Semiempirical Calculations on the Dipole Moment Enhancement in the Solid State*

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Dedicated to Prof. Dr. Jörg Fleischhauer on the occasion of his 65th birthday

The enhancement of the molecular dipole moment under the influence of the crystal lattice relative to the value for the corresponding isolated molecule has been calculated for the three low-pressure polymorphs of glycine using the semiempirical MINDO/3 *Hamiltonian*. In these calculations the influence of the lattice on an arbitrarily chosen reference molecule has been included by modifying the diagonal elements of the $\mathcal{H}^{\mathrm{core}}$ matrix. Starting from a set of atomic charges calculated for the isolated molecule an initial crystal lattice had been set up and included into the calculation of new self-consistent (SCF) charges for the reference molecule. The resulting set of new SCF charges was then used to replace the lattice charges from the preceding run, and a new SCF calculation was performed. This iterative process was continued until the difference between the electronic energies and the sum of the absolute values of the differences between the atomic charges from two subsequent SCF calculations was lower than 10^{-5} eV and 10^{-5} e_0, respectively. The results agree nicely with the experimental data obtained by other authors for α-glycine.

Key words: Dipole Moment Enhancement; Glycine; Calculations; Semiempirical Methods.

1. Introduction

If a molecule is transferred from the gas phase to the crystal lattice, its electron distribution will change under the influence of the field caused by the surrounding molecules of the solid. If the free molecule has a resulting dipole moment, this change of the electron distribution manifests itself in a change of its dipole moment. It is usually assumed that the dipole moment is higher in the solid state than for the unperturbed molecule in the gas phase [1]. Applying one of the available population analyses, the change of the molecular electron distribution will also be reflected by a change of the corresponding atomic charges. Thus it has been found that in molecular crystals which are crosslinked by hydrogen bonds the absolute values of the charges of those atoms which are involved in the hydrogen bridges will *increase* while, consequently, those in the central part of the molecule will *decrease*.

In this paper we examined the enhancement of the molecular dipole moment under the influence of the crystal lattice for the three low-pressure polymorphs of glycine[1] using a simple electrostatic model based on the semiempirical MINDO/3 Hamiltonian.

2. Computational Method

Starting from the structure of the reference molecule A, determined by X-ray structure determination [2 – 4], the crystal lattice has been generated by applying the corresponding space group symmetry. In the calculations only the reference molecule has been treated quantum-chemically, while the surrounding lattice molecules B $\neq$ A are represented only by their atomic point charges, calculated by means of the Mulliken population analysis. Similar approaches have been used by other authors, e.g. to study the influence of the crystal lattice on the geometry of acetamide [5] and formamide [7], to model the structure of the three poly-

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[1] A very recently discovered high-pressure polymorph of the same amino acid [13] will not be considered here.

Table 1. Dipole moments (in Debye, D) of the three low-pressure polymorphs of glycine in the gas phase ($\mu_{\rm gas}$) and in the crystal ($\mu_{\rm cry}$) according to the MINDO/3 method.

Polymorph	$\mu_{\rm gas}$	$\mu_{\rm cry}$	$\Delta\mu_{\rm cry,gas}$
α-glycine	12.18	14.69	2.52
β-glycine	12.18	14.40	2.22
γ-glycine	12.14	14.46	2.32

Table 2. Dipole moments (in D) of the three low-pressure polymorphs of glycine, calculated at experimental geometries in the solid state using the CCSD(T) method and different basis sets. *nbf* is the number of basis functions.

Polymorph	aug-cc-pVDZ	cc-pVTZ	6-311++G**
α-glycine	12.67	12.63	13.03
β-glycine	12.41	12.35	12.74
γ-glycine	12.44	12.40	12.81
nbf	160	220	145

morphs of glycine [6], to elucidate the effect of intermolecular interactions on the electronic field gradients in ice and liquid water [8, 10] and in solid ammonia, tetrazole, and imidazole [9]. A Morokuma-type analysis revealed that even in the case of hydrogen bonded water clusters mutual polarization of the molecules is the main effect, and that charge transfer is only of secondary importance [8, 10]. In the calculations described in this paper the influence of the crystal lattice on the reference molecule has been included by modifying the diagonal elements of the $\mathcal{H}^{\rm core}$ matrix of the atoms a of A according to

$$H_{\mu\mu,a} = {H_{\mu\mu,\rm a}}^0 - \sum_{\rm B}\sum_{\rm b} q_{\rm b}\cdot\Gamma_{\rm ab},$$

where

$${H_{\mu\mu,\rm a}}^0 = \langle\varphi_{\mu,\rm a}|\boldsymbol{h}^{\rm core}|\varphi_{\mu,\rm a}\rangle$$

($\varphi_{\mu,\rm a}$ is a basis function of atom a) is the corresponding matrix diagonal element of the $\boldsymbol{h}^{\rm core}$ operator of the unperturbed (isolated) reference molecule A, $q_{\rm b}$ is the net charge of atom b of any other lattice molecule B $\neq$ A, and $\Gamma_{\rm ab}$ is the two-center integral[2] used within the framework of the corresponding semiempirical method (here: MINDO/3 [11]). The summation over B includes all lattice molecules $\neq$ A up to a certain limit maintaining electrical neutrality.

The initial lattice is set up using the atomic charges obtained for the free molecule, and then an SCF calculation for A in the field of these charges is performed

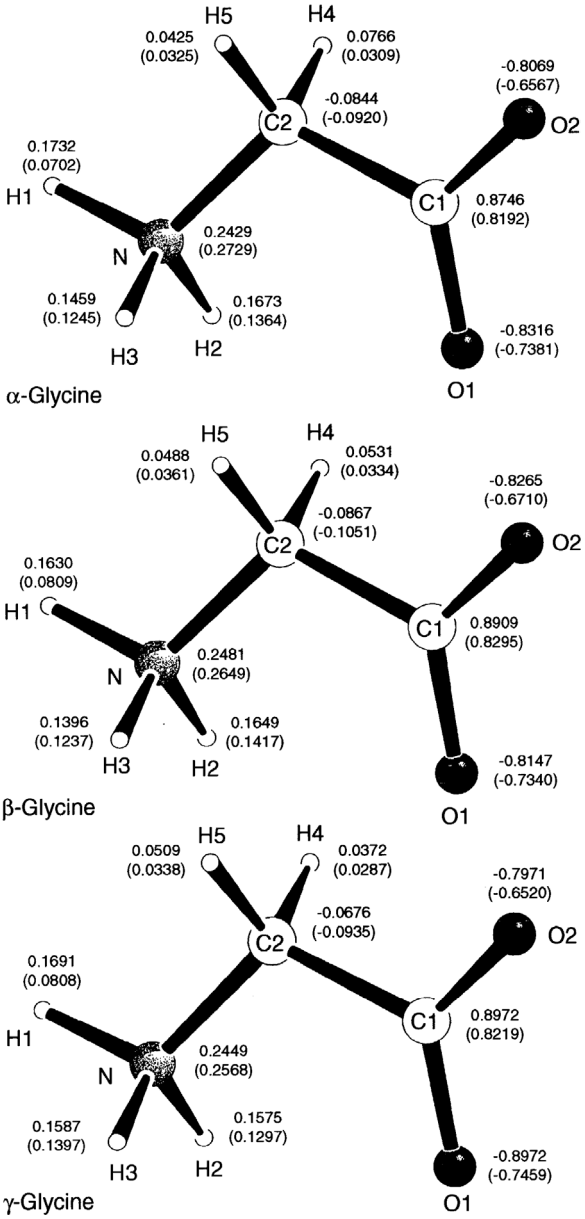

Fig. 1. Atomic charges (e_0, MINDO/3) of the three low-pressure polymorphs of glycine in the solid state. The numbers in parentheses are the corresponding values for the isolated molecule calculated for the same geometries.

(step 1). The old lattice charges are then replaced by the new self-consistent charges, and a new SCF calculation for the reference molecule follows (step 2). This iterative procedure is continued until the difference between (i) the electronic energy ($E_{\rm el}$) and (ii) the diagonal elements of the bond oder matrix of two subse-

[2] $\Gamma_{\rm ab} = 14.399\{r_{\rm ab}^2 + [7.1995(F^\circ({\rm a})^{-1} + F^\circ({\rm b})^{-1})]^2\}^{-1/2}$, where $r_{\rm ab}$ is the interatomic distance and F°(a) (F°(b)) an averaged one-centre coulomb integral of atom a (b) [11].

quent cycles drop below the defined convergency criteria (step n). The resulting dipole moment is assumed to be that of the molecule in the crystal lattice, and the lattice is said to be self-consistent.

To obtain the correct total energy ($E_{\mathrm{tot}} = E_{\mathrm{el}} + E_{\mathrm{core,core}}$) in each cycle, the term

$$\sum_{\mathrm{a}} \sum_{\mathrm{B}} \sum_{\mathrm{b}} q_{\mathrm{b}} \cdot Z_{\mathrm{a}} \cdot \Gamma_{\mathrm{ab}}$$

has to be added to the core repulsion energy ($E_{\mathrm{core,core}}$).

3. Results and Discussion

The changes of the Mulliken charges of the three polymorphs of glycine, calculated with the procedure described above, can be obtained from the numbers given in Fig. 1, where the values for the free molecules are given in parentheses. As expected, the absolute values of the charges of the atoms involved in hydrogen bonding increase. The corresponding changes of the dipole moments are given in Table 1. In order to estimate the reliability of the semiempirically calculated dipole moments, *ab initio* calculations have been performed using the same (experimental) geometries as in the MINDO/3 calculations. The results are listed in Table 2. The average difference between the semiempirically calculated dipole moments and those obtained at the CCSD(T)/cc-pVTZ level is 0.29D. Thus the used semiempirical method seems to give reliable results for the molecular dipole moments of the three polymorphs of glycine.

According to the calculations described above, the average increase of the dipole moments of the three polymorphs of glycine upon transfer from the gas phase to the solid state is 2.35D. Destro et al. [12] have recently determined the dipole moment of α-glycine in the solid state at 23 K by partitioning the experimental electron density. Using the monopole and dipole populations, and including a correction for scan truncation losses, they have obtained an experimental dipole moment of 14.9(3)D for α-glycine in the solid state, which agrees remarkably well with the semiempirical results presented in this paper.

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