Estimation of Lattice Energies of Organic Molecular Crystals by Combination of Experimentally Determined and Quantum-Chemically Calculated Quantities: A New Value for the Lattice Energy of α-Glycine

Gerhard Raabe

Institut für Organische Chemie; Rheinisch-Westfälische Technische Hochschule Aachen, Prof.-Pirlet-Straße 1, D-52074 Aachen

Reprint requests to Dr. G. R.; Fax: +49 241 8888 385, E-mail: gk016ra@cluster.rz.rwth-aachen.de

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Dedicated to Prof. Dr. Jörg Fleischhauer on the occasion of his 60th birthday

A new value for the lattice energy of α-glycine was determined by combination of the experimentally measured heat of sublimation taken from literature and the quantum-chemically calculated energy difference $E_{tot,gp} - E_{tot,cry}$, where $E_{tot,gp}$ is the total energy of the most stable form of the compound in the gas phase (carboxylic acid) and $E_{tot,cry}$ the total energy of the molecule as it occurs in its crystalline form (betaine). At the highest levels of *ab initio* theory employed in this study this energy difference is –(28±2) kcal/mol, indicating that older work overestimated this difference significantly. The reason for the overestimation of this energy difference was determined by means of additional *ab initio* calculations. The lattice energy of –(67±2)kcal/mol obtained using the new value for $E_{tot,gp} - E_{tot,cry}$ is significantly more positive than an older value of –103 kcal/mol frequently cited in the literature.

1. Introduction

The lattice energy (ΔE_{lat}) of a molecular crystal is defined as the change of energy associated with a process in which one mole of its initially infinitely separated (i. e. non-interacting) constituents[a)] combine to form a crystal lattice.

In the case of glycine, which is a betaine (H_3N^+-CH_2-COO^-) in the crystal lattice and in aqueous solution, approximate values for this energy can be obtained from the following cycle (*cf.* Fig. 1): in the first step one mole of crystalline glycine is dissolved in water and the change of energy associated with this process is the energy of solution (ΔE_{soln}). In the next step the betaine molecules are removed from the aqueous solution, and this hypothetical process requires the negative energy of solvation (ΔE_{solv}) of zwitterionic glycine.

Provided the structure of the betaine is essentially the same in the crystal and in the gas phase, the lattice energy can then be obtained from the relationship

$$\Delta E_{lat} = -\Delta E_{soln} + \Delta E_{solv}.$$

Based on a semiempirically estimated heat of hydration of $\Delta H_{solv} = -99.7$ kcal/mol and a value of $\Delta H_{soln} = 3.4$ kcal/mol for the heat of solution, Shimura [1] derived an approximate lattice energy of α-glycine of –103.1 kcal/mol.

Different from the lattice energy defined above the heat of sublimation (ΔH_{sub}) is the change of enthalpy associated with the evaporation of one mole of a crystalline solid resulting in the *most stable form* of the compound in the gas phase.

ΔH_{sub} and ΔE_{lat} are related to each other by the approximate relationship

$$\Delta E_{lat} = -\Delta H_{sub} - 2RT + \Delta E_{cry,gas},$$

where R is the gas constant, T the temperature, and $\Delta E_{cry,gas} = E_{tot,gp} - E_{tot,cry}$ the difference between the total energy of one mole of the most stable form of the isolated molecule in gas phase ($E_{tot,gp}$) and the total energy of a free molecule with a structure as it

[a)] The constituents are the betain molecules in their solid state geometry.

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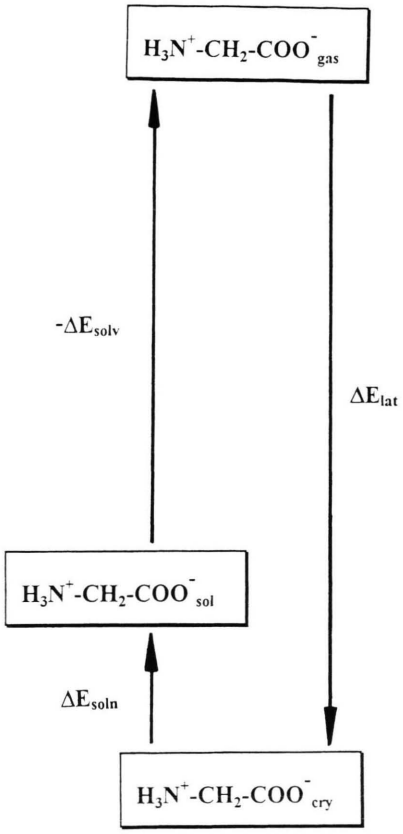

Fig. 1. Relationship between the energy of solution (ΔE_{soln}), the energy of solvation (ΔE_{solv}), and the lattice energy (ΔE_{lat}) of glycine. H_3N^+-CH_2-COO^-_{cry} is the betaine in the crystal lattice, H_3N^+-CH_2-COO^-_{sol} the solvated molecule in aqueous solution, and H_3N^+-CH_2-COO^-_{gas} the betaine in the gas phase.

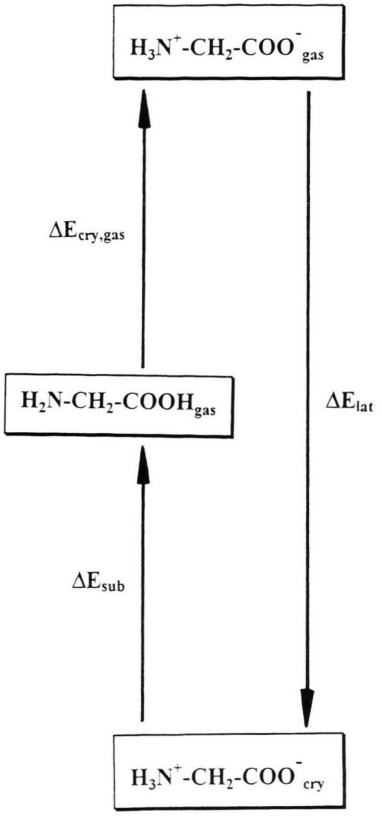

Fig. 2. Relationship between the energy of sublimation (ΔE_{sub}), the difference between the total energies of the betaine (H_3N^+-CH_2-COO^-_{gas}) and the most stable form of glycine (H_2N-CH_2-$COOH_{gas}$) in the gas phase, and the lattice energy (ΔE_{lat}).

occurs in the crystal ($E_{tot,cry}$). At room temperature $2RT$ is about 1.2 kcal/mol and, therefore, lies within the standard deviations usually associated with experimentally determined heats of formation [2]. The heat of sublimation of glycine has been determined several times in the past [3 - 8], and with one exception[b] the measured values cover the relatively narrow range between 30 and 35 kcal/mol.

In contrast to many other cases [9] $\Delta E_{cry,gas}$ differs significantly from zero for glycine, since the compound occurs as a betaine (H_3N^+-CH_2-COO^-) in the crystal and as a carboxylic acid (H_2N-CH_2-$COOH$) in the gas phase [10 - 13]. Combining their value for the heat of sublimation of α-glycine (31.2±0.5 kcal/mol) with the lattice energy given in [1], Takagi et al. [4] obtained a surprisingly high value of about –72 kcal/mol for the energy difference between the carboxylic acid and the betaine ($\Delta E_{cry,gas}$, *cf.* Fig. 2).

In a second approach, the same authors [4] used a sequence of hypothetical reactions to obtain an independent value for $\Delta E_{cry,gas}$:

$$H_2N\text{-}CH_2\text{-}COOH \rightarrow H_2N\text{-}CH_2\text{-}COO^\bullet + H^\bullet, \quad (1)$$

$$H_2N\text{-}CH_2\text{-}COO^\bullet + H^\bullet + e^- \rightarrow H_2N\text{-}CH_2\text{-}COO^- + H^\bullet, \quad (2)$$

$$H_2N\text{-}CH_2\text{-}COO^- + H^\bullet \rightarrow H_2N\text{-}CH_2\text{-}COO^- + H^+ + e^-, \quad (3)$$

$$H_2N\text{-}CH_2\text{-}COO^- + H^+ \rightarrow H_3N^+\text{-}CH_2\text{-}COO^-. \quad (4)$$

The changes of energy associated with steps (1), (2), (3), and (4) are the homolytic dissociation energy of an O-H bond (ΔE_D), the electron affinity (ΔE_A) of the resulting H_2N-CH_2-$COO^\bullet$ radical, the ionisation energy of a hydrogen atom (ΔE_I), and the energy of protonation (ΔE_P) of the amino group of the glycine anion

[b] In their mass spectrometric study of evaporation of α-amino acids Gaffney et al. [7] obtained a value of $\Delta H_{sub} = 23 \pm 1$ kcal/mol. See, however, [2].

$H_2N\text{-}CH_2\text{-}COO^-$. Using $\Delta E_D = 110.2$, $\Delta E_A = -87.7$[c], $\Delta E_I = 312.1$ and $\Delta E_P = -219$ kcal/mol[d], they obtained an even higher value of $\Delta E_{cry,gas} = -116$ kcal/mol.

An approximate value (δ) for $\Delta E_{cry,gas}$ is the difference between the total energies of the most stable isomer of the carboxylic acid in the gas phase and the betaine calculated by means of quantum chemical methods. Surprisingly high values for δ were obtained at the HF/STO-3G level (–87 kcal/mol), as well as with the CNDO/2 (–85 kcal/mol) and the PCILO method (–74 kcal/mol) [14]. Much lower values for the energy difference were calculated by Tse et al. (–29 kcal/mol) [15] and Wright et al. (–43 kcal/mol) [16]. In their studies they employed partly optimized structural parameters and the 4-31G and 6-31G basis set, respectively. Calculations by the author using some of the most popular semiempirical methods resulted in comparable values (MINDO/3: –33.8 kcal/mol, MNDO: –61.5 kcal/mol, PM3: –38.2 kcal/mol, AM1: –43.5 kcal/mol).

The computational results converged to the point that the most stable isomer of glycine in the gas phase is **2** (in Fig. 3), which is slightly lower in energy than **1**. Using standard bond lengths and angles Vishveshwara and Pople [17] obtained a value of $\Delta E_{1,2} = 2.2$ kcal/mol for this energy difference at the HF/4-31G level. Complete geometry optimizations with a smaller basis set (4-21G) by Sellers and Schäfer [18, 19] resulted in the same value. A similar result (1.9 kcal/mol) was reported by Siam et al. [20]. Inclusion of correlation corrections in single point calculations using HF-optimized structures only slightly decreases this energy difference. Thus, Jensen and Gordon [21] calculated a value of 1.5 kcal/mol for the energy difference between **1** and **2** at the MP2/6-31G*//HF/6-31G* level[e]. The importance of the inclusion of correlation energy into the calculation of the gradients was pointed out by Ramek et al. [22, 23] who obtained a significantly reduced value of $\Delta E_{1,2} = 0.7$ kcal/mol with the MP2/6-311G**//MP2/6-311G** method [22]. A further increase of the basis set in single point calculations at the MP2 level employing MP2/6-311++G**-optimized geometries by Császár [24] yielded a relative energy of 0.4 kcal/mol, indicating that both molecules might be of essentially the same energy.

While most[b] of the values of ΔH_{sub} from different sources lie consistently between 30 and 35 kcal/mol, both the experimentally determined and calculated values of $\Delta E_{cry,gas}$ and δ scatter widely (–29 - –116 kcal/mol!). To obtain a definite value for the energy difference between the betaine and the carboxylic acid, and thus to enable calculation of a reliable value of the lattice energy, the problem of the most stable form of glycine in the gas phase was reevaluated employing different methods and basis sets including geometry optimizations at the one-determinant as well as at the correlated level.

2. Computational Method

All *ab initio* calculations were performed employing the GAUSSIAN94 set of quantum chemical routines [25] running on a cluster of work stations at the Rechenzentrum der RWTH Aachen. All molecular structures under consideration were preoptimized at the one-determinant (*Hartree-Fock,* HF) level with the split valence 6-31G basis set [26 ,27]. In order to obtain more reliable geometries, polarization (*) [28] and diffuse (+) [29, 30] functions were then successively added to the basis set. Additional geometry optimizations were performed with the 6-311G basis set augmented with two sets of polarization and diffuse functions (6-311++G**). The 6-311G basis set [31] has a triple split in the valence s and p shells, combined with an inner shell representation by a single function with six Gaussians (valence triple-ζ). Finally, a basis set of full double-ζ quality (D95[f]) was complemented with (i) one set of six d-like functions on carbon ($\zeta_C = 0.75$), nitrogen ($\zeta_N = 0.80$), and oxygen ($\zeta_O = 0.85$) as well as a set of p-like functions on all hydrogens ($\zeta_H = 1.0$) and (ii) with additional diffuse functions on all atoms ($\zeta_O = 0.0845$, $\zeta_N = 0.0639$, $\zeta_C = 0.0438$, $\zeta_H = 0.0360$). The resulting basis sets were designated D95** and D95++**, respectively. The correlation energy was calculated by means of the Møller-Plesset perturbation theory [34] up to the fourth order (MP4). Core electrons were included in the MP2 calculations but were kept frozen (fc = frozen core) in the MP4 runs. In some cases the correlation energy was calculated employing HF-optimized

[c] This is the electron affinity of an oxygen atom.

[d] This is the proton affinity of ammonia.

[e] The abbreviation "method1/basis1//method2/basis2" means that the energy was calculated with method1 and basis set1 at a geometry that was optimized using method2 together with basis set2.

[f] This basis set is Dunning's [4s2p/2s] contraction [32] of Huzinaga's (9s5p/4s) set of Gaussian type orbitals [33].

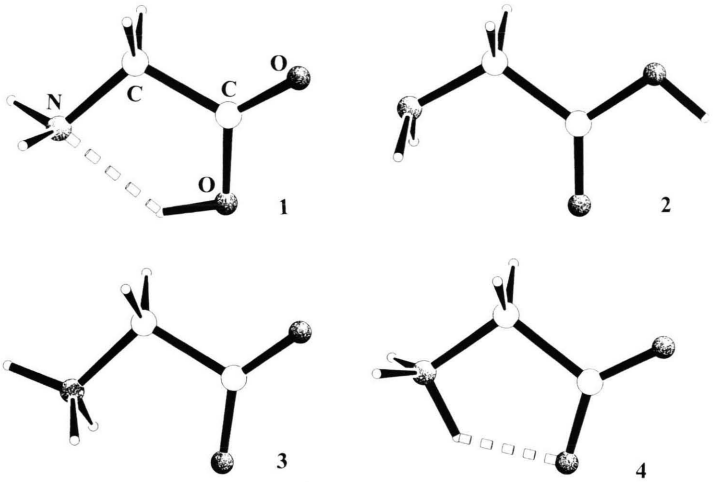

Fig. 3. The structures of glycine isomers obtained at the MP2/6-311++G** (**1** - **3**) and the HF/6-31+G* level (**4**).

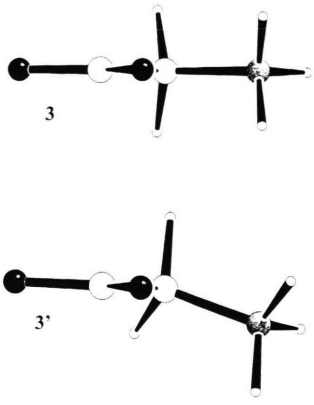

Fig. 4. The experimentally determined structure of the glycine betaine in the solid state (**3'**) [26] and the structure of an isolated betaine molecule in the gas phase (**3**) according to an MP2/6-311++G** geometry optimization.

geometries. Other geometry optimizations were performed including correlation corrections calculated by means of Møller-Plesset perturbation theory to the second (MP2) order. The stationary points located at the MP2/6-311++G** level were characterized by calculation of their normal frequencies.

Drawings of the molecules were generated using SCHAKAL [35].

3. Results and Discussion

Quantum chemical calculations were performed for the structures **1** - **4** of Figure 3. Total and relative energies are listed in Table 1 and 2, respectively.

In accordance with the results of Ding and Krogh-Jespersen [36] it was found that the optimized structure of the free betain (**3**) corresponds to a saddle point with one imaginary frequency in the spectrum of its normal vibrations. Structure **4** is still a stationary point at the HF/6-31G, HF/6-31G* and HF/6-31+G* level, however it collapses resulting in isomer **1**, not only as soon as polarisation functions are added to the hydrogen basis set (HF/6-31G**) but also if correlation energy is included in geometry optimizations with the 6-31+G* set of contracted Gaussian functions.

At all levels of the theory, **2** is the most stable isomer. The relative energies in Table 2 show that at the Hartree-Fock level structure **1** is by 2.7 - 3.0 kcal/mol less stable than **2**. Inclusion of correlation energy in single point calculations reduces the energy difference between **1** and **2** by 1.4 - 1.9 kcal/mol. If the geometry is optimized at the MP2 level, $\Delta E_{1,2}$ is further reduced by about 40% resulting in a value of 0.53 kcal/mol at the MP2/6-311++G**//MP2/6-311++G** level, which supports Ramek's statement that inclusion of correlation energy in geometry optimizations is important to obtain reliable relative energies [23].

The structures obtained with this method were characterized by calculation of their normal modes. As mentioned above, with one imaginary frequency in the spectrum of its normal vibrations betaine **3** cor-

Table 1. Total energies of **1** - **3** in Hartrees obtained with different methods and basis sets.

method1/basis1//method2/basis2[c)]	1	2	3
HF/6-31G*//HF/6-31G*	−282.826434	−282.831096	−282.781089
HF/6-31G**//HF/6-31G**	−282.843550	−282.848342	−282.794688
HF/6-31+G*//HF/6-31+G*	−282.836778	−282.841050	−282.795467
HF/6-31++G**//HF/6-31++G**	−282.854149	−282.858447	−282.808834
HF/6-311++G**//HF/6-311++G**	−282.921001	−282.925499	−282.875437
HF/D95**//HF/D95**	−282.906125	−282.910609	−282.858492
HF/D95++**//HF/D95++**	−282.910746	−282.915105	−282.864679
MP2/6-31G*//HF/6-31G*	−283.613022	−283.615370	−283.575324
MP2/6-31G**//HF/6-31G**	−283.660322	−283.662900	−283.618432
MP2/6-31+G*//HF/6-31+G*	−283.637153	−283.638691	−283.604608
MP2/6-31++G**//HF/6-31++G**	−283.684800	−283.686350	−283.647376
MP2/6-311++G**//HF/6-311++G**	−283.897407	−283.898867	−283.856745
MP2/D95**//HF/D95**	−283.766862	−283.768434	−283.726876
MP2/D95++**//HF/D95++**	−283.783946	−283.785341	−283.745882
MP2/6-31+G*//MP2/6-31+G*	−283.641720	−283.642731	−283.608857
MP2/6-311++G**//MP2/6-311++G**	−283.901103	−283.901953	−283.859952
MP2/D95++**//MP2/D95++**	−283.788241	−283.789064	−283.749723
MP4(*fc*)/6-31+G*//HF/6-31+G*	−283.673394	−283.675182	−283.640787
MP4(*fc*)/6-311++G**//HF/6-311++G**	−283.858012	−283.859531	−283.817663
MP4(*fc*)/D95++**//HF/D95++**	−283.769379	−283.770909	−283.731154

Table 2. Relative energies of **1** - **3** in kcal/mol obtained with different methods and basis sets.

method1/basis1//method2/basis2	**1**	**2**	**3**
HF/6-31G*//HF/6-31G*	2.93	0.00	31.38
HF/6-31G**//HF/6-31G**	3.01	0.00	33.67
HF/6-31+G*//HF/6-31+G*	2.68	0.00	28.60
HF/6-31++G**//HF/6-31++G**	2.70	0.00	31.13
HF/6-311++G**//HF/6-311++G**	2.82	0.00	31.41
HF/D95**//HF/D95**	2.81	0.00	32.70
HF/D95++**//HF/D95++**	2.74	0.00	31.64
MP2/6-31G*//HF/6-31G*	1.47	0.00	25.13
MP2/6-31G**//HF/6-31G**	1.62	0.00	27.90
MP2/6-31+G*//HF/6-31+G*	0.97	0.00	21.39
MP2/6-31++G**//HF/6-31++G**	0.97	0.00	24.46
MP2/6-311++G**//HF/6-311++G**	0.92	0.00	26.43
MP2/D95**//HF/D95**	0.99	0.00	26.08
MP2/D95++**//HF/D95++**	0.88	0.00	24.76
MP2/6-31+G*//MP2/6-31+G*	0.63	0.00	21.26
MP2/6-311++G**//MP2/6-311++G**	0.53	0.00	26.36
MP2/D95++**//MP2/D95++**	0.52	0.00	24.69
MP4(*fc*)/6-31+G*//HF/6-31+G*	1.12	0.00	21.58
MP4(*fc*)/6-311++G**//HF/6-311++G**	0.95	0.00	26.27
MP4(*fc*)/D95++**//HF/D95++**	0.96	0.00	24.95

responds to a saddle point, while **1** and **2** are local minima.

The results of all calculations further agree in that in the gas phase the betain is significantly higher in energy than both conformational isomers of the carboxylic acid. Using the smallest basis set (6-31G*), this energy difference (δ) amounts to –31.4 kcal/mol. Addition of p-like polarization functions to the hydrogen basis even increases the absolute value of this energy difference, while inclusion of diffuse functions reduces $|\delta|$. Inclusion of correlation energy (MP2) in single point calculations reduces $|\delta|$ by about 5 - 7 kcal/mol, and optimization of the structures at the MP2 level decreases $|\delta|$ by another 0.1 kcal/mol.

Carrying out the perturbation expansion to the fourth order (MP4) in single point calculations has only a small influence on δ. Thus $|\delta|$ is slightly increased ($\approx$0.2 kcal/mol) with the 6-31+G* and the D95++** basis sets. A slight decrease is obtained with the 6-311++G** set of contracted Gaussian functions, where $|\delta|$ is by about 0.2 kcal/mol smaller at the MP4 than at the MP2 level, indicating that a more complete inclusion of correlation energy might further reduce this energy difference. At the highest levels of theory employed in this study the energy difference δ between the most stable carboxylic acid and the betaine amounts to about –26 kcal/mol.

In order to find the reason for the striking difference between the best *ab initio* results of $\delta \approx -26$ kcal/mol and the –116 kcal/mol obtained by Takagi et al. [4] the set of hypothetical reactions (1) - (4) was re-examined at the MP4/6-311++G** level for closed shell species and with the UMP4/6-311++G** method for the radicals. These calculations were performed employing HF- and UHF/6-311++G** optimized structures. Using the corresponding total energies[g] of the radicals together with the value for the carboxylic acid results in ΔE_D = 117.2 kcal/mol. The electron affinity of the $H_2N\text{-}CH_2\text{-}COO^\bullet$ radical was calculated as the difference between its total energy and that of the glycine anion, and a value of ΔE_A = –80.6 kcal/mol was obtained in this way. The resulting values of ΔE_D and ΔE_A are not too different from those used in [4], and the same is true for the calculated value of ΔE_I = 313.6 kcal/mol. However, the *ab initio* energy of protonation at the glycine anion's nitrogen atom (ΔE_P = –323.9 kcal/mol) is by about 100 kcal/mol more negative than the value for the protonation energy of ammonia used for this step in [4]. It is, therefore, the use of the much too positive energy for this step which causes the overrating of the energy difference between the betaine and the carboxylic acid obtained in [4].

De Kruif et al. [3] reported a heat of sublimation of ΔH_{sub} = 32.6±0.5 kcal/mol, measured at T = 418.93 K. Using their value for the difference between the heat capacity of the solid and the corresponding gas of $\Delta c_p = -(14.3 \pm 4.8)$ cal·mol^{-1}·K^{-1} and the *Kirchhoff* equation results in an approximate value for the heat of sublimation of ΔH_{sub} = 38.6 kcal/mol at 0 K. Combining this value with δ = –26 kcal/mol results in a lattice energy for α-glycine of –65 kcal/mol. This value might be somewhat too positive, since the structures of the betaine molecule in the gas phase and in the solid state differ significantly (*cf.* Figure 4). To estimate the error possibly introduced employing the total energy of the optimized betaine structure, an additional single point calculation (MP4/6-311++G**) was performed using the experimentally determined structure [37]. The total energy calculated in this way is by about 4 kcal/mol higher than the one obtained from the calculations at the MP4/6-311++G**//HF/6-311++G** level, and the resulting lattice energy is –69 kcal/mol.

[g] $E_{tot}(H_2N\text{-}CH_2\text{-}COO^\bullet)$: –283.172996 a.u. ($\langle s^2 \rangle$ = 0.7582), $E_{tot}(H^\bullet)$: –0.499818 a.u., $E_{tot}(H_2N\text{-}CH_2\text{-}COO^-)$: –283.301446 a.u.

It is therefore concluded that the lattice energy of α-glycine is about –69 kcal/mol. This value is clearly at odds with the one derived by Shimura [1] emloying the heats of solution and solvation. A survey of the more recent literature, however, yielded values for the heat of solution of 3.6 and for the heat of solvation of –58.0 kcal/mol [12]. While the more recent value of ΔH_{soln} is almost identical with the one used in [1], the new value of ΔH_{solv} is by about 42 kcal/mol more positive than the semiempirically determined older heat of solvation. Use of the new data [12] to approximate the lattice energy results in a value of –62 kcal/mol, which is close to the lattice energy derived from ΔH_{sub} and δ.

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