# The Use of Quantum Chemical Semiempirical Methods to Calculate the Lattice Energies of Organic Molecular Crystals.
## Part I: The Three Polymorphs of Glycine

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A method to calculate the lattice energies of organic molecular crystals is described. It is based on the semiempirical quantum chemical MINDO/3 approximation but might also be used within the framework of any other quantum chemical method. The lattice energy is approximated by the sum of dispersion-, induction-, exchange repulsion-, and electrostatic energy. Different, however, from other schemes employed in this field, like for example the atom-atom-potential method, the variables in the expression for the lattice energy have not been fitted to reproduce experimental values and, therefore, the single contributions retain their original physical meaning. Moreover, the method offers the advantage that it may be directly applied to all compounds that can be treated within the framework of the underlying quantum chemical method. Thus, time consuming readjustment of the entire parameter set upon extension of the group of target molecules by another class of compounds becomes obsolete.

As an example, the lattice energies of the three polymorphs of glycine are calculated.

*Key words:* Lattice Energy; Glycine; Semiempirical Methods.

## 1. Introduction

Standard semiempirical methods allow rapid calculations of properties like vertical (Koopmans) ionization potentials, mean molecular polarizabilities, as well as polarizability tensors. Moreover, partitioning of the molecular dipole moment leads to atom-in-molecule polarizabilties and the corresponding atomic polarizability tensors. These quantities can be used to calculate the dispersion contribution to the lattice energy using either the London formula or the expression by Slater and Kirkwood. Together with easily available atomic charges, like those obtained for example by the Mulliken population analysis, the polarizabilities can also be used to calculate the induction energy. Moreover, the electrostatic energy can be evaluated employing either molecular or atomic multipole expansions. In most lattices the molecules are well separated from each other and the overlap between the single species is small. Thus, the unperturbed semiempirical molecular orbitals calculated for the isolated molecules might be used to evaluate the intermolecular repulsion energy due to overlap of the molecular electron densities. The major components of the lattice energy (dispersion-, induction-, exchange repulsion-, and electrostatic energy) can, therefore, be calculated directly, that is without any further adjustment of parameters.

An obvious shortcoming of this method is that all contributions to the lattice energy which are not explicitly included into the energy expression, as well as effects due to nonadditivity, are neglected. Since these effects are to a certain extent considered implicitly when adjusted potential parameters are used, the numerical results obtained by the procedure described in this paper may be not so close to their experimental counterparts as those obtained employing optimized interaction parameters.

The semiempirical method used in this study is the MINDO/3 approximation [1, 2]. The general

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methodology, however, is by no means confined to this method but can employ the results of any other standard semiempirical method like MNDO [3, 4], AM1 [5], and PM3 [6] as well.

## 2. Computational Method

The expression *"lattice energy"* as used in this paper describes the energy of interaction of a single reference molecule having a structure as it occurs in the solid state with all other molecules of the crystal lattice. Thus this energy neither includes energy differences due to structural changes that occur upon crystallization, nor differences between the vibrational energies of the molecule in the gas phase and the solid state.

The lattice energy ($\Delta E_\mathrm{lat}$)a) is approximated as the sum of dispersion- ($\Delta E_\mathrm{dis}$), electrostatic- ($\Delta E_\mathrm{els}$)b), induction- ($\Delta E_\mathrm{ind}$), and (closed shell) repulsion energy ($\Delta E_\mathrm{rep}$):

$$\Delta E_\mathrm{lat} = \Delta E_\mathrm{dis} + \Delta E_\mathrm{els} + \Delta E_\mathrm{ind} + \Delta E_\mathrm{rep}.$$

Within the framework of the most frequently used standard methods to compute $\Delta E_\mathrm{lat}$ [7], less complete expressions for the lattice energy are used. The single components of these expressions are calculated using parameters which result from a least squares fit of the approximate energy expression to so-called "experimental" lattice energies, usually obtained from experimentally determined enthalpies of sublimation

$$\Delta E_\mathrm{lat} = -\Delta H_\mathrm{sub} - 2RT + \delta,$$

where $\delta$ is the energy difference due to structural changes that occur upon sublimation [8]. If all the parameters occuring in such a truncated energy expression are adjusted together, the single contributions to the lattice energy mix and their original physical meaning is lost [7]. Direct calculation of these contributions by means of semiempirical methods and, of course, by more elaborate *ab initio* procedures, retains the original meaning of the components within the framework of the underlying method and thus facilitates the classification of solids as, for example, predominantly electrostatically ($\Delta E_\mathrm{els} < \Delta E_\mathrm{dis} + \Delta E_\mathrm{ind}$) or merely dipersively ($\Delta E_\mathrm{els} + \Delta E_\mathrm{ind} > \Delta E_\mathrm{dis}$) bonded crystals. Another advantage of this method is that it might be applied directly to all compounds which can be treated within the framework of the underlying quantum chemical method, and that it does not require any readjustment of parameters when a new class of compounds is included into the set of target molecules.

"Exact" formulae for the components of the lattice energy as derived from perturbation theory are given elsewhere, e. g. [7, 9 - 11] and are not reported here. Thus, the following discussion is confined to the common approximate expressions used in this paper, which are derived from the corresponding formulae obtained from perturbation theory introducing, in part, severe approximations, e. g. [7, 9 - 11].

## 3. The Components of the Lattice Energy

*(i) The electrostatic energy.* The electrostatic contribution to the lattice energy is approximated by a point charge model

$$\Delta E_\mathrm{els} = \frac{1}{2} \sum_a \sum_b q_a q_b r_{ab}^{-1}. \tag{1}$$

Here the first summation runs over all atoms $a$ of the reference molecule (A) and the second one covers the atoms $b$ of all other molecules (B) of the lattice. $q_a$ and $q_b$ are the (Mulliken) MINDO/3 charges of atoms $a$ and $b$, while $r_{ab}$ is their interatomic distance. Summation of the electrostatic energy was performed employing the Bertaut method [12, 13] in the version introduced by Williams [14 - 21] ("accelerated summation") employing a separation constant of $k = 0.3$ [14] and including direct as well as reciprocal space contributions.

*(ii) The dispersion energy.* First the well known London formula was used to calculate the dispersion contribution to the lattice energy

$$\Delta E_\mathrm{dis} = -\frac{3}{4} F_\mathrm{L} \sum_a \sum_b \alpha_a \alpha_b r_{ab}^{-6}, \tag{2}$$

$$F_\mathrm{L} = \frac{U_\mathrm{A} U_\mathrm{B}}{U_\mathrm{A} + U_\mathrm{B}},$$

where $U_\mathrm{A}$ and $U_\mathrm{B}$ are twice [22 - 26] the vertical

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a) In this paper, like in [8], the lattice energy is treated like a reaction energy; i. e. stabilizing contributions carry a negative sign.

b) The expression "electrostatic energy" might be misleading since the Hamiltonian describing the interacting closed shell species is essentially electrostatic and thus the entire energy of interaction is almost completely electrostatic in origin [46]. Here the term "electrostatic energy" describes those contributions to the lattice energy which arises from the interaction of the permanent electric moments of the unperturbed molecular charge distributions.

molecular ionisation potentials of the interacting molecules, approximated by the semiempirically calculated energies of their highest occupied molecular orbitals ($\varepsilon_{\mathrm{HOMO}}$, Koopmans' theorem [27]). $\alpha_a$ and $\alpha_b$ are scaled[c] atom-in-molecule polarizabilities calculated with the MINDO/3-FP method and Metzger's partitioning of the molecular dipole moment [28, 29]. In all cases considered in this paper molecules A and B belong to the same species. Thus, $F_{\mathrm{L}} = \frac{1}{2}U_{\mathrm{A}}$. In a second set of calculations the dispersion energy was obtained using the formula derived by Slater and Kirkwood:

$$\Delta E_{\mathrm{dis}} = -\frac{3}{4}\sum_a \sum_b F_{\mathrm{SK}}^{ab}\alpha_a\alpha_b r_{ab}^{-6}, \tag{3}$$

$$F_{\mathrm{SK}}^{ab} = \left\{\sqrt{\alpha_a/N_a} + \sqrt{\alpha_b/N_b}\right\}^{-1}.$$

In this expression $N_a$ and $N_b$ are the numbers of the "polarizable electrons" of atoms $a$ and $b$, approximated by the numbers of valence electrons [30]. Accelerated summation was employed to calculate the dispersion energy.

*(iii) The induction energy.* The induction energy is approximated by the expression

$$\Delta E_{\mathrm{ind}} = -\frac{1}{2}\sum_a [\boldsymbol{E}_a^{\mathrm{t}} \cdot \boldsymbol{\alpha}_a \cdot \boldsymbol{E}_a], \tag{4}$$

where $\boldsymbol{E}_a$ is the total electric field at the atom $a$ of the reference molecule caused by the atomic (Mulliken) charges of all other lattice atoms [28]. $\boldsymbol{\alpha}_a$ is the atom-in-molecule polarizablity tensor of atom $a$ calculated with the MINDO/3-FP method. This sum was evaluated directly and special precautions had to be taken in the case of $\gamma$-glycine with a high net cell dipole moment *(vide infra)*.

*(iv) The repulsion energy.* Destabilizing contributions to the lattice energy due to closed shell repulsion ("steric effects") were calculated employing an approximate expression for the exchange repulsion energy [7, 31 - 35]:

$$\Delta E_{\mathrm{rep}} = \tau \sum_k \sum_{\mathrm{B}} \sum_l \Big[\sum_{p,q} c_{kp}c_{lq}S_{pq}(r_{ab}^{-1/2})\Big]^2. \tag{5}$$

Indices $k$ and $l$ run over all occupied molecular orbitals of molecules A and B, calculated with the MINDO/3 method. $p$ and $q$ refer to the corresponding atomic orbitals at atoms $a$ and $b$ with LCAO-MO-coefficients $c_{kp}$ and $c_{lq}$, respectively ($p \in a, q \in b$). $S_{pq}$ is their overlap integral and $r_{ab}$ the distance between atoms $a$ and $b$. In a strict sense, $\tau$ is not only a function of the interacting atoms but also of the interatomic distance [7, 31 - 35]. In many cases, however, it is approximated by a constant, sometimes adjusted to fit the experimental results [31]. Murrell et al. [9] used values of $\tau$ = 1.016 and 1.319 for the interaction between two hydrogen- and two carbon atoms. A value of 1.0 was used in this study. In the calculation of the repulsion energy only overlap integrals between valence shells were considered, and they were calculated employing Slater type orbitals and orbital exponents optimized for molecular calculations [36]. Different from the standard MINDO/3 method, identical exponents were used for the 2s and 2p functions. Since the single contributions in square brackets decrease exponentially with the interatomic distance, accelerated summation is dispensable in this case and the sum was evaluted directly.

## 4. The Polymorphs of Glycine

As a test case glycine was chosen. Since the molecule is highly polar in the solid state, the electrostatic and the inductive energy might contribute significantly to the lattice energy[d]. Moreover, this molecule provides the opportunity to test the performance of the method in presence of hydrogen bridges. Three polymorphs of this amino acid, called $\alpha$-, $\beta$-, and $\gamma$-glycine, have been described in the literature [37 - 39]. Their solid state structures were determined by neutron diffraction in the case of $\alpha$-glycine [37], and by X-ray methods for the $\beta$-, and $\gamma$-polymorphs [38, 39][e] In all three modifications the molecule exists in the betaine structure ($H_3N^+$-$CH_2$-$COO^-$). To the best of the author's knowledge only one experimental study regarding the lattice energy of a single polymorph ($\alpha$-glycine) has been published so far

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[c] A scaling factor of 1.53846 applied to the MINDO/3-FP values results in molecular polarizabilities which are close to the so-called "experimental" polarizabilities calculated by means of the Lorenz-Lorenz equation.

[d] This is not necessarily the case since even for highly polar molecules the single pair contributions might cancel and result in net electrostatic and inductive contributions close to zero.

[c] $\alpha$-glycine [37]: space group $P2_1/n$ (No. 14) $a = 5.1054(6)$, $b = 11.9688(19)$, $c = 5.4645(9)$ Å, $\beta = 111.697(11)°$. $\beta$-glycine [38]: space group $P2_1$ (No. 4) $a = 5.077(4)$, $b = 6.268(6)$, $c = 5.380(9)$ Å, $\beta = 113.2°$. $\gamma$-glycine [39]: space group $P3_2$ (No. 145) $a = 7.037$, $c = 5.483$ Å.

Table 1. Experimentally determined structural parameters of the three polymorphs of glycine together with values for the free betaine optimized at the *ab initio* MP2/6-31+G* level. The numbers in parentheses are MP2/6-31+G*-optimized structural parameters obtained at fixed experimental dihedral angles. (Bond lengths in Å, bond angles in degrees). For numbering of atoms see Figure 1.

| | $\alpha$-glycine | $\beta$-glycine | $\gamma$-glycine | MP2/6-31+G* |
|---|---|---|---|---|
| C1-O2 | 1.251(1.243) | 1.257(1.244) | 1.237(1.244) | 1.243 |
| C1-O1 | 1.250(1.273) | 1.233(1.272) | 1.254(1.271) | 1.272 |
| C1-C2 | 1.526(1.562) | 1.521(1.562) | 1.527(1.559) | 1.565 |
| C2-N | 1.476(1.509) | 1.484(1.508) | 1.491(1.509) | 1.508 |
| C2-H4 | 1.090(1.092) | 1.097(1.091) | 1.094(1.092) | 1.091 |
| C2-H5 | 1.089(1.091) | 1.087(1.091) | 1.090(1.092) | 1.091 |
| N-H1 | 1.054(1.025) | 0.993(1.024) | 1.008(1.026) | 1.025 |
| N-H2 | 1.037(1.031) | 0.987(1.030) | 1.038(1.027) | 1.027 |
| N-H3 | 1.025(1.026) | 1.037(1.024) | 1.036(1.024) | 1.027 |
| O1-C1-O2 | 125.4(133.4) | 126.2(133.3) | 125.5(133.5) | 133.5 |
| C1-C2-N | 111.9(105.5) | 110.8(105.0) | 111.8(106.4) | 106.0 |
| O1-C1-C2 | 117.5(111.5) | 117.8(111.1) | 117.4(111.7) | 112.2 |
| O2-C1-C2 | 117.1(115.1) | 115.9(115.4) | 117.1(114.7) | 114.3 |

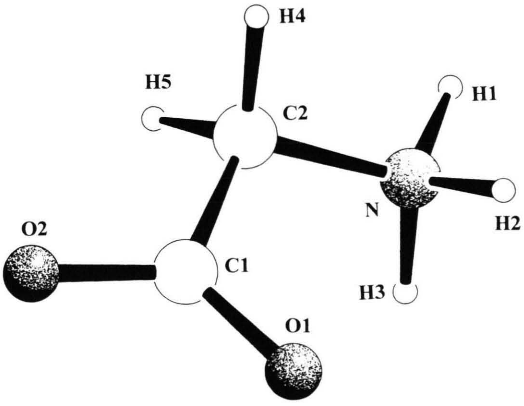

Fig. 1. Numbering of atoms in the glycine molecule used in Table 1.

[40, 42] and a value as negative as –103 kcal/mol was reported[a]. This value differs significantly from the lattice energy of about –69 kcal/mol derived recently [8] from experimentally determined enthalpy of sublimation 32.6 kcal/mol [42] and the difference between the total energies of the most stable isomers of glycine in the gas phase (carboxylic acid) and in the solid state (betaine).

According to experimental as well as computational results the most stable modification is the $\alpha$-form [39, 43 - 45], while the relative stability of the $\beta$- and $\gamma$-polymorph is less clear.

The experimentally determined parameters of the molecular structures in the solid state together with *ab initio* data (MP2/6-31+G*) for the isolated betaine are listed in Table 1. Some significant differences between experimental and calculated parameters are obvious. Although the large disparities in calculated and measured bond angles are most likely real and not artifacts (which might be caused for example by thermal motion of the molecules in the lattice), it is difficult to decide whether this is also the case for the differences between calculated and observed bond lengths. Therefore, an initial set of calculations was performed on the basis of experimentally determined molecular geometries. The results are given in Table 2. To estimate the effect of the uncertainty of the experimental data, three calculations were performed for each isomer. In the first calculation unchanged cell parameters were used, while in the second and third the reported standard deviations of the cell constants were added and subtracted, respectively. The larger difference between latter two values and that obtained with unchanged parameters was then used as an approximate value for the standard deviation of the corresponding calculated lattice energy. No standard deviations for the cell parameters were reported in the case of the $\gamma$-polymorph [39]. For the uncertainty of the cell constants of this compound a value of 0.006 Å was assumed, which is close to the average value of the correponding standard deviations of the $\beta$-form. The electrostatic contributions to the lattice energy are similar to those obtained by other authors [47] with different quantum chemical methods. The problems that might occur in the evaluation of the electrostatic contribution have been discussed in [47, 48]. Convergence problems, however, are not confined to the $r^{-1}$ sum but might also occur for other components. Thus, because the induction energy was calculated directly (i. e. without convergence acceleration), problems are to be expected especially in the case of $\gamma$-glycine for which a high resulting cell dipole moment along the $c$ axis was calculated (MINDO/3 charges, $\mu_c$ =30.1 D, see also [47]). Figure 2 shows the induction energy of $\gamma$-glycine as a function of the summation limit used in the direct calculation ($R_{\max}$)[f]. As typical for direct lattice sums, the function oscillates. At $R_{\max}$ = 80 Å the induction energy amounts to only –3.2 kcal/mol, which is just about 23.9% of the converged value (–13.4 kcal/mol, see

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[f] All molecules whose centers of gravity are closer to that of the reference molecule than $R_{\max}$ were included. Thus the maximum interatomic distance encountered in the summation is somewhat larger than $R_{\max}$.

Table 2. The lattice energies of the three polymorphs of glycine, calculated employing experimentally determined molecular structures (in kcal/mol).

| Polymorph | $\Delta E_{\mathrm{dis}}$ i) | $\Delta E_{\mathrm{els}}$ | $\Delta E_{\mathrm{ind}}$ | $\Delta E_{\mathrm{rep}}$ | $\Delta E_{\mathrm{lat}}$ i) |
|---|---|---|---|---|---|
| $\alpha$-glycine | –24.4/–29.1 | –35.7 | –14.9 | 16.5 | –58.5(0)/–63.2 |
| $\beta$-glycine | –20.3/–25.2 | –36.6 | –13.0 ii) | 11.2 | –58.6(2)/–63.6 |
| $\gamma$-glycine | –21.7/–26.6 | –37.1 | –13.4 iii) | 16.4 | –55.7(1)/–60.7 |

i) For the left / right values the formula of London / Slater and Kirkwood was used. ii) 46·2000·48 Å$^3$ block. iii) 63·63·2000 Å$^3$ block.

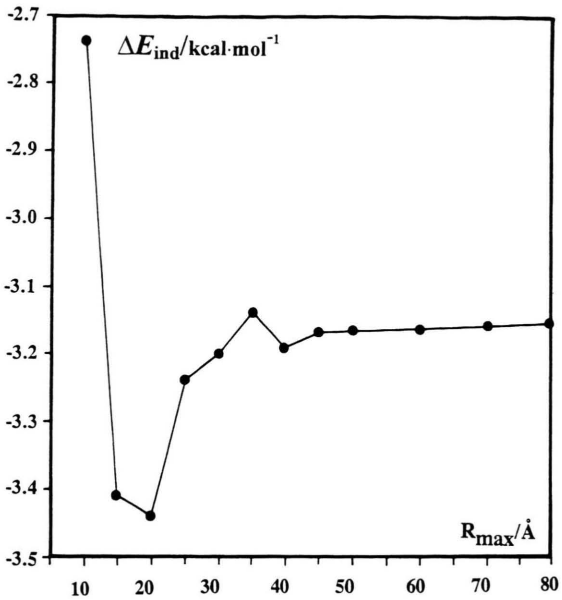

Fig. 2. The induction energy of the $\gamma$-glycine lattice as a function of the summation range. Direct summation. ($R_{\mathrm{max}}$ in Å, $\Delta E_{\mathrm{ind}}$ in kcal/mol).

Table 2). The convergence problems are not so severe as in the case of the electrostatic sum, where at $R_{\mathrm{max}}$ = 50 Å the sum covers –2 kcal/mol, only. Following the procedure suggested by Derissen and Voogd [45], the summation in the direction of the cell dipole moment was extended significantly and the calculation was performed for a 63·63·2000 Å$^3$ block. Compared with the value resulting from a summation over a 63·63·49 Å$^3$ box (–5.0 kcal/mol) the extension of the summation range results in a drop of the induction energy by more than 8 kcal/mol! The much lower cell dipole moment of the $\beta$-polymorph ($\mu_b$ = 3.9 D) is directed along the $b$ axis. As to be expected, extension of the summation range has a much less pronounced effect in this case. Going from a 46·56·48 Å$^3$ block to a 46·2000·48 Å$^3$ cell, the induction energy was lowered by only about 0.9 kcal/mol. Even such a small amount, however, might be of crucial importance in cases where the packing of molecular crystals has to be predicted, especially when the energy differences between different possible structures are small.

According to the calculations, the lattice energies of all three modifications lie within a relatively narrow range of about 4 kcal/mol. In general, the lattice energies reported in this paper are by about 9 - 14 kcal/mol less negative than those obtained by Derissen et al. ($\alpha$-glycine: –73.2, $\beta$-glycine: –69.0, $\gamma$-glycine: –71.8 kcal/mol [45]), which are close to the value for the $\alpha$-polymorph of –69 kcal/mol given in [8]. While the lattice energies of the $\alpha$- and $\beta$-polymorph are essentially identical, the least stabilizing value was obtained for the $\gamma$-form (*cf.* Table 2). The same relative stability of the $\beta$- and the $\gamma$-polymorph was obtained by Latajka et al. [44], while according to Derissen et al. [45] $\gamma$-glycine is by 2.8 kcal/mol more stable than the $\beta$-polymorph.

The crystal lattices of all three polymorphs are highly cross-linked by hydrogen bridges. Especially in the case of the $\beta$-polymorph the experimentally determined N-H bond lengths appear to be somewhat too short compared with the value expected for an N-H bond involved in N-H···O bridges (*cf.* Table 1). For the complex $(H_3N\text{-}H\cdots OH_2)^{\oplus}$ an N-H bond distance of about 1.06Å was obtained at the MP2/6-311G* level of *ab initio* theory. Thus in an additional set of calculations the N-H bond lengths of all polymorphs were fixed at 1.06 Å while experimental values were used for all other molecular structural parameters. The corresponding results are listed in Table 3.

Under these conditions the most stable polymorph is the $\beta$-modification. Essentially the same result is obtained when experimental bond- and dihedral angles are used in conjunction with MP2/6-31+G*-optimized bond lengths (Table 4).

Moreover, when the N-H bond lengths are fixed at 1.06 Å and MP2/6-31+G* values are used for the remaining interatomic distances together with experimental values for the bond and dihedral angles, the calculations also erroneously predict $\beta$-glycine to be the most stable polymorph (*cf.* Table 5).

It is of high importance to note that all deviations from the experimentally determined molecular geometry worsen the computational results. Thus, utmost care has to be exercised when it comes to the question

Table 3. The lattice energies of the three polymorphs of glycine listed below were calculated employing N-H bond lengths of 1.06 Å while all other structural parameters were fixed at experimental values (in kcal/mol).

| Polymorph | $\Delta E_{dis}$ i) | $\Delta E_{els}$ | $\Delta E_{ind}$ | $\Delta E_{rep}$ | $\Delta E_{lat}$ i) |
|---|---|---|---|---|---|
| α-glycine | −25.8/−30.5 | −35.8 | −15.3 | 17.2 | −59.7/−64.4 |
| β-glycine | −24.9/−29.8 | −36.2 | −14.5 ii) | 13.7 | −61.9/−66.8 |
| γ-glycine | −24.8/−29.6 | −36.8 | −15.0 iii) | 18.3 | −58.3/−63.1 |

Table 4. The lattice energies of the three polymorphs of glycine listed below were calculated employing MP2/6-31+G*-optimized bond lengths and experimentally determined bond- and dihedral angles (in kcal/mol).

| Polymorph | $\Delta E_{dis}$ i) | $\Delta E_{els}$ | $\Delta E_{ind}$ | $\Delta E_{rep}$ | $\Delta E_{lat}$ i) |
|---|---|---|---|---|---|
| α-glycine | −24.6/−29.3 | −35.5 | −14.6 | 17.5 | −57.2/−61.9 |
| β-glycine | −23.9/−28.8 | −36.4 | −13.8 ii) | 14.3 | −59.8/−64.7 |
| γ-glycine | −23.4/−28.2 | −37.0 | −14.3 iii) | 18.2 | −56.5/−61.3 |

Table 5. The lattice energies of the three polymorphs of glycine listed below were calculated employing N-H bond lengths of 1.06 Å while all other interatomic distances were optimized at the MP2/6-31+G* level. Bond angles and dihedral angels were fixed at the experimentally determined values (in kcal/mol).

| Polymorph | $\Delta E_{dis}$ i) | $\Delta E_{els}$ | $\Delta E_{ind}$ | $\Delta E_{rep}$ | $\Delta E_{lat}$ i) |
|---|---|---|---|---|---|
| α-glycine | −27.5/−32.2 | −35.3 | −16.0 | 19.3 | −59.5/−64.3 |
| β-glycine | −26.5/−31.8 | −36.3 | −15.3 ii) | 16.0 | −62.5/−67.4 |
| γ-glycine | −26.4/−31.1 | −36.8 | −15.6 iii) | 20.0 | −58.8/−63.5 |

i) For the left / right values the formula of London / Slater and Kirkwood was used. ii) 46·2000·48 Å$^3$ block. iii) 63·63·2000 Å$^3$ block.

whether a set of experimentally determined molecular structural parameters form a sound basis for a calculation of the lattice energy or not. For flexible molecules, like the amino acid glycine, there is no *a priori* choice for the molecular structure in the crystal lattice unless the geometry was optimized under the influence of the crystal field. Even then the question remains whether the positions of the atomic cores are the best choice for the centers of interaction or whether preference should be given to the corresponding maxima of electron density instead. Both centers will almost coincide in the case of atoms with a high electronegativity. Their positions might, however, differ significantly for atoms like hydrogen bonded to highly electronegative elements. Moreover, while the atomic cores might be the appropriate choice for one component of the lattice energy, the maxima of electron density may be better for another one. Thus in all cases where it is not obvious that the experimental data are in error (for example in the case of disorder or isotropically refined structures) the structures determined by diffraction methods should be used first. These initial calculations, however, should be followed by a careful examination about how meaningful changes of the molecular model influence the lattice energy.

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