminoacetaldehyde. Contours are labeled as in Figure 1.
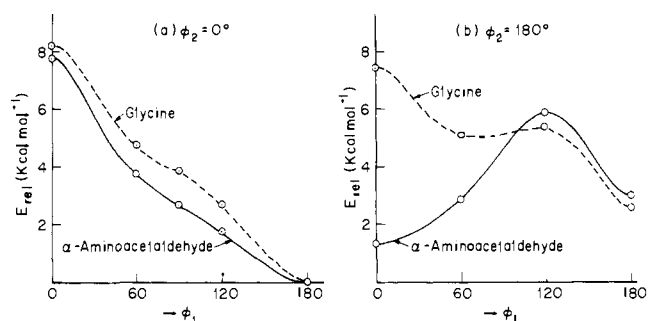
Figure 3. One-dimensional conformational profiles for glycine and α-aminoacetaldehyde. The energy is plotted as a function of φ_1. (a) φ_2 fixed at 0°. (b) φ_2 fixed at 180°.
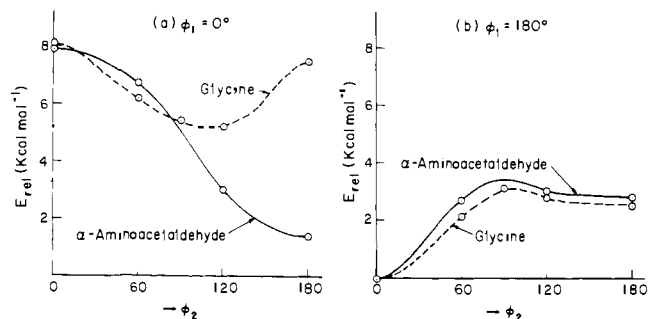
Figure 4. Analogue of Figure 3 for variation with respect to φ_2. (a) φ_1 fixed at 0°. (b) φ_1 fixed at 180°.

Both two-dimensional energy surfaces $E(\varphi_1, \varphi_2)$ show local minima at points other than (180, 0). For glycine, the contour plot (Figure 1) indicates a shallow minimum in the neighborhood of (−60, 120) about 4 kcal/mol above the global minimum. For α-aminoacetaldehyde, there is clearly a low-lying
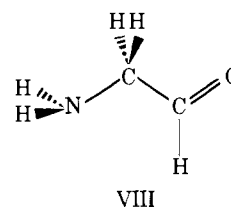
VIII

second local minimum at (0, 180) only 1.4 kcal/mol above VII. This corresponds to structure VIII.
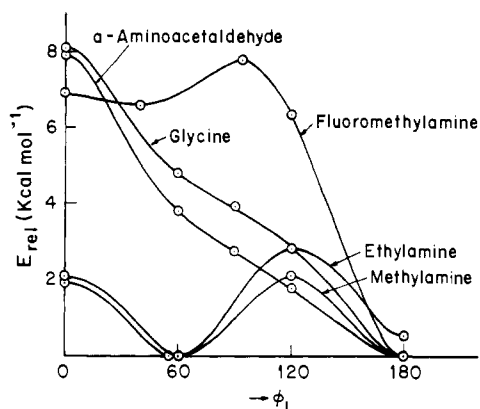
Figure 5. Potential energy variation with respect to φ_1 for glycine ($\varphi_2 = \varphi_3 = 0°$), α-acetaldehyde ($\varphi_2 = 0°$), fluoromethylamine, ethylamine, and methylamine.

A. C–N Bond Rotation.

We begin consideration of sections of the surfaces by comparing the C–N rotation with some other amines. Figure 5 compares the φ_1 potential energy variation (φ_2 being held at zero) with that for other amines. The nature of the curves depends on the substituent on the carbon atom. The normal threefold rotational barrier observed in methylamine[13] and ethylamine[13] does not exist for glycine and α-aminoacetaldehyde. Instead, only a single minimum exists at $\varphi_1 = 180°$. The rotational barrier is 8.1 kcal/mol and the maximum occurs at $\varphi_1 = 0°$. Fluoromethylamine shows somewhat similar behavior. It also has an energy of 6.9 kcal/mol at $\varphi_1 = 0°$, relative to the minimum at $\varphi_1 = 180°$. φ_1 rotation in glycine and α-aminoacetaldehyde resembles that of fluoromethylamine in that the $\varphi_1 = 120°$ conformation is more stable than the $\varphi_1 = 60°$ conformation, though the former is eclipsed. However, the energy difference between $\varphi_1 = 120$ and $60°$ is small in the case of fluoromethylamine, but is about 2 kcal/mol for glycine and α-aminoacetaldehyde. Further, the flat region between $\varphi_1 = 0$–$60°$ and the maximum at $\varphi_1 = 95°$ (7.8 kcal/mol) observed for fluoromethylamine are seen neither in glycine nor in α-aminoacetaldehyde for φ_1 rotation.

From the energy curves (with $\varphi_2 = 0$) of glycine and α-aminoacetaldehyde in Figure 5, it can be seen that the energy is a minimum at $\varphi_1 = 180°$ and increases monotonically up to $\varphi_1 = 0°$. The minimum may be due to direct interaction of carbonyl and amino groups (VI and VII), or the $\varphi_1 = 0°$ conformation may be destabilized by repulsive interaction of the nitrogen lone pair with the n lone pair electrons of the carbonyl group. The $\varphi_1 = 180$ or $120°$ conformations may also be stabilized by distorted intramolecular hydrogen bonds of the type N–H⋯O. Because of the difficulty in choosing a proper reference point for the theoretical study of intramolecular hydrogen bonds,[14] at present they can only be discussed in a qualitative manner.

Aside from energy, geometric considerations and charge distribution studies[15] have been the traditional approaches to the study of hydrogen bonds. From the geometric point of view, an ideal situation for hydrogen bond formation is to have angles N–H⋯O = $180°$ and H⋯O–C = $120°$.[15] The actual values of these angles are 106.0 and $87.7°$, respectively, in the ($120, 0$) conformation, and 92.0 and $79.6°$ in the ($180, 0$) conformation. At the ($180, 0$) conformation, the amino protons are symmetrically above and below the NCCO plane, giving a bifurcated pair of hydrogen bonds. The r(O⋯H) distances are 2.56 and 2.70 Å, respectively, in ($180, 0$) and ($120, 0$) conformations, the N⋯O distances in both cases being 2.65 Å. This is considerably smaller than the average N⋯O distance[16] observed for N–H⋯O hydrogen-bonded systems. The angles indicate highly distorted hydrogen bonds.

Table II. Population Analysis of N–H⋯O Linkage

Molecule	Atomic population shift[a]		
	Δq_N	Δq_H	Δq_O[b]
	Glycine		
($180, 0$)	0.015	−0.009	0.048
($120, 0$)	0.065	−0.047	0.041
	α-Aminoacetaldehyde		
($180, 0$)	0.012	−0.008	0.039
($120, 0$)	0.058	−0.045	0.044

[a] Δq values are defined relative to the ($0, 0$) conformation. Positive Δq values correspond to an increase in atomic electron population. [b] Oxygen atom of C=O bond.

The N–H⋯O charge distributions (Table II) indicate weak intramolecular hydrogen bonding when the ($0, 0$) conformation is taken as the reference point. There is a gain in the positive charge on the amino proton and in the negative charge on the nitrogen in the ($120, 0$) and ($180, 0$) conformations. The magnitude of these charge gains are comparatively greater for the ($120, 0$) than for the ($180, 0$) conformation. At ($120, 0$) a single hydrogen bond is formed with greater charge displacement. Nevertheless, the bifurcated structures VI and VII ($180, 0$) are more stable.

Rotation around the C–N bond discussed so far shows that both glycine and α-aminoacetaldehyde exhibit the same type of characteristics, when the amino nitrogen is cis with the carbonyl oxygen ($\varphi_2 = 0°$). As can be seen from Figure 3, this is not true for all values of φ_2. The energy curves for φ_1 rotation are similar for both molecules for $\varphi_2 = 0$ (Figure 3a) and $60°$. However, the potential energy curves for φ_1 rotation differ significantly from each other as φ_2 approaches a value of $180°$ (Figure 3b). This is due to the fact that the amino group approaches a proton in the case of α-aminoacetaldehyde, and a hydroxy group in the case of glycine. In fact, the ($0, 180$) conformation is a deep energy minimum in α-aminoacetaldehyde VIII, whereas it is an energy maximum in glycine. The maximum in glycine at ($0, 180$) is produced by the eclipsing of N–H bonds with C–H bonds and also by the lone pair repulsive interaction between nitrogen and the hydroxy oxygen. The minimum at ($0, 180$) in α-aminoacetaldehyde is interesting, since the minimum occurs in spite of the eclipsing of N–H bonds. It is discussed further in the following paragraphs.

As already noted, the ($0, 180$) conformation VIII of α-aminoacetaldehyde is a local minimum 1.4 kcal above the global minimum VII. Comparable minima are also found theoretically in hydroxy and fluoro analogues (Table III). Both rotomers ($\varphi_2 = 0$ and $180°$) have been detected experimentally for chloroacetaldehyde.[17]

In α-aminoacetaldehyde, the forces responsible for lowering the energy must be strong enough to offset the eclipsing of all three bonds at nitrogen with other single bonds. One of the reasons may be favorable dipole interaction of the amino group and the carbonyl group. The charge distribution on the aldehyde proton may also be effective in stabilizing the ($0, 180$) conformation. Table IV shows that the energy difference between $\varphi_2 = 180$ and $0°$ in various acetaldehydes depends on the nature of substituent on the α-carbon. In acetaldehyde and propionaldehyde, $\varphi_2 = 0°$ is more stable than $\varphi_2 = 180°$, the difference in energies being 0.7 and 1.3 kcal/mol, respectively. On the other hand, in acetaldehydes with electronegative substituents on α-carbon, the conformation $\varphi_2 = 180°$ is more stable than $\varphi_2 = 0°$ ($\varphi_1 = 0°$ for glycolaldehyde and aminoacetaldehyde). The energy differences are 4.1, 5.8, and 6.5 kcal/mol, respectively, in fluoro-, hydroxy-, and aminoacetaldehydes. This increase is associated with an increase in the

Table III. Comparative Studies on Acetaldehydes with Electronegative Substituents on α-Carbon ($\varphi_1 = 0°$ for Hydroxy and Amino Aldehydes)

Substituent α-carbon	Dihedral angle φ_2, deg	Rel energy, kcal/mol	Dipole moment, D	Charge Densities on Aldehyde H	O	Heavy atom on α-carbon
F[a]	0	4.1	4.8	0.818	8.489	9.426
	60	6.3	4.1	0.811	8.487	9.430
	120	3.3	2.6	0.803	8.502	9.440
	180	0	1.2	0.793	8.520	9.447
OH[b]	0	7.2	5.3	0.838	8.489	8.720
	60	7.7	4.8	0.831	8.491	8.729
	120	4.1	3.9	0.823	8.508	8.739
	180	1.3	3.5	0.807	8.527	8.751
NH$_2$[c]	0	7.9	5.0	0.838	8.496	7.756
	60	6.7	4.7	0.832	8.522	7.773
	120	3.0	4.3	0.824	8.540	7.800
	180	1.4	4.0	0.806	8.547	7.810

[a] The energies are relative to the minimum energy conformation at $\varphi_2 = 180°$ and total energy for this conformation is -251.404974 au. [b] The energies are relative to $\varphi_1 = 180$, $\varphi_2 = 0$, $\varphi_3 = 0°$ conformation. The results are based on experimental geometry. For further details see Table II of the preceding paper. [c] Energies are relative to $\varphi_1 = 180$, $\varphi_2 = 0$, $\varphi_3 = 0°$ conformation. See footnote of Table I.

Table IV. Energy and Charge Density (on Aldehyde Proton) Differences in Aldehydes, for Conformations with C=O Bond Eclipsed and Staggered

Molecule	Structures 1	2	$\Delta E(1 - 2)$,[a] kcal/mol	$\Delta P(1 - 2)$[b] on aldehyde H
Acetaldehyde			-0.7	0.0036
Propionaldehyde			-1.3	0.0004
Fluoroacetaldehyde			4.1	0.025
Glycolaldehyde			5.8	0.031
α-Aminoaceteldehyde			6.5	0.032

[a] Difference in the energy between structures 1 and 2. The values are positive if structure 2 has lower energy. [b] ΔP = difference in the charge density on the aldehyde hydrogen atom between structure 1 (C=O bond eclipsed) and structure 2 (C=O staggered). Positive values indicate an increase in positive charge in structure 2.

positive character of the aldehyde proton. In fact, Table III shows that the aldehyde proton steadily loses electron density on varying φ_2 from 0 to 180° in acetaldehydes substituted with F, OH, or NH$_2$. A gain in electron density by the electronegative atom is also observed. Since the positive charge on the proton is an important factor in the formation of hydrogen bonds,[18] a C–H⋯X (X = F, OH, or NH$_2$) bond[19] may stabilize the (0, 180) conformation. However, the geometry can allow for only a highly distorted hydrogen bond structure and as mentioned before, a quantitative assessment of intramolecular hydrogen bond strength is not possible at present. As can be noted from Table III, the decrease in dipole moment values are associated with a decrease in the electron density on the aldehyde proton and an increase in the electron density on the electronegative atom on α-carbon. Thus, the change in the
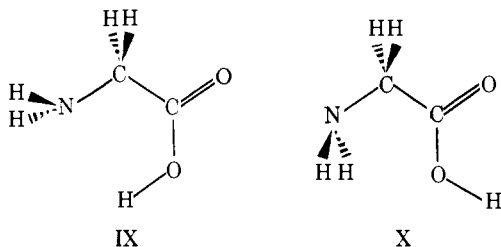
electron densities observed can have an effect in stabilizing (0, 180) conformation either indirectly by influencing the dipolar interactions or directly by the formation of an intramolecular hydrogen bond.

B. C–C Bond Rotation. Next we consider rotation around the C–C bond in these amines and compare them with their hydroxy analogues. φ_2 rotation produces similar curves for glycine and φ-aminoacetaldehyde when $\varphi_1 = 180°$ (Figure 4b). The region between $\varphi_2 = 90$–180° is almost flat with a slight minimum at 180°. On the other hand, there is no corresponding flat region in the hydroxy analogues and a definite minimum exists at the (180, 180) conformation. However, the minimum at (180, 180) in glycolic acid lies 2.7 kcal/mol above (180, 0); in glycolaldehyde this difference is 6.2 kcal/mol. On the other hand, in both glycine and α-aminoacetaldehyde the

(180, 180) conformations have roughly the same energies above (180, 0) (2.6 kcal/mol in glycine and 2.9 kcal/mol in α-aminoacetaldehyde). The stability of the (180, 180) conformation in glycolic acid over the corresponding conformation in glycolaldehyde has been attributed to the intramolecular hydrogen bond.[8] Since the (180, 180) conformation in glycine and α-aminoacetaldehyde have roughly the same energies over the (180, 0) conformation, the corresponding bifurcated intramolecular hydrogen bonds of the type N–H⋯OH are apparently less effective in glycine. However, the energy difference between the (180, 0) and (180, 180) conformations in glycine and α-aminoacetaldehyde is smaller than in glycolaldehyde.

φ_2 rotation in glycine and α-aminoacetaldehyde is sensitive to φ_1 values. φ_2 rotation curves for glycine and α-aminoacetaldehyde in Figure 4b ($\varphi_1 = 180°$) are similar, but they are significantly different in Figure 4a ($\varphi_1 = 0°$). In Figure 4a, both glycine and α-aminoacetaldehyde have energy maxima at $\varphi_2 = 0°$. This can be attributed to the repulsive interaction between the lone pair electrons of the nitrogen and n-electrons of the carbonyl group. Also the three single bonds at nitrogen are eclipsed with other single bonds. As φ_2 approaches 180°, glycine has again a maximum, now due to the interaction of the nitrogen lone pair electrons with the lone pair on the hydroxy oxygen. As φ_2 approaches 180° for α-aminoacetaldehyde, on the other hand, an energy minimum is found. This is the same minimum at (0, 180) which was discussed earlier (structure VIII).

C. C–O Bond Rotation. Finally we consider the rotation around C–O bond of the carboxylic group in glycine (φ_3 rotation). When φ_1 is fixed at 0° and φ_2 at 180°, φ_3 has a minimum at 180°, represented by structure IX, and this structure has an energy of 2.2 kcal/mol above structure VI. The energy of this conformation of glycine is 0.4 kcal/mol lower than that of structure X, which has the (180, 180) con-

formation. The preference (0.4 kcal/mol) for structure IX over X is reasonably interpreted as being due to a hydrogen bond between the amino nitrogen and the hydroxy group in IX. The strength of this apparently overcomes other features favoring X. The eclipsing of the NH_2 and CH_2 groups destabilizes IX by about 2.1 kcal/mol (from comparable studies of methylamine[13]) and the abnormal trans HOC=O conformation destabilizes it further by about 6.3 kcal/mol (from comparable studies of formic acid[12]). Hence, apart from the internal hydrogen bonding, IX should be less stable than X by 8.4 kcal/mol. The N⋯H–O bond must therefore stabilize IX by about 8.8 kcal/mol. It may be noted that, in glycolic acid,[8] the analogue of structure X is 2.7 kcal/mol *more* stable than the analogue of IX. This difference may well be due to the greater electron donor character of the amino group compared with hydroxyl.

Although it is known that the cis orientation of the carboxylic group is preferred in formic acid,[12,20,21] the trans orientation is also observed in some crystals[22] where the carboxylic

hydroxy group is involved in intramolecular hydrogen bonding. Microwave studies[23] on 2-fluoroacetic acid reveal the presence of $\varphi_2 = \varphi_3 = 180°$ isomers, which are about 0.6 kcal/mol higher in energy than the $\varphi_2 = \varphi_3 = 0°$ conformations (STO-3G calculated difference between these two conformations is 1.1 kcal/mol).

IV. Conclusions

The principal conclusions of this work may be summarized as follows:

(1) For both glycine and α-aminoacetaldehyde the most stable conformation found is one in which the NH_2 group forms two distorted intramolecular bifurcated hydrogen bonds with the carbonyl oxygen (structures VI and VII).

(2) The aldehyde has an important second local minimum in the potential surface (VIII) in which there is an attractive interaction between the aldehyde hydrogen and the lone pair of electrons on nitrogen. This interaction also has some characteristics of a distorted hydrogen bond.

(3) Glycine has another stable structure (IX) in which the carbonyl group shows the abnormal trans HOC=O arrangement, but is lowered in energy by an O–H⋯N hydrogen bond.

(4) These conclusions about the conformations of these amines closely parallel features of the potential surfaces of the corresponding hydroxy compounds.

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