Chemical Physics Letters 514 (2011) 21–25

Contents lists available at SciVerse ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Comparative study of CCSD(T) and DFT methods: Electronic (hyper)polarizabilities of glycine

Andrea Alparone *

Department of Chemistry, University of Catania, viale A. Doria 6, Catania 95125, Italy

ARTICLE INFO

Article history:
Received 2 July 2011
In final form 8 August 2011
Available online 12 August 2011

ABSTRACT

Static electronic (hyper)polarizabilities of the two lowest-energy conformations of glycine have been computed in the gas phase by using high-level *ab initio* and DFT methods with the POL, LPOLX-ds and LPOLX-fl Sadlej basis sets. Response electric properties from Hartree–Fock, Møller–Plesset and DFT computations have been compared to those calculated with Coupled-Cluster levels. Long-range corrected CAM-B3LYP and ωB97X-D functionals are superior to B3LYP, B3PW91 and mPW1PW91 especially to predict first- and second-order hyperpolarizabilities. The results obtained with the POL, LPOLX-ds and LPOLX-fl basis sets have minor differences. The effects of the different conformation on the response electric properties have been illustrated.

1. Introduction

Naturally occurring amino acids are the building blocks of peptides, proteins and enzymes and determine many of their important biological functionalities. A great deal of experimental and theoretical work has been carried out to characterize bio- and physico-chemical properties of individual amino acids and peptides. Electric susceptibility studies of glycine- and alanine-based peptides have been used to elucidate conformational and folding features [1,2]. Furthermore, there is a growing attention in exploring linear and nonlinear optical (NLO) properties of amino acids [3–15] and oligopeptides [7,15–17]. Thermal stable chromophore/peptide complexes are promising candidates for building efficient NLO devices [18]. Organic crystals based on amino acids are potentially appealing NLO materials for Second Harmonic Generation (SHG) applications [19,20]. However, Fleck and Petrosyan have lately reviewed in detail the principal troubles when characterizing SHG amino acid-based crystals [20]. Second-order hyperpolarizability of arginine, threonine, serine, alanine, proline, phenylalanine, histidine, tryptophan and tyrosine have been obtained by means of Z-scan measurements in aqueous solutions [9,10]. Recently, first-order hyperpolarizabilities of phenylalanine, tryptophan, tyrosine and of the tripeptide lysine–tryptophan–lysine have been investigated by using the hyper-Rayleigh scattering technique [15]. Thus, development and validation of relatively low-cost computational strategies to predict accurate response electric properties of important bio-molecular materials such as amino acids and peptides is clearly of great interest.

In the present work we focused our attention on the electronic (hyper)polarizabilities of glycine. Two different molecular conformations were investigated on a homogeneous theoretical ground (Figure 1): form **A** which exhibits a bifurcated $NH_2\cdots O{=}C$ hydrogen bond and form **B** which is characterized by a single $O{-}H\cdots NH_2$ hydrogen bond. In the vacuum **A** and **B** structures are the lowest-energy isomers of glycine [11,21,22]. Response electric properties can be determined accurately by using correlated wave function-based methods and Density Functional Theory (DFT), provided that sufficiently flexible basis sets including diffuse and polarization functions are used. However, it is well established that DFT methods with no long-range corrections are in trouble especially when dealing with (hyper)polarizabilities of extended systems [23]. On the other hand, novel functionals with long-range corrections are proven to give good estimates of response electric properties at minor computational cost of correlated *ab initio* methods [24,25].

Dipole moment and static electronic (hyper)polarizabilities of the lowest-energy conformations of glycine were computed in the gas phase at the Hartree–Fock (HF), Møller–Plesset perturbation theory (MPn), Coupled Cluster (CC) and DFT levels. The performances of the long-range corrected functionals the CAM-B3LYP [26] and ωB97X-D [27] were evaluated with respect to the highest-level *ab initio* method CCSD(T). The CAM-B3LYP functional has been employed with success to predict charge transfer excitations of a glycine dipeptide model system, in very good agreement with CASPT2 results [26]. We also considered the traditional B3LYP, B3PW91 and mPW1PW91 functionals as implemented in the GAUSSIAN 09 program [28]. These functionals have been extensively employed for (hyper)polarizability calculations [29–33]. Additionally, we explored whether response electric properties are potentially useful to distinguish the investigated conformations. Nonlinear

---

* Fax: +39 95 580138.
E-mail address: agalparone@unict.it

0009-2614/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2011.08.010

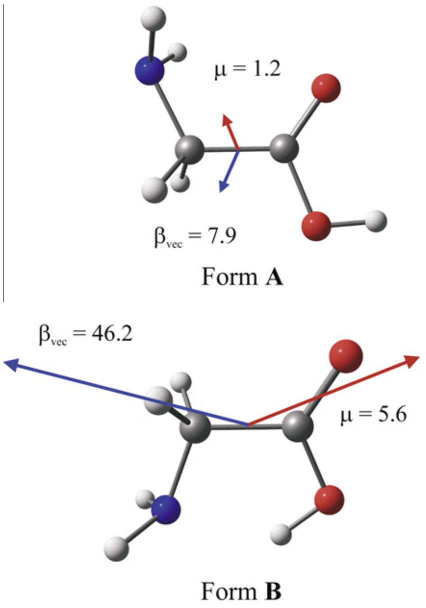

Figure 1. Molecular structures and CCSD(T)/POL dipole moment μ (D) and mean dipole first hyperpolarizability β_{vec} (a.u.) of glycine forms.

optical methodologies are currently adopted to characterize and identify structural features [34,35].

2. Computational methods

All calculations were performed using the GAUSSIAN 09 [28] and PC-GAMESS programs [36,37]. Molecular structures were optimized using the B3LYP functional with the 6-311++G** basis set. Vibrational analysis confirmed that the investigated structures are true minima on the potential energy surfaces (no imaginary frequencies). Dipole moment (μ), static electronic dipole polarizability (α), first- (β) and second-order hyperpolarizability (γ) values were computed analytically at the HF level by using the Time-Dependent HF method [38]. Correlated *ab initio* (MP2, MP4-SDTQ, CCSD and CCSD(T)) and DFT (B3LYP, B3PW91, mPW1PW91, CAM-B3LYP and ωB97X-D) α, β, and γ values were determined through the numerical differentiation procedure described in details in Ref. [39], using a field strength of 0.005 a.u. The accuracy of this approach was validated at the HF level, by comparing the response electric properties obtained by both analytical and numerical procedures. Present computations were carried out with the POL Sadlej basis sets, specifically built for electric response properties [40,41]. The POL basis sets consist of [3s2p] and [5s3p2d] functions, respectively, for H atom and first-row heavy atoms (C, N, O). As widely documented in the literature, POL basis sets are proven to give reliable estimates for electric (hyper)polarizabilities of small and medium-sized molecules [29,30,40–44]. The effects of basis sets were checked at the HF and MP2 levels, by comparing the response electric properties obtained with the POL and the more extended LPOLX-ds and LPOLX-fl basis sets [45]. These basis sets are recognized to produce very accurate (hyper)polarizability values [45,46]. The LPOLX-ds and LPOLX-fl basis sets for H atom consist of [4s3p] and [5s4p3d] functions, respectively, while for first-row heavy atoms (C, N, O) they consist of [6s5p3d] and [7s6p4d3f] functions, respectively.

We report the dipole moment (μ), the isotropically averaged polarizability ($<\alpha>$), the polarizability anisotropy ($\Delta\alpha$), the isotropically averaged first- (β_{vec}) and second-order ($<\gamma>$) hyperpolarizabilities, which are defined, respectively, as [47]:

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \tag{1}$$

$$<\alpha> = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$

$$\Delta\alpha = \left\{\frac{1}{2}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)\right]\right\}^{1/2} \tag{3}$$

$$\beta_{\mathrm{vec}} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \tag{4}$$

where β_i ($i = x, y, z$) is given by, $\beta_i = \frac{1}{3}\sum_{j=x,y,z}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$ and

$$<\gamma> = \frac{1}{15}\sum_{i,j}(\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji}) \tag{5}$$

where $i, j = x, y, z$.

3. Results and discussion

As well-known in the literature [11,21,22], glycine **A** is the lowest-energy isomer. At the CCSD(T)/POL//B3LYP/6-311++G** level, form **B** is predicted to lie 1.9 kJ/mol above form **A**, in reasonable agreement with the previously reported CCSD(T)/CBS datum (2.6 kJ/mol) [22]. Table S1 of the Supplementary data collects the structural parameters of the studied conformations together with the available microwave experimental data for comparison [48]. The results show that the B3LYP/6-311++G** geometry of form **A** is in satisfactory agreement with experiment, the largest discrepancies being found for the C—N bond length (0.017 Å) and H—N—H angle (6.2°). Additionally, the present geometries are in fair agreement with those previously calculated at the CCSD/DZP [21] and B97-1/cc-pVDZ [11] levels.

3.1. Effect of the basis set and theoretical level

It is well-known the crucial role of basis set and level of calculation in predicting adequately electronic (hyper)polarizabilities. Because of the heavy computational cost of CC computations, it is important to survey efficient DFT methods and basis sets for obtaining accurate (hyper)polarizabilities. In Table 1 are listed the μ,$<\alpha>$, $\Delta\alpha$, β_{vec}, and $<\gamma>$ values of the investigated conformations. The results show that the enlargement of basis sets (POL → LPOLX-fl) has only a negligible effect on the dipole moment and polarizabilities, increasing μ,$<\alpha>$ and $\Delta\alpha$ values by 0.1–0.5%, 0.2–0.3% and 0.5–0.7%, respectively. For the β_{vec} and $<\gamma>$ data the discrepancies are slightly more pronounced, being 2.4–3.0% and 4.4–4.5%, respectively. Note that the hyperpolarizability calculation with the LPOLX-fl basis sets requires a CPU time of two orders of magnitude higher than that with the POL basis sets, being currently impracticable for high-level correlated computations. In addition, for the **A** form we investigated the basis set effects at correlated level (MP2/POL → MP2/LPOLX-ds). The results summarized in Table S2 of the Supplementary data reveal that the performances of the POL basis sets for correlated γ values are quite similar to those obtained from the HF calculations, while those for β values are only slightly worsened. Therefore, the use of the POL basis sets for subsequent correlated calculations can be considered a good compromise between accuracy and computational cost.

Dipole moments of glycine conformers are available from microwave measurements [49]. At the highest-level CCSD(T)/POL, the μ values are predicted to be 1.16 D for glycine **A** and 5.62 D for glycine **B**, in satisfactory agreement with the experimental data [49] of 1.10 D (+5%) and 5.45 D (+3%), respectively, as well as with previous CCSD(T)/aug-cc-pVDZ estimates [11] of 1.28 and 5.46 D,