Radicals and Ions of Glycine: An ab Initio Study of the Structures and Gas-Phase Thermochemistry

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Abstract: The structures of glycine and the related radicals and ions were optimized at both HF/6-31G(D) and MP2/6-31G(D) levels. The vibrational frequencies were calculated at the HF/6-31G(D) or MP2/6-31G(D) levels and the total energies of these molecules were evaluated at the G2(MP2) level. Proton affinities (PAs) and bond dissociation energies (BDEs) were found. The PAs and BDEs demonstrate that there is a strong captodative stabilizing effect for the C-centered radicals. Thus for H_2NCH_2COOH the C–H BDE is relatively low, 331 kJ mol^{-1}. Using the G2(MP2) energies, the glycine ionization potential (894 kJ mol^{-1}) and the acyloxyl radical electron affinity (358 kJ mol^{-1}) were also derived. Values of C_p°, S°, $H^\circ - H_0^\circ$, $\Delta_f H^\circ$, and $\Delta_f G^\circ$ at 298 K were calculated. The recommended values of $\Delta_f H_{298}^\circ$ (in kJ mol^{-1}) are as follows: $H_3NCH_2COOH^+$ (249), $H_3NCHCOOH^{\cdot+}$ (454), H_2-$NCH_2COOH^{\cdot+}$ (502), $H_3NCH_2COO^{\cdot+}$ (547), $H_2NCHC(OH)_2^{\cdot+}$ (399), H_2NCH_2COOH (−392), $H_2NCHCOOH^{\cdot}$ (−279), $HNCH_2COOH^{\cdot}$ (−181), $H_2NCH_2COO^{\cdot}$ (−138), $H_2NCH_2COO^-$ (−491), $H_2NCHCOO^{\cdot-}$ (−346), and $HNCH_2COO^{\cdot-}$ (−303).

1. Introduction

Glycine is the simplest of the α-amino acids, and as an important model compound in biophysics and biochemistry, it has been the subject of many experimental[1-6] and theoretical investigations.[7-19] The −N−C−C(O)− structure, which occurs in glycine, is a fundamental building block in the α-amino acids and proteins derived from them.[20,21] The same group of atoms is also present in many heterocycles of biological importance. Damage to these molecules frequently creates ionic or free radical species centered in the −N−C−C(O)− unit.[22,23] Knowl-

edge of the structural and thermochemical properties of such intermediates is therefore of great interest in toxicology, pharmacology, and radiation biology.[24-26]

Ab initio calculations carried out with modern electronic structure methods, such as implemented in the Gaussian 92 molecular orbital package,[27] are a valuable source of structural information for both closed and open shell systems. In addition, they can be used to provide thermochemical information.[28,29] In fact when absolute G2(MP2)[30] energies are used in isodesmic reactions in conjunction with reliable experimental heats of formation for related systems, they can be expected to yield thermochemical data which are reliable to within ±10 kJ mol^{-1} or better.[28,29] For these reasons we have conducted G2(MP2) level[30] calculations on glycine and the O-, N-, and C-centered ions and radicals that may be formed from it. Similar calculations on the ions and radicals of formic and acetic acids were reported earlier.[29]

The most thorough theoretical studies of glycine to date are due to Jensen and Gordon[18] and the present authors.[19] One of the glycine-derived radicals has been investigated at high level by Leroy et al.[28] In this work, we extend the study to provide new structural and thermodynamic information for the radicals and ions of glycine, and we reinvestigate the three most stable glycine conformers in the gas phase at the G2(MP2) level with

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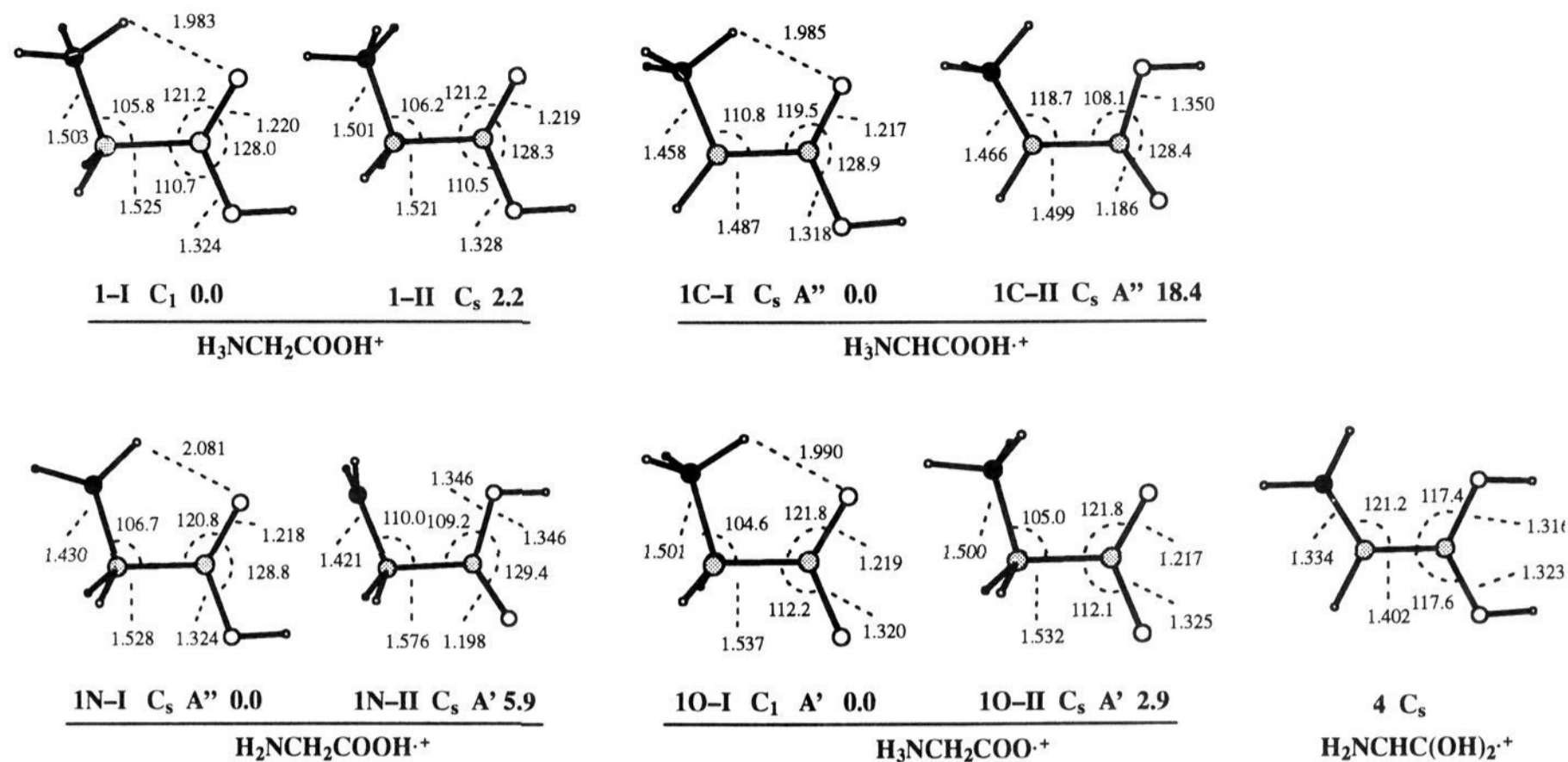(25) Stadtman, E. R. *Annu. Rev. Biochem.* **1993,** *62,* 797.

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1–I C₁ 0.0   **1–II Cₛ 2.2**   **1C–I Cₛ A" 0.0**   **1C–II Cₛ A" 18.4**

H₃NCH₂COOH⁺   H₃NCHCOOH·⁺

1N–I Cₛ A" 0.0   **1N–II Cₛ A' 5.9**   **1O–I C₁ A' 0.0**   **1O–II Cₛ A' 2.9**   **4 Cₛ**

H₂NCH₂COOH·⁺   H₃NCH₂COO·⁺   H₂NCHC(OH)₂·⁺

Figure 1. MP2/6-31G(D) optimized structures for cations. Filled circles represent nitrogen atoms and shaded circles carbon atoms. Large open circles are oxygen and small open circles hydrogen. Bond lengths are in angstroms and angles in degrees. Relative energies are in kilojoules per mole.

the objective of refining existing estimates of relative stabilities. The work is intended to lay the foundation for a study of such species in solution currently in progress. It also serves to provide comparisons with gas-phase experimental results. In section 2, we briefly describe the levels of ab initio theory used and the computational procedure. In section 3 we present the results, reporting the optimized geometries at the MP2/6-31G-(D) level, and the G2(MP2) energies. Thermochemical results are reported and compared with available experimental data in section 4. Then we discuss the general features of these calculated results in the light of available literature data. Finally our conclusions are stated in section 5.

2. Computation Details

Ab Initio Calculations. All ab initio calculations presented here were performed with the Gaussian 92 molecular orbital packages.[27] All species were calculated at the G2(MP2) level of theory.[30] The G2-(MP2) procedure includes a geometry optimization at the level of second-order Moller–Plesset perturbation theory with the 6-31G(D) basis set (MP2/6-31G(D)) and two single-point post-Hartree–Fock (HF) calculations, i.e. QCISD(T)/6-311G(D,P) and MP2/6-311+G(3DF,2P), on the MP2 optimized geometry in order to obtain an accurate estimate of the correlation energy. Harmonic frequencies are required by the G2(MP2) procedure at the HF/6-31G(D) level, scaled by 0.8929, for an estimate of the zero-point vibrational energy. Compared with the G2 theory,[31] the G2(MP2) method provides a similar level of accuracy, but with a significant saving in computational time and disk storage. Thus it can be applied to systems of moderate size.[30]

All of the structures discussed in this study (and shown in Figures 1–3) were obtained by unconstrained (C₁) optimization at (U)HF/6-31G(D) and (U)MP2/6-31G(D) levels, and therefore are local minima in their lowest electronic states. Where optimization yielded symmetric structures, symmetry-ordained equivalences were imposed on the parameters and the energy and symmetry of the lowest electronic state were determined by direct calculation. Harmonic frequency analysis at the (U)HF/6-31G(D) level yielded all real frequencies for all structures in Figures 1–3. In two cases where optimization at the MP2 level led to significant changes in the HF-predicted geometries,

harmonic frequency analysis was repeated at the (U)MP2/6-31G(D) level in order to verify the nature of the stationary points as minima. In these cases, the scaled MP2 ZPE was used in place of the prescribed HF ZPE for the G2(MP2) procedure.[30]

Thermodynamic Functions. Ideal gas thermodynamic functions C_p^o, S^o, $H^o - H_0^o$, $\Delta_f H^o$, and $\Delta_f G^o$ at 298.15 K and 1 bar of pressure were calculated by standard statistical thermodynamic methods based on the rigid rotor–harmonic oscillator model[32] and using the frequencies obtained at HF/6-31G(D) or MP2/6-31G(D) levels. In the standard statistical methods, hindered internal rotations are treated as vibrational motions rather than as free or hindered rotors. This approximation may entail some error in the calculated thermodynamic functions C_P^o, S^o, and $H^o - H_0^o$, which could be avoided in a more detailed treatment,[19] as in a few cases of the present study where the $-NH_3$ group torsional motion was treated as a rigid free rotator in calculating C_p^o, S^o, and $H^o - H_0^o$.

Heats of formation at 0 K, $\Delta_f H_0^o$, for all species were derived from their stabilities calculated at the G2(MP2) level relative to glycine, for which the experimental heat of formation was used. The calculated values of $H^o - H_0^o$ were used to evaluate heats of formation at 298.15 K. For ionic species the "ion convention", defined in ref 33, was followed. For some of the radicals the method of isodesmic reactions was used. The additional calculations required for the isodesmic reactions were also carried out at the G2(MP2) level. For all species studied, values of $\Delta_f G_{298}^o$ were derived from the most accurate values of $\Delta_f H_{298}^o$ and the entropy change of the formation reaction. The values of S_{298}^o for the elements were taken from Wagman et al.[34]

3. Computational Results and Discussion

The organization of the discussion and the identification of the structures is shown in Scheme 1. The present paper deals *solely with the gas-phase chemistry.* However, in anticipation of a solution-phase study, glycine-derived structures are arranged in Scheme 1 from left to right in order of their state in aqueous

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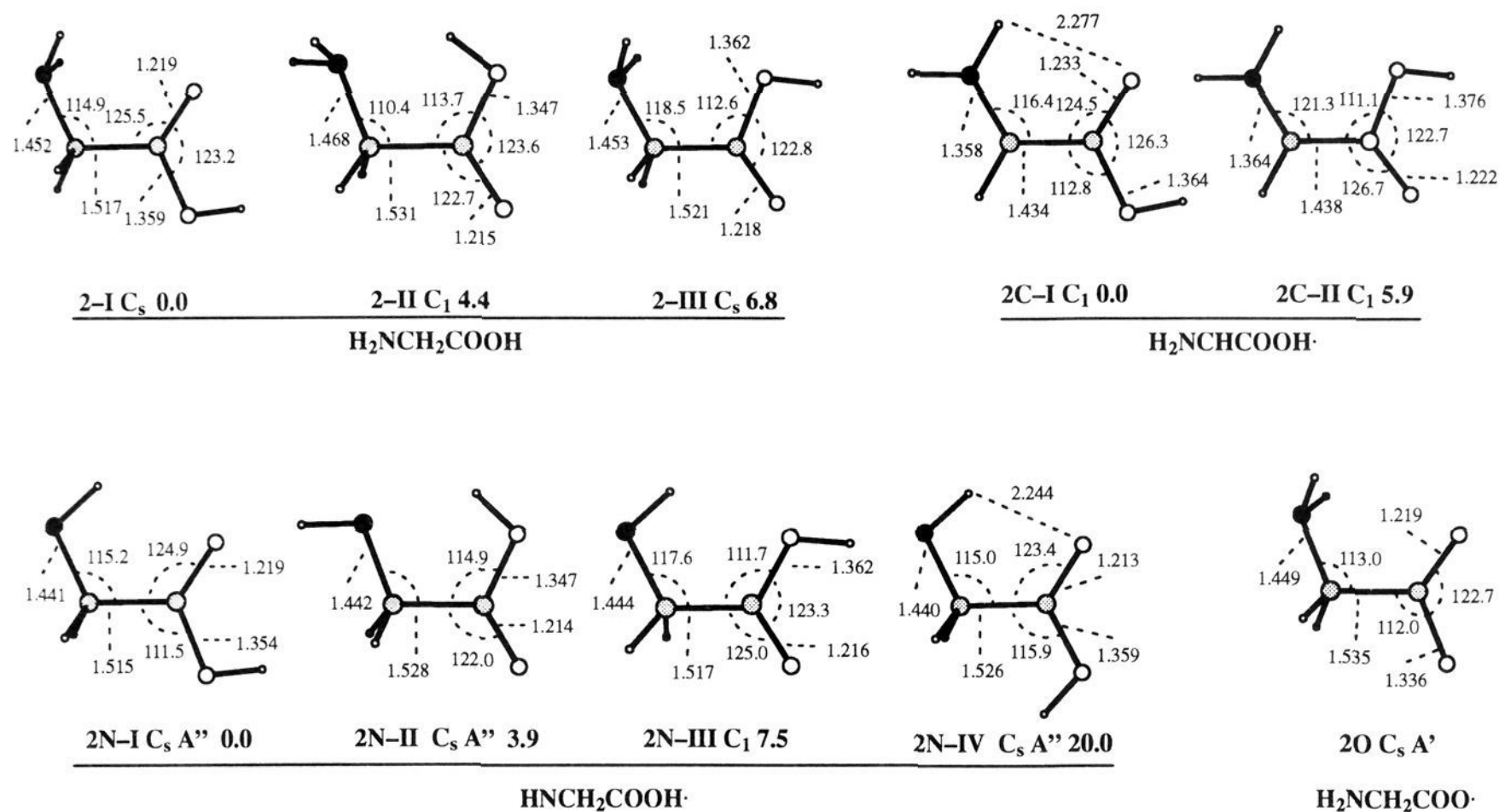
Figure 2. MP2/6-31G(D) optimized structures for neutral molecules. Filled circles represent nitrogen atoms and shaded circles carbon atoms. Large open circles are oxygen and small open circles hydrogen. Bond lengths are in angstroms and angles in degrees. Relative energies are in kilojoules per mole.
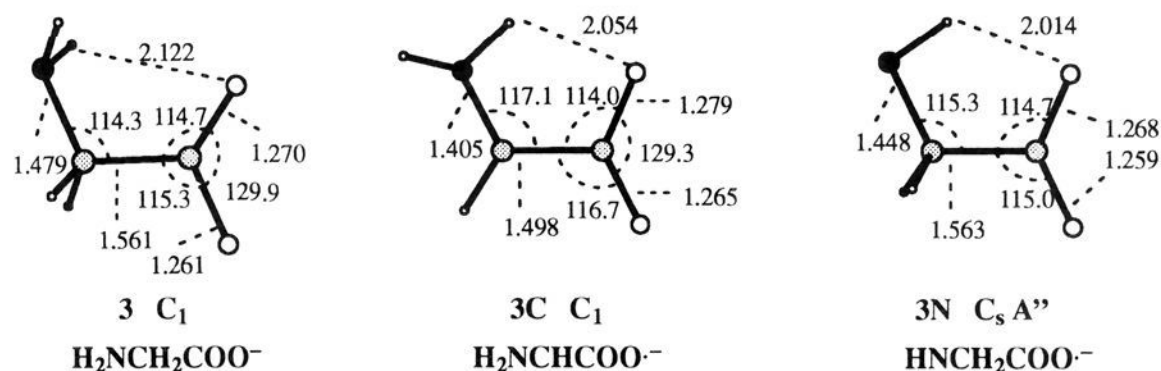
Figure 3. MP2/6-31G(D) optimized structures for anions. Filled circles represent nitrogen atoms and shaded circles carbon atoms. Large open circles are oxygen and small open circles hydrogen. Bond lengths are in angstroms and angles in degrees. Relative energies are in kilojoules per mole.

Scheme 1

	Cations	Neutral specis	Anions
	$H_2NCHC(OH)_2^{\cdot+}$ **4**		
	$H_3NCH_2COO^{\cdot+}$ **1O**	$H_2NCH_2COO^{\cdot}$ **2O**	
Radicals	$H_2NCH_2COOH^{\cdot+}$ **1N**	$HNCH_2COOH^{\cdot}$ **2N**	$HNCH_2COO^-$ **3N**
	$H_3NCHCOOH^{\cdot+}$ **1C**	$H_2NCHCOOH^{\cdot}$ **2C**	$H_2NCHCOO^{\cdot-}$ **3C**
Close–shell systems	$H_3NCH_2COOH^+$ **1**	H_2NCH_2COOH **2**	$H_2NCH_2COO^-$ **3**

solution of increasing pH. Thus, structures **1**, **2**, and **3** identify protonated glycine, neutral glycine, and glycine anion, respectively.

Free radical species may be derived from **1**, **2**, or **3** by the removal of a hydrogen atom. The symbol of the corresponding element is used to designate whether H• is removed from the N, C, or O atom. Thus, structure **2C** would represent the free radical which is obtained by removal of H• from the carbon atom of neutral glycine, **2**. One free radical, structure $H_2NCHC-(OH)_2^{\cdot+}$ (**4**), arises from tautomerization of **1N** or **1C**.

Almost all species exist in more than one conformational form. When conformations must be designated these are

Table 1. Vibrational Zero-Point Energies (ZPE, at HF/6-31G(D)) and Total and Relative G2(MP2) Energies

species	symbol	ZPE, kJ mol^{-1}	G2(MP2), hartree	Δ(G2(MP2)), kJ mol^{-1}	$\langle S^2 \rangle$
H$_3$NCH$_2$COOH$^+$	1-I	252.1^a	−284.345 78^b	−882.1	
	1-II	268.7	−284.344 93	−879.9	
H$_3$NCHCOOH$^{\cdot+}$	1C-I	227.0	−283.682 51	859.3	0.793
	1C-II	225.1	−283.675 50	877.7	0.815
H$_2$NCH$_2$COOH$^{\cdot+}$	1N-I	221.7	−283.669 27	894.0	0.763
	1N-II	220.7	−283.667 02	899.9	0.755
H$_3$NCH$_2$COO$^{\cdot+}$	1O-I	216.7^a	−283.651 66^b	940.3	0.759
	1O-II	231.1	−283.650 55	943.2	0.759
H$_2$NCHC(OH)$_2^{\cdot+}$	4	224.4	−283.701 25	810.1	0.772
H$_2$NCH$_2$COOH	2-I	227.5	−284.009 79	0.0	
	2-II	229.2	−284.008 11	4.4	
	2-III	227.5	−284.007 21	6.8	
H$_2$NCHCOOH$^{\cdot}$	2C-I	189.1	−283.380 64	1651.8	0.778
	2C-II	188.8	−283.378 40	1657.7	0.792
HNCH$_2$COOH$^{\cdot}$	2N-I	186.1	−283.348 94	1735.1	0.760
	2N-II	187.2	−283.347 45	1739.0	0.761
	2N-III	186.0	−283.346 06	1742.6	0.760
	2N-IV	185.3	−283.341 30	1755.1	0.760
H$_2$NCH$_2$COO$^{\cdot}$	2O	189.6	−283.330 49	1783.5	0.758
H$_2$NCH$_2$COO$^-$	3	190.5	−283.466 77	1425.7	
H$_2$NCHCOO$^{\cdot-}$	3C	151.4	−282.824 98	3110.7	0.766
HNCH$_2$COO$^{\cdot-}$	3N	149.3	−282.814 46	3138.3	0.760

^{a} Calculated at the MP2/6-31G(D) level. ^{b} 0.95 × ZPE(MP2/6-31G(D)) in place of 0.89 × ZPE(HF/6-31G(D)).

identified by appended roman numerals in order of increasing relative energy. Thus **1O-I** is the lowest energy conformer of the free radical obtained by removal of the H atom on oxygen from the protonated form, **1**, of glycine. The MP2/6-31G(D) structures of all the species discussed are shown in Figures 1−3. The vibrational ZPEs evaluated at the HF/6-31G(D) or MP2/6-31G(D) levels and the total energies and relative energies calculated at the G2(MP2) level of ab initio calculations are collected in Table 1.

The Protonated Glycine Cation, H$_3$NCH$_2$COOH$^+$ 1-I and 1-II. Two conformers were studied for the protonated glycine. Structure **1-II** (Figure 1) closely resembles structure **2-I** of neutral glycine (Figure 2) and has C_s symmetry. There are only minor changes in the geometric parameters describing the local structure of the CH$_2$COOH group due to the proton addition on the nitrogen atom (cf. **2-I** in Figure 2). The C−N bond is longer by 0.05 Å and the NCC angle is narrowed by 9° in going from neutral glycine to this cation. The −NH$_3$ carries a large portion of the positive charge, this being 0.6 as calculated from the Mulliken population.

Rotating the −NH$_3$ group in structure **1-II** by 60° leads to another possible stable conformer, which has a strong hydrogen bond between the in-plane H atom of the −NH$_3$ group and the oxygen of the −COO group but an unfavored eclipsed arrangement between the H atoms of the −NH$_3$ and −CH$_2$ groups. MP2/6-31G(D) optimization with no symmetry constraints gives structure **1-I**, as plotted in Figure 1, which is a minimum on the MP2/6-31G(D) surface as confirmed by the frequency calculation. The interaction between the eclipsed hydrogen atoms is reduced by a rotation of the −NH$_3$ and −COO groups in such a way as to maintain the strong hydrogen bonding interaction (H···O distance 1.983 Å). The other parameters are similar to those of structure **1-II**. At the G2(MP2) level, structure **1-I** is more stable by 2.2 kJ mol^{-1} than structure **1-II**.

The Cationic Radicals: H$_3$NCHCOOH$^{\cdot+}$ (1C), H$_2$NCH$_2$COOH$^{\cdot+}$ (1N), H$_3$NCH$_2$COO$^{\cdot+}$ (1O), and H$_2$NCHC(OH)$_2^{\cdot+}$ (4). Two conformers were studied for H$_3$NCHCOOH$^{\cdot+}$ (1C). Both structures, **1C-I** and **1C-II** (Figure 1), have C_s symmetry and are in the ^{2}A$''$ electronic state. In **1C-I**, the distance between the in-plane H atom of the −NH$_3$ group and the O atom is found

to be 1.985 Å, much shorter than the corresponding van der Waals separation (2.6 Å)[35] and indicating a strong hydrogen bonding interaction. Conformer **1C-II** is related to **1C-I** by a 180° rotation around the C−C bond. The differences between the geometric parameters in these two conformers are mainly due to the hydrogen bonding interaction in **1C-I** which is absent in **1C-II**. In going from structure **1C-I** to **1C-II**, the NCC bond angle opened up by 8° (see Figure 1), both the NH and CC bonds are longer by 0.012 Å, and the CN bond is longer by 0.008 Å. At the G2(MP2) level, **1C-II** is 18.4 kJ mol above structure **1C-I**.

As in the case of structure **1-I**, **1O-I** has a C_1 symmetry to achieve a semistaggered arrangement of hydrogen atoms and to keep the hydrogen bonding interaction. The H atom of −NH$_3$ is out of the molecular plane by 20° and the hydrogen bond is 1.990 Å. Conformer **1O-II** of H$_3$NCH$_2$COO$^{\cdot+}$ is a σ radical (^{2}A$'$ state) with C_s symmetry. Structure **1O-II** has the preferred staggered arrangement for the H atoms of −CH$_2$ and −NH$_3$ groups but reduced H bonding interaction. At the G2(MP2) level, structure **1O-II** is less stable by 2.9 kJ mol^{-1} than **1O-I**. The corresponding geometric parameters of structures **1O-I** and **1O-II** are similar. The unpaired spin density is largely localized to the distal oxygen of the −CO$_2$ group in both structures **1O-I** and **1O-II**.[36]

Two minima were located for radical cation H$_2$NCH$_2$COOH$^{\cdot+}$ (**1N**, Figure 1). Structure **1N-I** is a ^{2}A$''$ radical with C_s symmetry. Both the positive charge and the unpaired spin density are localized to the −NH$_2$ group. There is a strong hydrogen bonding interaction between one H atom of the −NH$_2$ group and the carboxyl O atom, as indicated by the smaller separation than that of van der Waals (2.081 vs 2.6 Å). Rotation of the −NH$_2$ group through 90° permits an attractive 3-electron interaction between the N and an oxygen atom of the −CO$_2$H group. This attraction is not sufficient to outweigh the energetic advantage of the hydrogen bond when the more basic carbonyl oxygen atom is presented to N, but it does lead to a stable structure **1N-II** when the less basic OH group is presented to the −NH$_2^{\cdot+}$ group. The molecular point group of structure **1N-II** is also C_s. The H$_2$NC− group is almost planar (within 1° deviation). At the G2(MP2) level, **1N-II** is less stable than **1N-I** by 5.9 kJ mol^{-1}.

H$_2$NCHC(OH)$_2^{\cdot+}$ (**4**, Figure 1) was found to be significantly more stable than the other cationic radicals (by 49.2, 83.9, and 130.2 kJ mol^{-1} relative to H$_3$NCHCOOH$^{\cdot+}$ (**1C**), H$_2$NCH$_2$COOH$^{\cdot+}$ (**1N**), and H$_3$NCH$_2$COO$^{\cdot+}$ (**1O**), respectively) at the G2(MP2) level. The optimized structure has C_1 symmetry at the HF/6-31G(D) level with the two hydroxy groups turned out of the average molecular plane by about 15°. However, the MP2/6-31G(D) optimized structure has C_s symmetry (a planar radical in a ^{2}A$''$ electronic state). Carbon-centered radicals like **4**, which have both π donor (−NH$_2$) and π acceptor (−C(OH)$_2^+$) substituents, have been shown[37] to be more stable than with

(35) The van der Waals radii are 1.2, 1.4, and 1.5 Å for H, O, and N atoms, respectively, as given in *Handbook of Chemistry and Physics*; Chemical Rubber Publishing Co.: Cleveland, OH.

(36) The results from our recent investigation of the structures of formyloxyl radicals[51] suggest that there are three electronic states which lie within 10 kJ mol^{-1} of each other. All are σ radicals. Two have C_{2v} symmetry (^{2}A$_1$ and ^{2}B$_2$) and the third has a "broken symmetry" structure with C_s symmetry (^{2}A$'$). In acetyloxyl,[51] the ^{2}A$_1$-like state is destabilized by 22 kJ mol^{-1} and the ^{2}A$'$-like state by 10 kJ mol^{-1} relative to the ^{2}B$_2$-like state. In glycine-derived species, the −CO$_2$ group resides in a lower symmetry environment than in either formyloxyl or acetyloxyl. Attempts to converge to a ^{2}B$_2$-like state (with approximately equal CO bonds) invariably resulted in the ^{2}A$'$-like geometry with long and short CO bonds and localized spin. In formyloxyl, the lowest acyloxyl π radical is more than 50 kJ mol^{-1} higher. Such radicals are not considered to be important in the description of the thermochemistry of the radicals of glycine.

either substituent alone. The consequences of the extra stabilization, termed "captodative effect",[38] on derived properties are discussed below.

Glycine, H₂NCH₂COOH (2), the Parent Molecule. Thorough studies on the glycine conformations have been carried out by the present authors[19] and others.[18] The relative energies of the three lowest energy conformers, **2-I**, **2-II**, and **2-III** of neutral glycine (Figure 2) were reexamined at the G2(MP2) level. With respect to the **2-I** conformer, structures **2-II** and **2-III** are found to be 4.4 and 6.8 kJ mol⁻¹, respectively, less stable. The previously determined values of 5.7 and 6.4 kJ mol⁻¹ (MP2/6-31+G(D) + ZPE level[19]) are in good agreement with the present G2(MP2) results.

The Neutral Radicals HNCH₂COOH• (2N), H₂NCHCOOH• (2C), and H₂NCH₂COO• (2O) (Figure 2). Four conformers, related by the C−C, C−N, and C−O rotations, are examined for HNCH₂COOH• (**2N**). The most stable conformer **2N-I** is a ²A″ radical with C_s symmetry and has the same internal configuration as the most stable glycine structure **2-I**. Rotating around C−C, C−N, and C−O by 180° leads to structure **2N-II**, a ²A″ radical lying 3.9 kJ mol⁻¹ above **2N-I** at the G2-(MP2) level. Starting with structure **2N-I** and rotating around the C−C bond by about 150° led to structure **2N-III**, with C_1 symmetry (one of the H atoms in the −CH₂ group tends to eclipse the carbonyl oxygen atom). Conformer **2N-III** is 7.5 kJ mol⁻¹ above structure **2N-I**. This relative energy differs by less than 1 kJ mol⁻¹ from the corresponding value for glycine (energy difference between structures **2-I** and **2-III**). A 180° rotation around the C−O bond from structure **2N-I** results in conformer **2N-IV** (²A″ state). At the G2(MP2) level, the energy cost due to adoption of the *s*-trans configuration of the −COOH group is found to be 20 kJ mol⁻¹, comparable to that of glycine (25 kJ mol⁻¹ at the MP2/6-31+G(D) + ZPE level).[19]

The most stable conformer of the carbon free radical H₂NCHCOOH• (**2C**) has C_1 symmetry (**2C-I** of Figure 2). Except for the H atoms of the NH₂ group, all other nuclei are essentially in the same plane. The unpaired spin density is predominantly on the α-center but also delocalized over the other heavy atoms, with a value of 0.18 on the nitrogen atom. A rotation around the C−C bond by 180° led to another C_1 conformer, structure **2C-II** (Figure 2), which is 5.9 kJ mol⁻¹ higher than structure **2C-I** at the G2(MP2) level. The spin densities on the α-center and the nitrogen atom of **2C-II** are similar to that of **2C-I**, but there is a small redistribution of spin density between the two ends of the C−O single bond of the −COOH group.

The optimized H₂NCH₂COO• structure (**2O**, Figure 2) has C_s symmetry.[36] The ground state is ²A′ (a σ radical). The unpaired spin is localized at the oxygen atom which forms a "single" bond (bond length 1.336 Å, see Figure 2) with the C atom.

The Glycine Anion: H₂NCH₂COO⁻ (3, Figure 3). H₂NCH₂COO⁻ has C_1 symmetry and is characterized by a N−H•••O hydrogen bond which results in an eclipsed arrangement between the other carboxyl oxygen atom and a hydrogen atom of the CH₂ group. The hydrogen bonding interaction is relatively strong, as indicated by a short H•••O separation (2.122 vs 2.6 Å of the van der Waals distance) and dissimilarity of the two CO bonds (1.261 vs 1.270 Å).

The Anionic Radicals: HNCH₂COO•⁻ (3N) and H₂-NCHCOO•⁻ (3C). HNCH₂COO•⁻ (**3N**) is a nitrogen centered

radical with C_s symmetry (Figure 3). The C−C bond length is 1.563 Å, essentially unchanged from glycine anion **3**, while the N−H•••O separation has decreased. The optimized structure **3C** for H₂NCHCOO•⁻ has C_1 symmetry and a short N−H•••O separation, an indication of H bonding. The local NH₂C− structure is tetrahedral, with an average (two HNC and one HNH angles) bond angle of 109.4°. Although formally in the same category as **4**, and to a lesser extent **1C** and **2C**, less stabilization of the carbon-centered radical by the carboxyl(ate) group is expected since the negatively charged carboxylate group is not a good π acceptor.

An Estimation on the Relative Stabilities of Zwitterion Species H₃N⁺CH₂COO⁻ and H₃N⁺CHCOO•⁻. Previous studies[19,39] indicate that the zwitterion form of glycine does not exist as a stationary structure in the gas phase. However, it is known that this form is the dominant structure in aqueous solution. As the present work is intended to lay the foundation for a study of glycine and its derived radicals in aqueous solution, we estimated the G2(MP2) energies for H₃N⁺CH₂COO⁻ (**5**) and H₃N⁺CHCOO•⁻ (**5C**).

5 C_s 5C C_s ²A″
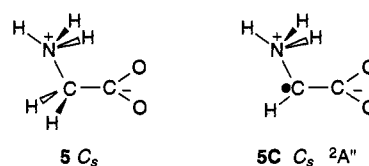
With C_s constraint and orientation of the −NH₃ group in such a way as to prevent proton transfer, MP2/6-31G(D) optimization led to stationary points for both **5** and **5C**. Frequency calculations gave one and two imaginary frequencies for H₃N⁺CH₂COO⁻ (**5**) and H₃N⁺CHCOO•⁻ (**5C**), respectively. Using 0.95 × ZPE(MP2) in place of 0.89 × ZPE(HF)), the "G2-(MP2)" energy for H₃N⁺CH₂COO⁻ (**5**) is −283.968 89 hartrees. Thus **5** is 107.4 kJ mol⁻¹ above the neutral glycine H₂NCH₂COOH (**2**) and is essentially the same as the previous value (106.5 kJ mol⁻¹) calculated at a lower level.[19] The similarly estimated "G2(MP2)" energy for H₃N⁺CHCOO•⁻ (**5C**) is −283.310 87 hartrees, or 1727.6 kJ mol⁻¹ above H₃N⁺CH₂COO⁻ (**5**).

4. Thermochemistry

Values of the thermodynamic functions C_P°, S°, and $H^\circ − H_0^\circ$ obtained from the calculated vibrational frequencies are given in Table 2. Values of $\Delta_f H_{(c)298}^\circ$ and $\Delta_f G_{(c)298}^\circ$ were obtained as described in the subsection below.

Heats and Free Energies of Formation. The heat of formation of crystalline glycine at 298 K and 1 bar, $\Delta_f H_{(c)298}^\circ$, is well established. The value given in the recent NBS compilation,[34] −528.1 kJ mol⁻¹, agrees well with −528.6 kJ mol⁻¹ selected earlier by Cox and Pilcher.[40] The heat of formation of gaseous glycine under standard conditions, $\Delta_f H_{(g)298}^\circ$, is calculated by addition of the heat of sublimation ΔH_{s298}° derived as follows. Heats of sublimation for the 408−470 K temperature range, $\Delta H_{s(408-470)}^\circ$, have been measured in several laboratories.[41,42] The results give an average of 133.7 ± 3.2 kJ mol⁻¹, and the temperature dependence, if any, is clearly less than the standard deviation of these values.[42] Taking the mean upper temperature of the experiments (429 K), the correction of $\Delta H_{s(408-470)}^\circ$ to 298 K is $\int_{298}^{429} (C_{P(c)} − C_{P(g)})\, dT$.

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Table 2. Ideal Gas Thermodynamic Properties at 298.15 K

| | | | | | $\Delta_f H^{\circ\,b}$ | | |
	symbol	$C_P^{\circ\,a}$	$S^{\circ\,a}$	$H^{\circ} - H_0^{\circ\,b}$	Δ(G2(MP2))	rec	$\Delta_f G^{\circ\,b}$
$H_3NCH_2COOH^{+\,c}$	1	83.8	321.8	16.7	250	249	363
$H_3NCHCOOH^{\bullet+}$	1C	90.7	318.5	17.8	468	454	549
$H_2NCH_2COOH^{\bullet+}$	1N	89.8	314.2	17.2	502	502	599
$H_3NCH_2COO^{\bullet+\,c}$	1O	80.3	320.8	16.5	547	547	642
$H_2NCHC(OH)_2^{\bullet+}$	4	96.0	318.9	18.2	419	399	494
H_2NCH_2COOH	2	87.5	313.1	17.4	−392	−392	−295
$H_2NCHCOOH^{\bullet}$	2C	89.9	311.5	17.2	−265	−279	−201
$HNCH_2COOH^{\bullet}$	2N	85.4	317.0	17.2	−182	−181	−105
$H_2NCH_2COO^{\bullet}$	2O	83.3	319.3	17.1	−133	−138	−62
$H_2NCH_2COO^{-}$	3	80.8	310.4	16.8	−491	−491	−413
$H_2NCHCOO^{\bullet-}$	3C	82.3	310.4	16.6	−331	−346	−287
$HNCH_2COO^{\bullet-}$	3N	78.4	314.4	16.3	−304	−303	−245

^{a} JK^{-1} mol^{-1}. ^{b} kJ mol^{-1}. ^{c} 0.95 × MP2/6-31G(D) frequencies were used. The −NH$_3$ group rotations were treated as free rotors.

Table 3. Heats of Formation (kJ mol^{-1}) from Isodesmic Reactions

| | | $\Delta_F H^{\circ}_{298}$ | |
compound	isodesmic reaction	Δ(G2(MP2))	isodesmic reaction
$H_2NCHC(OH)_2^{\bullet+}$ (4)	$H_2CC(OH)_2^{\bullet+} + H_2NCH_2COOH^{\bullet+} \rightarrow CH_3COOH^{\bullet+} + H_2NCHC(OH)_2^{\bullet+}$	419	398.5
$H_3NCHCOOH^{\bullet+}$ (1C)	$H_3NCHCOOH^{\bullet+} + CH_3COOH \rightarrow H_3NCH_2COOH^{+} + CH_2COOH^{\bullet}$	−468	456.6
	$H_3NCHCOOH^{\bullet+} + H_2NCH_2CH_3 \rightarrow H_3NCH_2COOH^{+} + H_2NCHCH_3^{\bullet}$		451.4
	average		454.0
$H_2NCHCOOH^{\bullet}$ (2C)	$H_2NCHCOOH^{\bullet} + CH_3^{\bullet} \rightarrow H_2NCH_2^{\bullet} + CH_2COOH^{\bullet}$	−265	−275.9^a
	$H_2NCHCOOH^{\bullet} + CH_3COOH \rightarrow H_2NCH_2COOH + CH_2COOH^{\bullet}$		−277.2
	$H_2NCHCOOH^{\bullet} + H_2NCH_2CH_3 \rightarrow H_2NCH_2COOH + H_2NCHCH_3^{\bullet}$		−282.5
	average		−278.5
$HNCH_2COOH^{\bullet}$ (2N)	$HNCH_2COOH^{\bullet} + H_2NCH_3 \rightarrow H_2NCH_2COOH + HNCH_3^{\bullet}$	−182	−181.3
$H_2NCH_2COO^{\bullet}$ (2O)	$H_2NCH_2COO^{\bullet} + HONO \rightarrow H_2NCH_2COOH + NO_2^{\bullet}$	−133	−138.4
	$H_2NCH_2COO^{\bullet} + CH_3COOH \rightarrow H_2NCH_2COOH + CH_3COO^{\bullet}$		−137.8
	average		−138.1
$H_2NCHCOO^{\bullet-}$ (3C)	$H_2NCHCOO^{\bullet-} + CH_3COOH \rightarrow H_2NCH_2COO^{-} + CH_2COOH^{\bullet}$	−331	−343.0
	$H_2NCHCOO^{\bullet-} + H_2NCH_2CH_3 \rightarrow H_2NCH_2COO^{-} + H_2NCHCH_3^{\bullet}$		−348.3
	average		−345.7
$HNCH_2COO^{\bullet-}$ (3N)	$HNCH_2COO^{\bullet-} + H_2NCH_3 \rightarrow H_2NCH_2COO^{-} + HNCH_3^{\bullet}$	−304	−303.0

^{a} From ref 28.

This integral requires a knowledge of $C_{P(c)}$ and $C_{P(g)}$, the heat capacities for crystalline and gaseous glycine, respectively, but is expected to be small.[40] Data for $C_{P(g)}$ did not exist in the past, but good estimates are now available from the ab initio study in ref 19. Accurate experimental data for $C_{P(c)}$ exist up to 300 K[43] and reasonable extrapolations to 429 K can be made. Using this information we find $\int_{298}^{429} (C_{P(c)} - C_{P(g)})\,dT$ equal to 1.7 ± 0.2 kJ mol^{-1} for the studies which gave $\Delta H^{\circ}_{s(408-470)} = 133.7 \pm 3.2$ kJ mol^{-1}. Thus ΔH°_{s298} is 135.4 ± 3.4 kJ mol^{-1}.

On the basis of the above values of ΔH°_{s298} and $\Delta_f H^{\circ}_{(c)298}$, one finds $\Delta_f H^{\circ}_{(g)298} = -392.7$ kJ mol^{-1}. Lias et al.[33] have recently reported a value of -391 ± 5 kJ mol^{-1}, and Cox and Pilcher's earlier recommendation[40] was -392.1 ± 0.6 kJ mol^{-1}. In this paper we use -392 ± 5 kJ mol^{-1} as the best value of $\Delta_f H^{\circ}_{(g)298}$ for glycine. The gas-phase heat of formation of every other species was calculated from this and the Δ(G2-(MP2)) energy of the species, given in Table 1. Corrections to 298 K were made on the basis of the $H^{\circ} - H_0^{\circ}$ data in Table 2. These values of $\Delta_f H^{\circ}_{(g)298}$ are given in column six of Table 2 under the heading $\Delta_f H^{\circ}(\Delta$(G2(MP2))).

Use of the differences in the G2(MP2) energies of the radical species and the experimental value of $\Delta_f H^{\circ}_{(g)298}$ for glycine in the procedure described above (instead of calculating them directly by the G2(MP2) procedure[44]) is expected to reduce residual errors arising from electron correlation effects. For
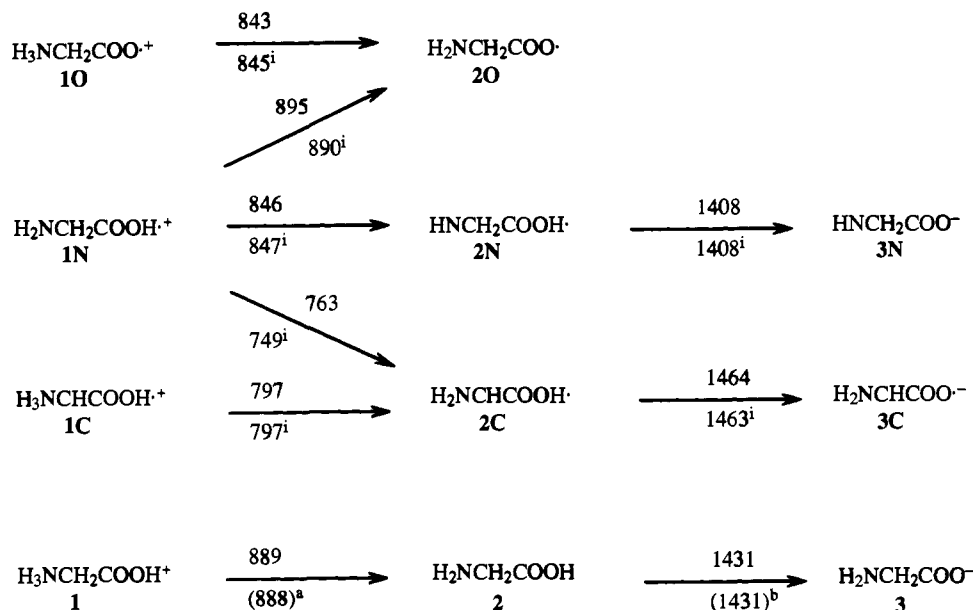
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some of the open shell species, where the error may be more severe, we carried out calculations of $\Delta_f H^{\circ}_{(g)298}$ based on isodesmic reactions. Table 3 contains the results. These values of $\Delta_f H^{\circ}_{(g)298}$ have been given in column seven of Table 2 as the recommended values of $\Delta_f H^{\circ}_{(g)298}$, $\Delta_f H^{\circ}$(rec). For all other species, closed or open shell, $\Delta_f H^{\circ}$(rec) was taken from the Δ-(G2(MP2))-derived values. The values of $\Delta_f G^{\circ}_{(g)298}$ in column eight of Table 2 were derived from the values of $\Delta_f H^{\circ}$(rec) and entropy data, as explained in section 2.

It is interesting to compare the values of $\Delta_f H^{\circ}_{(g)298}$ for the five species in Table 3 calculated from the isodesmic reactions and from the Δ(G2(MP2)) procedure relating them to the experimental $\Delta_f H^{\circ}_{(g)298}$ of glycine. The average discrepancy of 7.4 kJ mol^{-1} is about what one expects in G2(MP2) calculations. However, the fact that the only significant errors (13−20 kJ mol^{-1}) occur with the C-centered radicals $H_2NCHCO_2H^{\bullet}$ (2C), $H_2NCHCO_2^{\bullet-}$ (3C), and $H_2NCHC(OH)_2^{\bullet+}$ (4), suggests that special circumstances which are not as well described by the G2(MP2) procedure arise in the bonding of these species. This is discussed further below.

Ionization Potentials and Proton Affinities. Enthalpies of deprotonation and/or ionization at 1 bar of pressure and 298 K for the closed shell parent species and the open shell radicals or radical ions calculated from differences in the G2(MP2) energies are shown in Figure 4. For the five cases where isodesmic reactions were carried out, the enthalpy changes were also obtained from the values of $\Delta_f H^{\circ}$(rec) and $\Delta_f H^{\circ}_{(g)298}$ of $H^+_{(g)}$, 1530 kJ mol^{-1},[33] to check internal consistency. Those

$H_3NCH_2COO^{-+}$ **10** $\xrightarrow[845^i]{843}$ $H_2NCH_2COO \cdot$ **20**

$\nearrow \; 895 \; / \; 890^i$

$H_2NCH_2COOH^{\cdot +}$ **1N** $\xrightarrow[847^i]{846}$ $HNCH_2COOH \cdot$ **2N** $\xrightarrow[1408^i]{1408}$ $HNCH_2COO^-$ **3N**

$\searrow \; 763 \; / \; 749^i$

$H_3NCHCOOH^{\cdot +}$ **1C** $\xrightarrow[797^i]{797}$ $H_2NCHCOOH \cdot$ **2C** $\xrightarrow[1463^i]{1464}$ $H_2NCHCOO^{\cdot -}$ **3C**

$H_3NCH_2COOH^+$ **1** $\xrightarrow[(888)^a]{889}$ H_2NCH_2COOH **2** $\xrightarrow[(1431)^b]{1431}$ $H_2NCH_2COO^-$ **3**

Figure 4. Enthalpies of deprotonation from relative G2(MP2) energies with correction to 298 K. These are numerically equal to the proton affinities (PAs) of the products. Superscripts "i" denote values calculated from $\Delta_f H^\circ_{298}$(rec); Values in parentheses are experimental averages from (superscript a) refs 33, 50, and 53 and (superscript b) refs 33, 54, 50, and 55.

cases have been indicated by a superscript "i". In addition, available experimental results are given in parentheses.

The calculated ionization potential of glycine is 894 kJ mol^{-1}. A precise experimental IP is not available, but the lowest band in the photoelectron spectrum of glycine[6] exhibits a maximum at 965 kJ mol^{-1} and a threshold in the region of 870−905 kJ mol^{-1}. The IP calculated here lies in this threshold range. The fact that it is significantly higher than the IPs of methylamine and ethylamine, which are 866[33] (873.2 kJ mol^{-1} calculated[45]) and 855[33] kJ mol^{-1}, respectively, implies that the carboxyl group lowers the energy of the N lone pair orbital, with which the lowest IP of glycine is associated.[6]

The reliability of $\Delta_f H^\circ_{(g)298}$ for $H_3NCH_2COOH^+$ and $H_2NCH_2CO_2^-$ in Table 2 is confirmed by the excellent agreement in Figure 4 between the G2(MP2) proton affinities of the nitrogen site of H_2NCH_2COOH and the carboxylate site of $H_2NCH_2COO^-$, respectively, and the corresponding experimental values. These values of $\Delta_f H^\circ_{(g)298}$ are also in accord with those in ref 33.

The PAs of the open shell species in Figure 4 are also of interest. First one must note the difference between $\Delta_f H^\circ_{(g)298}$ for species **2C** calculated from the isodesmic reactions and $\Delta_f H^\circ_{(g)298}$ for glycine (cf. Table 3). This causes a 14 kJ mol^{-1} discrepancy between the PA for formation of **1N** from that species calculated from G2(MP2) energies and from values of $\Delta_f H^\circ$(rec). Apart from this all of the PAs derived from the data for isodesmic reaction agree with those from G2(MP2) energy differences within 5 kJ mol^{-1}. The parent ion species, **1N**, plays a central role and it is regrettable that the adiabatic IP has not been obtained with greater precision. However, the PAs in Figure 4 show that the enthalpy of this species ties in well with those of **20** and **2N**, which were derived from isodesmic reactions.

The PAs of the O-centered, N-centered, and C-centered radicals, **20**, **2N**, and **2C**, to form **1N** decrease in that order. Thus in the deprotonation of **1N** the last of these is highly favored compared to the others. Indeed species **2C** has a particularly stable structure, which is a manifestation of the

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Table 4. Bond Dissociation Energies (kJ mol^{-1}) at 298 K

	parent species			
bond	$H_3NCH_2COOH^+$ (1)	H_2NCH_2COOH (2)	$H_2NCH_2COO^-$ (3)	$H_3N^+CH_2COO^-$ (5)
O−H	516	472		
N−H	471	429	406	
C−H	423	331, 334^a	363	415

^{a} From ref 28.

captodative effect.[38] Evidence for this also comes from a comparison of the carboxylate PAs of **3C**, **3N**, and **3** in Figure 4. The PA of **3C** is seen to be some 30 kJ mol^{-1} larger than that of **3**. Evidently, the extra stabilization of **2C** is not present in **3C**. The opposite situation seems to hold for the N-centered radical **3N**. Here the PA is 20 kJ mol^{-1} smaller than that of **3**, a possible consequence of the stronger hydrogen bonding in **3N**.

Bond Dissociation Energies and Electron Affinities. Bond dissociation energies for bonds to hydrogen in structures **1**, **2**, **3**, and **5** are shown in Table 4. The bond dissociation energies decrease in the order O−H > N−H > C−H. Protonation at N is seen to enhance the bond dissociation energies of all three bond types. Both of these trends and the decrease in N−H bond strength observed on deprotonation at the −COOH group of **2** are in accord with normal behavior, where stabilization of the radical form increases with electron availability in the molecular framework. The really striking feature of Table 4 is the very small value of D_{C-H} of neutral glycine, which was observed previously.[28] This must be attributed to the very strong stabilization of structure **2C** by the captodative effect[38] which was already noted above in connection with the proton affinities. Again, this is not matched in the deprotonated $H_2NCHCOO^{\cdot -}$ form **3C**, since deprotonation at the −COOH group of **2C** enhances the strength of the C−H bond.

More relevant from the point of the solution chemistry of glycine is the C−H bond dissociation energy of the zwitterionic form of glycine, namely **5**. This is estimated to be 415 kJ mol^{-1} by comparison of the "G2(MP2)" energies of **5**, **5C** (see above), and the hydrogen atom (1312.8 kJ mol^{-1}). Thus, the C−H bond dissociation energy of the zwitterion **5** is substantially larger

than that of neutral glycine **2** and the glycine anion **3** and somewhat smaller than that of the protonated form **1**.

There are no experimental measurements of the above energies for glycine per se, but comparisons may be made with results for related molecules. For example, the values of D_{N-H} for forms **1** and **2** may be compared with 449 and 423 kJ mol^{-1} for the corresponding methylamine species. Evidently the electron withdrawing effect of the $-COOH$ group raises D_{N-H}. The effect on D_{C-H}, however, is the opposite, since the 423 and 331 kJ mol^{-1} values in Table 4 for forms **1** and **2** of glycine are smaller than 448 and 400 kJ mol^{-1}, the $C-H$ bond dissociation energies for the corresponding species of methylamine (calculated from data in ref 33), respectively. The values of $D_{C-H} = 331$ and 363 kJ mol^{-1} for forms **2** and **3** in Table 4 may also be compared with 407 and 400 kJ mol^{-1} for CH$_3$-COOH and CH$_3$COO$^-$, respectively (calculated from data in ref 29). The fact that the $C-H$ bonds of glycine are weaker than both the methylamine and the acetic acid bonds indicates that there is a synergism in the effect of the $-NH_2$ and the $-COOH$ groups on the stabilization of the carbon-centered radicals of glycine, as expected for the captodative effect. Also the effect is largest in the neutral radical, where $-COOH$ is the acceptor. When the NH$_2$ donor group is replaced by the inductively withdrawing $-NH_3^+$ group this destabilizes the radical center, as has been previously shown,[37] and D_{C-H} rises dramatically.

The present value of D_{O-H} for neutral glycine is slightly larger than the 460 kJ mol^{-1} value for acetic acid, derived from our isodesmic reaction results in ref 29. The available experimental values of D_{O-H} of acetic acid are even smaller (434,[46] and 443[47] kJ mol^{-1}), and close to the value for methanol (435 kJ mol^{-1}).[33] However, there is experimental evidence that when other electronegative atoms are attached to the C atom the O$-H$ bond dissociation energy rises. Thus D_{O-H} in CF$_3$OH has been reported to be 502 ± 13 kJ mol^{-1}.[48] Secondly, the rapid decomposition of R$-CO_2^{\bullet}$ radicals may complicate the experimental thermochemistry.[29] The present conclusion is that D_{O-H} for glycine is similar to, if not slightly larger than, that of acetic acid, and that both probably have larger O$-H$ bond energies than previously reported.

Although we will discuss the solution properties in greater detail in a forthcoming publication, it may be noted that the trends observed in Table 4 are expected to hold in aqueous solution as well, since solution energies of the closed shell and H-atom removed species should be similar.

From the G2(MP2) energies the EA of neutral glycyloxyl, structure **20**, is 358 kJ mol^{-1}, slightly larger than that for acetyloxyl: experimental[49] 318 kJ mol^{-1}; calculated[29] 324 kJ mol^{-1}. This difference is in accord with the larger stabilization by polarization in the glycyl anion.[50]

Table 5. G2(MP2) Energies and Experimental Heats of Formation (298 K) for Compounds Used in Isodesmic Reactions

compound	E(G2(MP2)), hartree	$\Delta_f H^{\circ}_{298}$, kJ mol^{-1}
HNCH$_3$	−95.005 97	182[a]
H$_2$NCH$_3$	−95.664 52	23.0[a]
H$_2$NCHCH$_3^{\bullet}$	−134.244 51	109[a]
H$_2$NCH$_2$CH$_3$	−134.891 37	−47.5[a]
H$_2$CC(OH)$_2^{\bullet+}$	−228.382 27	503[a]
NO$_2^{\bullet}$	−204.830 47[b]	33.1[c]
HONO (cis)	−205.455 07[b]	−76.7[d]
CH$_2$COOH$^{\bullet}$	−228.090 42[b]	−243[b]
CH$_3$COOH	−228.747 73[b]	−432[c]
CH$_3$COO$^{\bullet}$	−228.072 69[b]	−190[b]
CH$_3$COOH$^{\bullet+}$	−228.354 23[b]	−597[a]

[a] From ref 33. [b] From ref 29. [c] From ref 34. [d] From ref 52.

5. Summary

The ab inito calculations have provided optimized structures for glycine, and its related radicals and ions, as well as absolute G2(MP2) energies and heats of formation. Differences in G2-(MP2) energies of the parent molecules and the ions gave the IP, EA, and PAs. The PA values for closed shell species are in good agreement with the experimental values.

Gas-phase heats of formation for the ions and radicals were derived from the experimental heat of formation of glycine and the difference between the G2(MP2) energy of that compound and those of the other species. Several values of $\Delta_f H^{\circ}_{(g)298}$ of open shell species were checked against values derived from isodesmic reactions involving radicals with closely similar bonding. The agreement was within ±3 kJ mol^{-1} except for radical systems with captodative stabilization, where the former method tended to underestimate the radical stabilization by about 12 kJ mol^{-1}. Recommended values of heats of formation at 298 K are as follows (in kJ mol^{-1}): HNCH$_2$COO$^{\bullet-}$ (−303), H$_2$NCHCOO$^{\bullet-}$ (−346), H$_2$NCH$_2$COO$^{\bullet}$ (−138), HNCH$_2$COOH$^{\bullet}$ (−181), and H$_2$NCHCOOH$^{\bullet}$ (279).

The calculated value of D_{O-H} for neutral glycine, 472 kJ mol^{-1}, is similar to, if not slightly larger than, that of acetic acid and both are larger than previously reported. The C$-H$ bonds of neutral glycine are exceptionally weak, $D_{C-H} = 331$ kJ mol^{-1}.

The EA of glycyloxyl from the G2(MP2) energies is 358 kJ mol^{-1}.

The ionization potential of neutral glycine is 894 kJ mol^{-1}.

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