Conformers of dehydrogenated glycine isomers

Erik M. Orján | András B. Nacsa | Gábor Czakó

Abstract
We report a comprehensive ab initio investigation of the conformers of dehydrogenated glycine radicals using the STO-3G, 3-21G, and aug-cc-pVDZ (aVDZ) basis sets and the UHF and UMP2 (H₂N-CH-COOH and HN-CH₂-COOH) as well as MCSCF and MRCI (H₂N-CH₂-COO) methods via two different conformational search strategies generating initial structures for optimizations by (a) removing H atoms from glycine conformers and (b) scanning torsional angles describing internal rotation along the CC, CN, and CO (except for H₂N-CH₂-COO) bonds of the radicals. We find four H₂N-CH-COOH {InCH, IIInCH, IIInCH, IVnCH} and seven HN-CH₂-COOH {IpNH, IIpNH, IIInNH, IVpNH, VnNH, VIpNH, VIIpNH} conformers with classical(adiabatic) relative energies of {0.00(0.00), 1.57(1.55), 5.25(5.03), 9.85(9.72)} and {0.00(0.00), 0.78(1.06), 1.93(2.08), 3.34(3.16), 3.93(3.29), 5.00(4.86), 9.27(8.87)} kcal/mol, respectively, obtained with UCCSD(T)-F12b/aug-cc-pVTZ(+UCCSD(T)-F12b/aVDZ ZPE correction) and four H₂N-CH₂-COO {IpCOO, IIpCOO, IpCOO, IIpCOO} conformers with MRCI-F12+Q/aVDZ ZPE correction energies of {0.00(0.00), 1.65(1.64), 1.78(1.75), 2.21(2.21)} kcal/mol, where n and p denote C₁ and C₂ symmetry. The MRCI-F12+Q [UCCSD(T)-F12b] InCH → IpNH and InCH → IpCOO classical(adiabatic) isomerization energies are 18.51(17.32)[21.20(20.01)] and 31.88(31.66) kcal/mol, respectively.

KEYWORDS
ab initio, amino acids, conformational search, explicitly correlated, glycine radical conformers

1 | INTRODUCTION

Reactive free radicals can damage biomolecules in the human body causing serious diseases. One of the most harmful radicals is OH, which may abstract a hydrogen atom from proteins thereby damaging their structure and functionality. Hydrogen abstraction can occur from the backbone and the amino-acid side chains of the polypeptides. The accurate theoretical description of such processes is extremely challenging, because one should deal with macromolecules in aqueous environment. The simplest model system of proteins is their smallest building block, which is the amino acid glycine, which is zwitterionic (+H₃N-CH₂-COO⁻) in solution and neutral (H₂N-CH₂-COOH) in the gas phase. The conformers and properties of gaseous glycine were thoroughly investigated by various electronic structure theories and experimental techniques during the past couple of decades.[1-12] Radicals can abstract a H atom by breaking the CH, NH, or OH bond resulting in a dehydrogenated glycine radical H₂N-CH-COOH, HN-CH₂-COOH, or H₂N-CH₂-COO, respectively. The OH + glycine reaction and the structures and energetics of the glycine radicals have been extensively investigated focusing mainly on the CH abstraction channel and the lowest energy conformer of H₂N-CH-COOH.[13-24] This may be explained by the fact that the C-terminal channels are energetically favored over NH and OH bond cleavages[13,16] and CH abstraction may happen in proteins, whereas the amino and carboxyl groups form peptide bonds, where OH bond does not exist and the electronic structure of the NH bond is altered. Nevertheless, a

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited. © 2020 The Authors. Journal of Computational Chemistry published by Wiley Periodicals LLC.
few studies reported several conformers of all the three isomer radicals derived from homolytic CH, NH, and OH bond dissociation. The above-mentioned theoretical studies employed density functional theory (usually B3LYP) and the MP2 method with double- and triple-zeta basis sets (usually 6-31G* and 6–311+ +G**). The use of the more sophisticated and accurate CCSD(T) method is rare and only employed for single-point energy computations.

In the present study, we report a comprehensive ab initio study of the conformers of gas-phase glycine radicals considering CH, NH, and OH bond dissociations. We go beyond the accuracy of the previous studies by applying the explicitly correlated CCSD(T)-F12b method to obtain benchmark structures and relative energies of the conformers of gas-phase glycine radicals considering CH, NH, and OH bond dissociations. We aim to find new conformers of the dehydrogenated glycine radicals. Besides the high-level ab initio investigation of the glycine radicals, we test different computational strategies to determine all the possible conformers of the title system, which techniques may become useful for mapping the conformational space of other similar or even larger systems.

The motivation of the present study is multiple-fold: (a) We determine conformers of glycine with the state-of-the-art explicitly correlated CCSD(T)-F12b method, for the first time, thereby confirming and/or improving previous work. (b) We aim to find new conformers for the dehydrogenated glycine radicals, thereby complementing previous incomplete studies. (c) We provide benchmark structures and energetics for the conformers of glycine radicals. (d) As the topology of the potential energy surface may sensitively depend on the level of electronic structure theory, we test different ab initio methods, including also multi-reference techniques, and basis sets to find radical conformers. Knowing the performance of the low-level methods can provide useful guidance for the investigations of larger systems, when the use of high-level theories is not feasible. (e) The present benchmark characterization of the dehydrogenated glycine radicals may be the first step toward the study of the OH + glycine reaction.

In Section 2, we describe the computational details including the introduction of two different conformational search strategies. The results are presented and discussed in Section 3. The article ends with summary and conclusions in Section 4.

2 | COMPUTATIONAL DETAILS

2.1 | Conformers of glycine

Following the pioneering electronic structure studies reporting eight conformers (see Figure 1) of the gaseous glycine, we optimize these conformers and compute their harmonic frequencies using the second-order Møller–Plesset perturbation theory (MP2) combined with the correlation-consistent aug-cc-pV(DZ) basis set. Then, we further optimize the obtained structures by the explicitly correlated coupled-cluster singles, doubles, and perturbative triples method (CCSD(T)-F12b) using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Besides MP2, the harmonic frequencies are also computed at the CCSD(T)-F12b/aug-cc-pVDZ level of theory.

2.2 | Conformers of dehydrogenated glycine isomers

Our goal is to determine all the possible conformers of the dehydrogenated glycine radicals. To achieve this goal we investigate two different strategies and various levels of electronic structure theory as detailed below.

2.2.1 | Strategy I

As a first, simple, chemically motivated strategy we remove one H atom from the central C atom, the amino or the carboxyl group of each of the eight glycine conformers. Since the two CH2 and NH2 hydrogen atoms are equivalent in the three C3 glycine geometries and different in the five C5 structures, the H abstraction leads to 3 + 2 × 5 = 13, 3 + 2 × 5 = 13, and eight different initial radical geometries for the H2N-CH-COOH, HN-CH2-COOH, and H2N-CH2-COO isomers, respectively. In the case of H2N-CH-COOH and HN-CH2-COOH we perform geometry optimizations starting from the above two times 13 initial structures using the following levels of theory: UHF/STO-3G, UHF/3-21G, UHF/aug-cc-pVDZ, UMP2/STO-3G, UMP2/3-21G, and UMP2/aug-cc-pVDZ. For the 8 H2N-CH2-COO geometries we experience convergence problems in Hartree–Fock (both ROHF and UHF); thus, the use of the multi-configurational self-consistent field (MCSCF) and multi-reference configuration interaction (MRCI) methods is found to be necessary. Therefore, we optimize the H2N-CH-COO geometries using the MCSCF/STO-3G, MCSCF/3-21G, MCSCF/aug-cc-pVDZ, MRCI/STO-3G, MRCI/3-21G, and MRCI/aug-cc-pVDZ levels of theory starting from the eight initial structures. The MCSCF computations utilize a small active space of five electrons on three spatial orbitals and we compute the ground electronic state only. During all the correlation computations in this study, the core electrons are kept frozen.

2.2.2 | Strategy II

In order to ensure that we have found all the possible conformers with Strategy I, we perform a more systematic mapping of the conformational space of the glycine radicals. Starting from the lowest-energy conformer obtained by Strategy I for each of the three isomers, we generate 63 steps (6 different angle values as 0° and 360° are equivalent). The torsional motions describe the internal rotations of the [NH2, COOH, OH], [NH, COOH, OH], [NH2, COO] groups for H2N-CH-COOH, HN-CH2-COOH, and H2N-CH2-COO, respectively, as shown in Figure 2. From the above 216, 216, and...
36 structures we initiate geometry optimizations using the ab initio methods and basis sets described in Section 2.2.1. From the unique conformers obtained by the lower levels of theory using either Strategy I or II UMP2/aug-cc-pVDZ (H₂N-CH-COOH and HN-CH₂-COOH) and MRCI/aug-cc-pVDZ (H₂N-CH₂-COO) optimizations are initiated to assign each conformer to one of the UMP2/aug-cc-pVDZ or MRCI/aug-cc-pVDZ structures or to verify a new conformer. Note that for the MCSCF conformers obtained from Strategy II this assignment is not performed owing to the large number of conformers.
2.2.3 | Benchmark structures and energies

The final UMP2/aug-cc-pVDZ conformers obtained by Strategies I and II are further optimized using the ROHF-based UCCSD(T)-F12b[35] method with the aug-cc-pVDZ (geometry and frequency computation) and aug-cc-pVTZ (geometry) basis sets. Thus, the best classical relative energies of the H₂N-CH₃-COOH and HN-CH₂-COOH conformers are obtained at the UCCSD(T)-F12b/aug-cc-pVTZ level of theory and the adiabatic relative energies include UCCSD(T)-F12b/aug-cc-pVDZ zero-point energy corrections. For the H₂N-CH₃-COOH conformers the classical relative energies are determined using the Davidson-corrected[26] MRCl+Q[34] and MRCl-F12+Q[37] methods with the aug-cc-pVDZ basis set at the MRCl/aug-cc-pVDZ geometries and the adiabatic relative energies are obtained utilizing MRCl/aug-cc-pVDZ zero-point energy (ZPE) corrections. In order to compare the energies of all the glycidyl radical isomers, MRCl+Q/aug-cc-pVDZ and MRCl-F12+Q/aug-cc-pVDZ energies are also computed for the H₂N-CH₃-COOH and HN-CH₂-COOH conformers at the UCCSD(T)-F12b/aug-cc-pVTZ geometries. Furthermore, MRCl/aug-cc-pVDZ frequencies are determined for the lowest-energy H₂N-CH₃-COOH conformer to obtain ZPE-corrected isomerization energy between H₂N-CH₃-COOH and H₂N-CH₂-COOH. All the ab initio computations in this study are performed using the MOLPRO[38] program package.

3 | RESULTS AND DISCUSSION

3.1 | Conformers of glycine

The structures and relative energies of the eight conformers (minima) of glycine are given in Figure 1 and Table 1, respectively. The notation of the conformers follows previous studies,[1–4] that is, roman numbers increase with the energy of Cₛ structures and p and n refer to planar (Cₛ symmetry) and nonplanar (C₁ symmetry) arrangements of the N-C-COOH atoms, respectively. Three conformers (Ip, VIp, and VIIp) have C₁ symmetry, whereas in five cases (IIn, IIIn, IV, Vn, and VIIIn) lone-electron-pair repulsion effects favor symmetry breaking; thus, the minima are nonsymmetric and the Cₛ structures (not shown in Figure 1) correspond to saddle points.[11] The symmetry-breaking stabilizer effects change the energy order of the III and IV conformers, that is, IVn is below III in by about 0.5 kcal/mol in agreement with previous studies.[1,4] For the glycine conformers the MP2/aug-cc-pVDZ level of theory provides remarkably accurate relative energies with only about 0.1 kcal/mol mean and 0.2 kcal/mol maximum differences from the CCSD(T)-F12b/aug-cc-pVDZ results as shown in Table 1. The CCSD (T)-F12b relative energies obtained with the aug-cc-pVDZ and aug-cc-pVTZ basis sets agree within 0.00–0.03 kcal/mol showing the excellent basis-convergence of the explicitly-correlated CCSD(T)-F12b method. The present CCSD(T)-F12b/aug-cc-pVTZ classical relative energies are in excellent agreement (the average absolute deviation is less than 0.1 kcal/mol) with the final predictions of Császár,[5] confirming that the “conservative” error bar estimate of ±0.3 kcal/mol given in Császár[1] was really conservative. Furthermore, the present benchmark classical relative energies reproduce the CCSD(T)/complete-basis-set(CBS) results of Balabin[6] within 0.03 kcal/mol on average, showing the superiority of the CCSD(T)-F12b method over the traditional and more time-consuming CCSD(T) CBS-extrapolation techniques. As Table 1 shows the ZPE corrections are between −0.3 and +0.4 kcal/mol with varying signs, where MP2 and CCSD(T)-F12b are in good agreement again. These ZPE corrections are clearly not negligible considering that the CCSD(T)-F12b classical relative energies are basis-set-converged within about 0.03 kcal/mol. The final adiabatic relative energies are in the same order as the classical ones, confirming the Ip, IIn, IV, Vn, VIp, VIIp, and VIIIIn energy order of previous theoretical predictions.[1,4]

3.2 | Conformers of dehydrogenated glycine isomers

3.2.1 | Strategy I

Geometry optimizations initiated from the eight glycine conformers after removing different H atoms result in 4, 7, and 4 conformers.

| TABLE 1 | Classical and adiabatic relative energies (kcal/mol) of glycine conformers obtained at different levels of theorya |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Classical        | CCSD(T)-F12b/aVDZ | CCSD(T)-F12b/aVTZ | ΔZPE            | Adiabaticb      |                  |
|                | MP2/aVDZ         | MP2/aVDZ         |                  |                  | MP2/aVDZ         |                  |
| Ip              | 0.00             | 0.00             | 0.00             | +0.00            | 0.00             | 0.00             |
| IIn             | 0.54             | 0.66             | 0.68             | +0.28            | +0.35            | 1.03             |
| IIIn            | 1.59             | 1.73             | 1.73             | +0.06            | +0.04            | 1.65             |
| IV              | 1.25             | 1.23             | 1.23             | −0.01            | −0.02            | 1.24             |
| Vn              | 2.43             | 2.59             | 2.62             | +0.08            | +0.08            | 2.51             |
| VIp             | 4.86             | 4.79             | 4.80             | −0.15            | −0.17            | 4.71             |
| VIIp            | 6.06             | 5.92             | 5.89             | −0.18            | −0.10            | 5.88             |
| VIIIn           | 6.25             | 6.05             | 6.06             | −0.25            | −0.14            | 6.00             |

aResults correspond to optimized geometries obtained by MP2/aug-cc-pVDZ, CCSD(T)-F12b/aug-cc-pVDZ, and CCSD(T)-F12b/aug-cc-pVTZ.

bClassical relative energy plus zero-point energy correction (ΔZPE).

CcSD(T)/aug-cc-pVTZ classical relative energy plus CCSD(T)/aug-cc-pVDZ ΔZPE.
(minima) for the H$_2$N-CH-COOH, HN-CH$_2$-COOH, and H$_2$N-CH$_2$-COO radicals as shown in Figure 3. Similar to glycine, the radical con-
formers are denoted by roman numbers reflecting the UMP2/aug-cc-
pVDZ or MRCI/aug-cc-pVDZ energy order, p and n denote C$_s$ and C$_1$
point-group symmetry, respectively, and subscripts CH, NH, and COO
denote the radical isomer.

All the four H$_2$N-CH-COOH conformers are nonsymmetric and
related to each other by internal rotations along the CC and CO axes.

Torsional motion of the NH$_2$ group does not result in additional min-
ima. Removing H atoms from glycine conformers {I$_p$, I$_{II}$, II$IN$, IV$_n$, V$_n$, V$_{II}P$, V$_{II}I$} results in radical conformers {I$_{CH}$, IV$_{CH}$, I$_{II}$$_{CH}$, II$In$$_{CH}$, I$_{II}$In$_{CH}$, IV$_n$$_{CH}$, II$In$$_{CH}$, I$_{II}$In$_{CH}$} regardless which H atom is removed from
the C$_s$ structures and which level of theory is used as shown in
Table 2. The sole exemption is the case of V$_n$-H$_7$ (see Table 2) at the
UMP2/STO-3G level, which results in I$_{CH}$ instead of I$_{II}$$_{CH}$. As seen
above, each radical conformer is obtained from two glycine
conformers, which have the same COOH conformation, but different NH2 arrangements. UMP2 with both the 3-21G and aug-cc-pVDZ basis sets gives the qualitatively same four conformers with 2–3 kcal/mol basis-set effects and with the same energy order. At the UMP2/STO-3G level the energy order changes and six different conformers are obtained as conformers with relative energies of 0.73 and 3.13 kcal/mol are both assigned (based on further UMP2/aug-cc-pVDZ optimizations) to InCH and the IVnCH conformer is split to relative energies of 2.74 and 5.59 kcal/mol. Considering the structures of the above four UMP2/STO-3G conformers, the ones at 0.73, 3.13,

| TABLE 2 | Relative energies (kcal/mol) of H2N-CH-COOH conformers obtained from the eight glycine conformers at different levels of theorya |
|---|---|---|---|---|---|
| Initial structureb | UHF | | | | |
| | STO-3G | 3-21G | aVDZ | STO-3G | 3-21G | aVDZ |
| Ip-H7 | 2.97 (InCH) | 8.81 (InCH) | 3.13 (InCH) | 14.92 (InCH) | 11.85 (InCH) |
| In-H7 | 2.74 (InCH) | 8.81 (InCH) | 14.92 (InCH) | 11.85 (InCH) |
| Il-H7 | 2.74 (InCH) | 8.81 (InCH) | 14.92 (InCH) | 11.85 (InCH) |
| Iln-H7 | 0.00 (InCH) | 1.16 (InCH) | 0.00 (InCH) | 0.00 (InCH) |
| lIVn-H7 | 0.73 (InCH) | 2.32 (InCH) | 2.32 (InCH) |
| lIVn-H8 | 3.13 (InCH) | 11.85 (InCH) | 11.85 (InCH) |
| lIVn-H9 | 0.73 (InCH) | 2.32 (InCH) | 2.32 (InCH) |
| lIVn-H10 | 3.13 (InCH) | 11.85 (InCH) | 11.85 (InCH) |
| Vn-H7 | 2.97 (InCH) | 8.81 (InCH) | 14.92 (InCH) | 11.85 (InCH) |
| Vn-H8 | 2.97 (InCH) | 8.81 (InCH) | 14.92 (InCH) | 11.85 (InCH) |
| Vn-H9 | 2.97 (InCH) | 8.81 (InCH) | 14.92 (InCH) | 11.85 (InCH) |
| Vn-H10 | 2.97 (InCH) | 8.81 (InCH) | 14.92 (InCH) | 11.85 (InCH) |
| VIIp-H7 | 4.79 (VIpNH) | 8.39 (VIpNH) | 5.89 (VIpNH) | 5.03 (VIpNH) |
| VIIp-H8 | 4.79 (VIpNH) | 8.39 (VIpNH) | 5.89 (VIpNH) | 5.03 (VIpNH) |
| VIIp-H9 | 4.79 (VIpNH) | 8.39 (VIpNH) | 5.89 (VIpNH) | 5.03 (VIpNH) |
| VIIp-H10 | 4.79 (VIpNH) | 8.39 (VIpNH) | 5.89 (VIpNH) | 5.03 (VIpNH) |

aThe assignment of the conformers (see Figure 3), obtained by UMP2/aug-cc-pVDZ computations initiated from the lower-level optimized structure, are shown in parentheses.
bInitial structure of the geometry optimization obtained by removing the indicated H atom from the given glycine conformer (see Figure 1).
cUHF convergence problems or the optimization did not converge within 100 steps. 
2.74, and 5.59 kcal/mol look like InCH, InCH, IVnCH, and IVnCH, respectively, in agreement with the assignments. However, it is important to note that all the conformers obtained at UMP2/STO-3G have large imaginary frequencies. Furthermore, in four cases the UMP2/STO-3G optimizations are not converged as seen in Table 2. Using the UHF method with the STO-3G basis each of the four conformers is obtained once and the other optimizations are not converged due to UHF convergence problems or the optimization procedure reaches a maximum of 100 steps. At the UHF/3-21G level four conformers are obtained, two optimizations fail, and the energy order of InCH and IVnCH reverses. Using UHF/aug-cc-pVDZ there is no convergence problem, but this level results in seven conformers (different energies) as InCH splits into 0.00 and 0.09 kcal/mol, IVnCH into 5.94 and 6.04 kcal/mol, and IVnCH into 8.81 and 9.64 kcal/mol. There is no qualitative difference between the structures of the conformers which are assigned to the same minimum with UMP2/aug-cc-pVDZ.

In the case of the HN-CH$_2$-COOH radical, all the optimizations converge successfully (see Table 3). The UMP2/aug-cc-pVDZ level of theory results in 7 conformers, from which only two (IIIp$^\prime$NH and Vn$^\prime$NH) do not have $C_s$ symmetry as shown in Figure 3. The structures and energy order of the radical conformers are similar to the corresponding parent glycine geometries as {Ip, In, III, IVn, Vn, Vlp, VIIp, VIIln} result in {Ip$\_\text{NH}$, IIn$\_\text{NH}$, IIIp$\_\text{NH}$, IVp$\_\text{NH}$, IIIn$\_\text{NH}$, Vlp$\_\text{NH}$, VIIp$\_\text{NH}$, VIIIIp$\_\text{NH}$}. The fact that the removal of different H atoms from the amino group of IVn, Vn, and VIIIn provides different radical conformers differing in the conformation of the NH group is expected considering the twisted orientation of the NH$_2$ group of these glycine conformers (see Figure 1). Comparing the structures of the eight glycine and seven radical conformers, one can notice that the VIIp-like radical conformer is missing as optimization initiated from VIIp results in IIp$\_\text{NH}$, which has the same COOH conformation, but the NH group rotates into a favorable HN$\_\text{NH}$/C$_1$/C$_1$/C$_1$HO arrangement, instead of the repulsive NH$\_\text{NH}$/C$_1$/C$_1$/C$_1$HO.

As Table 3 shows the lower levels of theory roughly give similar result; Ip$\_\text{NH}$ is always the lowest energy conformer, the energy orders are similar, though IIp$\_\text{NH}$ and IIIn$\_\text{NH}$ as well as often IVp$\_\text{NH}$ and IVn$\_\text{NH}$ are reversed. VIIp$\_\text{NH}$ is only obtained at the UHF/STO-3G, UHF/aug-cc-pVDZ, and UMP2/aug-cc-pVDZ levels, whereas using the other methods and bases the removal of both H atoms from VIIIn provides the energetically favored Vlp$\_\text{NH}$ conformer. Furthermore, at the UHF/STO-3G and UHF/3-21G levels some of the optimizations initiated from IIIIn and Vn result in a $C_s$ structure IIIp$\_\text{NH}$ (Figure 4), which is a transition state connecting two

![Transition-state structures of HN-CH$_2$-COOH](Color figure can be viewed at wileyonlinelibrary.com)

TABLE 4 Relative energies (kcal/mol) of H$_2$N-CH$_2$-COO conformers obtained from the eight glycine conformers at different levels of theory$^a$

| Initial structure$^b$ | MCSCF | MRCI |
|----------------------|-------|------|
|                      | STO-3G | 3-21G | aVDZ | STO-3G | 3-21G | aVDZ |
| Ip$\_\text{H}_6$     | 0.00 (Ip$\_\text{COO}$) | 0.00 (Ip$\_\text{COO}$) | 0.00 (Ip$\_\text{COO}$) | 0.00 (Ip$\_\text{COO}$) | 0.00 (Ip$\_\text{COO}$) | 0.00 (Ip$\_\text{COO}$) |
| IIn$\_\text{H}_6$    | 1.41 (IVn$\_\text{COO}$) | 2.34 (IVn$\_\text{COO}$) | 2.89$^c$ | 1.52 (IVn$\_\text{COO}$) | 2.91 (IVn$\_\text{COO}$) | 2.96$^d$ |
| IIIIn$\_\text{H}_6$ | 1.60 (IIIp$\_\text{COO}$) | 2.66 (IIIp$\_\text{COO}$) | 1.64 (IIIp$\_\text{COO}$) | 1.19 (IIIp$\_\text{COO}$) | 2.92 (IIIp$\_\text{COO}$) | 1.64 (IIIp$\_\text{COO}$) |
| IVn$\_\text{H}_6$    | 2.03 (IVn$\_\text{COO}$) | _ | _ | _ | 4.52$^e$ (IVn$\_\text{COO}$) | 2.21 (IVn$\_\text{COO}$) |
| Vn$\_\text{H}_6$     | 0.00 (Ip$\_\text{COO}$) | 0.00 (Ip$\_\text{COO}$) | 0.00 (Ip$\_\text{COO}$) | 0.00$^e$ (Ip$\_\text{COO}$) | 0.00 (Ip$\_\text{COO}$) | 0.00 (Ip$\_\text{COO}$) |
| Vlp$\_\text{H}_6$    | 1.98 (IIIp$\_\text{COO}$) | 2.46$^f$ (IVn$\_\text{COO}$) | _ | _ | 3.43$^f$ (IVn$\_\text{COO}$) | _ |
| VIIp$\_\text{H}_6$   | _ | 0.00 (Ip$\_\text{COO}$) | _ | _ | 0.00 (Ip$\_\text{COO}$) | 1.64 (IIIp$\_\text{COO}$) |

$^a$The assignment of the conformers (see Figure 3), obtained by MRCI/aug-cc-pVDZ computations initiated from the lower-level optimized structure, are shown in parentheses.

$^b$Initial structure of the geometry optimization obtained by removing the indicated H atom from the given glycine conformer (see Figure 1).

$^c$Further MRCI/aug-cc-pVDZ optimization fails.

$^d$Frequency computation fails (imaginary frequencies are suspected).

$^e$Imaginary frequencies are obtained.

$^f$MOLPRO computations fail.
C₁-IlInNH enantiomers. Thus, in the case of UHF/3-21G both IlInNH and VIIpNH are missing. At the UMP2/STO-3G level one of the optimizations starting from IlIn results in IpNH instead of IlInNH, nevertheless in this case IlInNH is also obtained by removing the other H atom. Additional conformers (minima) are not found using the lower levels of theory.

For the H₂N-CH₂-COO radical MRCI/aug-cc-pVDZ finds four conformers as shown in Table 4 and Figure 3. There are two C₃ conformers (IpCOO and IlIpCOO), which differ in the conformation of the COO group, and there are two C₁ conformers (IlInCOO and IVnCOO), where the NH₂ group is twisted (Figure 3). (Note that an additional fifth conformer is also obtained from IIIn, which seems to be a IVnCOO-like TS structure with C₃ symmetry, but its saddle-point character cannot be confirmed, because the frequency computation does not converge for this conformer.) As shown in Table 4 IpCOO is obtained from Ip and VIlp at every level of theory, as expected, because these two glycine conformers have the same NH₂ and COO arrangements as IpCOO. IlInCOO is found by removing the hydroxyl H atom from IVn, again at every level of theory, due to the similar conformations. Considering structural similarity, we expect IlInCOO from VIIIn as well, as we find using MRCI/aug-cc-pVDZ. However, the other levels either do not converge or result in IpCOO, where the NH₂ group turns into an energetically favored symmetric orientation. In most cases we obtain IlIpCOO from the structurally similar IlIn, except with the STO-3G basis, where new conformers are obtained that relax into IpCOO. In the case of MCSCF/STO-3G the new conformer has an IpCOO/IlIpCOO-like structure with twisted COO group (C₁ symmetry), which relaxes to IpCOO at the MRCI/aug-cc-pVDZ level (Table 4). IlIpCOO is also expected from the very similar and also planar VIIlp, but this happens only at the MCSCF/STO-3G level, the other levels converge only with 3-21G resulting in IVnCOO, where the NH₂ group is twisted breaking the C₁ symmetry. The conformation of IVnCOO is related to IIIn and Vn, and indeed, the converged optimizations always result in IVnCOO from the dehydrogenated IIIn and Vn. However, when
convergence problem does not occur and IVn\textsubscript{COO} is obtained from both IIn and Vn, and in some cases from VII\textsubscript{p}, the energies of the IVn\textsubscript{COO}-like conformers are always different (see Table 4). Thus, additional conformers, which are IVn\textsubscript{COO}-like minima at the lowest energies and C\textsubscript{s} saddle points or twisted C\textsubscript{1} minimum (MCSCF/STO-3G) at the higher energies (highest energy MRCI/3-21G conformer has no symmetry with a twisted COO group), are found at lower levels of theory, which all result in the same IVn\textsubscript{COO} conformer with further MRCI/aug-cc-pVDZ optimizations.

3.2.2 | Strategy II

Starting geometry optimizations from the 216 initial structures using the UMP2 method with the aug-cc-pVDZ basis set results in four different H\textsubscript{2}N-CH-COOH conformers with equal probability as shown in Figure 5. These conformers are the same as the ones obtained from Strategy I and shown in Figure 3. At the UMP2/3-21G level again the same four conformers are obtained with similar probability showing that the well around each minimum covers similar size of the configuration space. At the UMP2/STO-3G, UHF/STO-3G, UHF/3-21G, and UHF/aug-cc-pVDZ levels of theory the configuration space is more structured resulting in 18, 25, 7, and 17 conformers, respectively. The conformers, which were found with Strategy I are usually obtained with the highest probabilities. If we further optimize the above conformers using the UMP2/aug-cc-pVDZ level, all of them converge to the above-mentioned four different minimum structures as shown in Figure 5; thus, we can be confident that at higher level of theory four conformers of H\textsubscript{2}N-CH-COOH exist and Strategy II does not reveal any new conformer beyond the ones found via Strategy I.
In the case of the HN-CH₂-COOH isomer, the Strategy II with UMP2/aug-cc-pVDZ provides seven conformers (minima) like Strategy I and four transition states (saddle points) as shown in Figure 6. The transition states, shown in Figure 4, connects the two enantiomer structures of IllpNH and VnNH via Illp'NH and Vp'NH as mentioned earlier, VnIll'NH represents a COOH torsional barrier between IllpNH and IlIpNH, and VIlIp'NH is the “missing” conformer with repulsive NH—HO arrangement, which turns out being a saddle point. These transition-state geometries, {Illp'NH, Vp'NH, VnIll'NH, VIlIp'NH}, are obtained only {3, 5, 2, 1} times from the 216 initial structures as shown in Figure 6. The IlIpNH minimum is obtained 49 times, whereas the other minima are found about 20–30 times. The larger probability of the IlIpNH conformer can be explained by the fact that both Ill- and VIlp-like geometries result in IlIpNH as discussed at Strategy I (Table 3). The UMP2 method with the 3-21G and STO-3G basis sets basically provide the same seven conformers as in the case of the aug-cc-pVDZ basis. It is important to note that Strategy II finds VIlpNH 17 and 5 times with 3-21G and STO-3G, respectively; whereas this conformer was missing using the above small basis sets with Strategy I. Using the UHF method the conformational potential is more rugged resulting in many conformers; some of them correspond to the ones found with Strategy I and the other usually have small probabilities as shown in Figure 6. These small probability conformers vanish with further optimizations at the UMP2/aug-cc-pVDZ level and at the end all the conformers relax to the structures shown in Figures 3 and 4.

For H₂N-CH₂-COO the 36 optimizations provide 4 conformers at the MRCI/aug-cc-pVDZ level of theory as shown in Figure 7. The conformers {IpCOO, IIlnCOO, IIPCOO, IVnCOO} are obtained {8, 4, 4, 5} times, whereas 15 optimizations fail due to convergence problems. MRCI/3-21G gives 5 conformers, but the two different structures at 2.91 and 4.52 kcal/mol both converge to the same IVnCOO conformer at the MRCI/aug-cc-pVDZ level. Interestingly, Strategy I found a sixth conformer at 3.43 kcal/mol, which was also assigned to IVnCOO however,
this sixth conformer is not seen with Strategy II. Using MRCl/STO-3G six conformers are obtained, which all assigned to the same four minima with further MRCl/aug-cc-pVDZ optimizations as shown in Figure 7. Strategy I gave four conformers at the MRCl/STO-3G level, but IIpCOO was missing, which is found with Strategy II, albeit only once. Furthermore, Strategy II finds an additional conformer at 2.05 kcal/mol, which is assigned to IVnCOO. In the case of the MCSCF method 14, 14, and 15 conformers are found with the STO-3G, 3-21G, and aug-cc-pVDZ basis sets, respectively, showing again that the potential energy surface is more structured at lower levels of theory. Here many conformers are found only 1 or 2 times from the 36 optimizations, and only a few of them, which were also obtained with Strategy I, are found 4–9 times. Owing to the large number of conformers, we do not perform MRCI/aug-cc-pVDZ optimization for each geometry, nevertheless, on the basis of our previous findings we assume that all these conformers would result in the same four minima as seen using MRCI (Figure 7).

### 3.2.3 Benchmark structures and energies

The high-level UCCSD(T)-F12b geometry optimizations with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, initiated from the UMP2/

---

**Table 5** Classical and adiabatic relative energies (kcal/mol) of the H$_2$N-CH-COOH conformers obtained at different levels of theory$^{a}$

| Classical | Adiabatic$^b$ | ΔZPE |
|-----------|---------------|------|
| MP2/ aVDZ | CCSD(T)- F12b/aVDZ | MP2/ aVDZ |
| CCSD(T)- F12b/aVTZ | CCSD(T)- F12b/aVTZ | CCSD(T)- F12b/aVTZ |

$^a$Results correspond to optimized geometries obtained by UMP2/aug-cc-pVDZ, UCCSD(T)-F12b/aug-cc-pVDZ, and UCCSD(T)-F12b/aug-cc-pVTZ.

$^b$Classical relative energy plus zero-point energy correction (ΔZPE).

**Table 6** Classical and adiabatic relative energies (kcal/mol) of the HN-CH$_2$-COOH conformers obtained at different levels of theory$^{a}$

| Classical | Adiabatic$^b$ | ΔZPE |
|-----------|---------------|------|
| MP2/ aVDZ | CCSD(T)- F12b/aVDZ | MP2/ aVDZ |
| CCSD(T)- F12b/aVTZ | CCSD(T)- F12b/aVTZ | CCSD(T)- F12b/aVTZ |

$^a$Results correspond to optimized geometries obtained by UMP2/aug-cc-pVDZ, UCCSD(T)-F12b/aug-cc-pVDZ, and UCCSD(T)-F12b/aug-cc-pVTZ.

$^b$Classical relative energy plus zero-point energy correction (ΔZPE).

**Table 7** Classical and adiabatic relative energies (kcal/mol) of the HN-CH$_2$-COOH transition states obtained at different levels of theory$^{a}$

| Classical | Adiabatic$^b$ | ΔZPE |
|-----------|---------------|------|
| MP2/ aVDZ | CCSD(T)- F12b/aVDZ | MP2/ aVDZ |
| CCSD(T)- F12b/aVTZ | CCSD(T)- F12b/aVTZ | CCSD(T)- F12b/aVTZ |

$^a$Results correspond to optimized geometries obtained by UMP2/aug-cc-pVDZ, UCCSD(T)-F12b/aug-cc-pVDZ, and UCCSD(T)-F12b/aug-cc-pVTZ.

$^b$Classical relative energy plus zero-point energy correction (ΔZPE).

$^c$UCCSD(T)/aug-cc-pVTZ classical relative energy plus UCCSD(T)/aug-cc-pVDZ ΔZPE.
aug-cc-pVDZ conformers, give four minima for H$_2$N-CH-COOH and seven minima (and four transition states) for HN-CH$_2$-COOH; thus, none of the UMP2/aug-cc-pVDZ conformers disappears at higher levels of theory. As Table 5 shows the MP2/aug-cc-pVDZ level significantly overestimates the relative energies of the H$_2$N-CH-COOH conformers as the UCCSD(T)-F12b/aug-cc-pVDZ data are lower by 0.80, 0.54, and 2.08 kcal/mol for IInCH, IIIpCH, and IVnCH, respectively. The UCCSD(T)-F12b relative energies with the aug-cc-pVDZ and aug-cc-pVTZ basis sets agree within 0.05 (IInCH), 0.01 (IIIpCH), and 0.08 (IVnCH) kcal/mol, showing the excellent basis-set-convergence of the explicitly-correlated UCCSD(T)-F12b method. The benchmark (UCCSD(T)-F12b/aug-cc-pVTZ) relative energies of the [IInCH, IIIpCH, IVnCH, IVpNH] conformers are [0.00, 1.57, 5.25, 9.85] kcal/mol. Applying UCCSD(T)-F12b/aug-cc-pVDZ ZPE corrections of [0.00, −0.02, −0.22, −0.13] kcal/mol, we obtain the following benchmark adiabatic relative energies: [0.00, 1.55, 5.03, 9.72] kcal/mol.

The best classical and adiabatic relative energies of the HN-CH$_2$-COOH conformers are given in Table 6 (minima) and Table 7 (transition states). Here UMP2/aug-cc-pVDZ fortuitously provides reasonably accurate relative energies with only 0.1–0.2 kcal/mol deviations from the UCCSD(T)-F12b/aug-cc-pVDZ data (the maximum difference is 0.27 kcal/mol for IVpNH). UCCSD(T)-F12b again shows rapid convergence; thus, the final UCCSD(T)-F12b/aug-cc-pVTZ classical relative energies are definitely basis-set converged within ±0.1 kcal/mol or better. The ZPE corrections are between −0.4 and +0.3 kcal/mol for the minima and −0.8 and −0.1 kcal/mol for the transition states as shown in Tables 6 and 7, respectively. The relative energies of the seven conformers span a roughly 10 kcal/mol range, and the energy order is the same with UMP2/aug-cc-pVDZ, UCCSD(T)-F12b/aug-cc-pVDZ, and MRCI+Q, MRCI-F12+Q using the aug-cc-pVDZ basis set.

Table 8: Classical and adiabatic relative energies (kcal/mol) of the H$_2$N-CH$_2$-COO conformers obtained with MRCI, MRCI+Q, and MRCI-F12+Q using the aug-cc-pVDZ basis set.

| Classical | Adiabatic |
|-----------|-----------|
|            | MRCI+Q    | MRCI-F12+Q |
| IInCOO     | 0.00      | 0.00       |
| IIIpCOO    | 1.62      | 1.61       |
| IVnCOO     | 1.82      | 1.78       |
| IVpNH      | 2.21      | 2.21       |

Table 9: Classical and adiabatic relative energies (kcal/mol) of the dehydrogenated glycine conformers obtained with the MRCI+Q, MRCI-F12+Q, and UCCSD(T)-F12b methods.

| Classical | Adiabatic |
|-----------|-----------|
|            | MRCI+Q    | MRCI-F12+Q | CCSD(T)-F12b |
| IInCH      | 0.00      | 0.00       | 0.00         |
| IIIpCOO    | 1.62      | 1.61       | 1.57         |
| IVnCOO     | 1.82      | 1.78       | 1.75         |
| IVpNH      | 2.21      | 2.21       | 2.21         |

*Results correspond to optimized geometries obtained by MRCI/aug-cc-pVDZ.

Classical relative energy plus zero-point energy correction (ΔZPE).

Classical relative energy plus MRCI/aug-cc-pVDZ ΔZPE.

Classical relative energy plus MRCI/aug-cc-pVDZ ΔZPE.
aug-cc-pVDZ, and UCCSD(T)/aug-cc-pVTZ regardless ZPE correction. The classical energy of the \( \text{III}p_{\text{NH}} \) transition state is above the energy of \( \text{IIIn}_{\text{NH}} \) by 0.30, 0.35, and 0.32 kcal/mol at the UMP2/aug-cc-pVDZ, UCCSD(T)-F12b/aug-cc-pVDZ, and UCCSD(T)/aug-cc-pVTZ levels, respectively, whereas the corresponding adiabatic energy differences are 0.36, 0.02, and –0.02 kcal/mol. Thus, classically the nonsymmetric \( \text{IIIn}_{\text{NH}} \) structure is clearly favored, whereas the ZPE-corrected energies of \( \text{IIIn}_{\text{NH}} \) and \( \text{IIlp}_{\text{NH}} \) are almost the same at the highest levels of theory. In the case of \( \text{Vlp}_{\text{NH}} \) versus \( \text{Vn}_{\text{NH}} \), the classical energies show a low barrier of about 0.1 kcal/mol and the adiabatic barrier heights are also positive about 0.7 kcal/mol (UMP2) and 0.1–0.2 kcal/mol (UCCSD(T)-F12b). \( \text{VIIlp}_{\text{NH}} \) is clearly above \( \text{VIIp}_{\text{NH}} \) by 0.8–0.9 kcal/mol classically and 0.8–1.5 kcal/mol adiabatically and \( \text{VIIlp}_{\text{NH}} \) has significantly higher energy than any other conformer of \( \text{HN}-\text{CH}_{2}-\text{COOH} \).

The four conformers of the \( \text{HN}-\text{CH}_{2}-\text{COOH} \) radical are very close to each other in energy, as the classical(adiabatic) relative energies of \( \{\text{Ip}_{\text{COO}}, \text{In}_{\text{COO}}, \text{III}_{\text{pCOO}}, \text{IV}_{\text{nCOO}}\} \) are \( (0.00(0.00), 1.64(1.63), 1.82(1.79), 2.21(2.21)) \) kcal/mol at the MRCl/aug-cc-pVDZ level of theory as shown in Table 8. The Davidson corrections (+Q), which estimate the dynamical correlation effects beyond double excitations, are found to be small \( (0.00–0.04 \text{ kcal/mol}) \) as seen in Table 8. Furthermore, the basis-set effects beyond aug-cc-pVDZ are also negligible, because the standard MRCl+Q and explicitly correlated MRCl-F12+Q relative energies again agree within \( 0.00–0.04 \text{ kcal/mol} \) (Table 8).

Comparison of the benchmark classical and adiabatic energies of all the conformers of the \( \text{H}_{2}\text{N}-\text{CH}-\text{COOH}, \text{HN}-\text{CH}_{2}-\text{COOH}, \) and \( \text{H}_{2}\text{N}-\text{CH}_{2}-\text{COO} \) radicals is shown in Table 9. The lowest energy conformer is \( \text{In}_{\text{CH}} \); the classical(adiabatic) MRCl-F12+Q energies of \( \text{Ip}_{\text{COO}} \) and \( \text{Ip}_{\text{COO}} \) are \( 18.51(17.32) \) and \( 31.88(31.66) \) kcal/mol relative to \( \text{In}_{\text{CH}} \), respectively. The energies of all the conformers of \( \text{HN}-\text{CH}-\text{COOH} \) are below the energy of \( \text{Ip}_{\text{NH}} \) and all the \( \text{HN}-\text{CH}_{2}-\text{COOH} \) conformers are below \( \text{Ip}_{\text{COO}} \). Thus, we can conclude that H abstraction is thermodynamically preferred from the \( \text{CH}_{2} \) group of glycine, followed by the H abstraction from the amino and carboxyl groups in increasing energy order. For the conformers of \( \text{H}_{2}\text{N}-\text{CH}-\text{COOH} \) and \( \text{HN}-\text{CH}_{2}-\text{COOH} \) both MRCl (specifically MRCl+Q and MRCl-F12+Q) and CCSD(T)-F12b relative energies are available, which are in good agreement with only about 0.2 kcal/mol mean and 0.6 kcal/mol maximum absolute deviations if we consider the energies of the conformers relative to \( \text{In}_{\text{CH}} \) and \( \text{Ip}_{\text{NH}} \), respectively. However, for the classical(adiabatic) energy gap between the \( \text{In}_{\text{CH}} \) and \( \text{Ip}_{\text{NH}} \) conformers, MRCl+Q, MRCl-F12+Q, and CCSD(T)-F12b give 16.66(15.47), 18.51 (17.32), and 21.20(20.01) kcal/mol, respectively. Considering the energy difference between \( \text{In}_{\text{CH}} \) and \( \text{Ip}_{\text{COO}} \), the MRCl+Q and MRCl-F12+Q classical(adiabatic) results are 29.18(28.96) and 31.88(31.66) kcal/mol, respectively, which are above the corresponding energies of 25.64(24.05) and 28.11(26.52) kcal/mol of the highest-energy conformer of \( \text{HN}-\text{CH}_{2}-\text{COOH} \) (\( \text{VIIp}_{\text{NH}} \)), whereas the CCSD(T)-F12b energy of \( \text{VIIp}_{\text{NH}} \) is above the classical MRCl+Q energy of \( \text{Ip}_{\text{COO}} \). Nevertheless, the presumably more accurate MRCl-F12+Q energy of \( \text{Ip}_{\text{COO}} \) is clearly above the CCSD(T)-F12b energy of \( \text{VIIp}_{\text{NH}} \).

### SUMMARY AND CONCLUSIONS

We have determined the first explicitly-correlated CCSD(T)-F12b/aug-cc-pVTZ structures and relative energies of the eight conformers of glycine confirming the predictions of previous studies.\(^{[1,4]}\) Furthermore, we report a comprehensive ab initio investigation of the conformers and isomers of dehydrogenated glycine radicals revealing 4, 7 (+4 TS), and 4 conformers for \( \text{H}_{2}\text{N}-\text{CH}-\text{COOH}, \text{HN}-\text{CH}_{2}-\text{COOH}, \) and \( \text{H}_{2}\text{N}-\text{CH}_{2}-\text{COO} \), respectively. The four conformers of \( \text{H}_{2}\text{N}-\text{CH}-\text{COOH} \) are nonsymmetric (\( C_{3} \)), whereas the conformers of the other two isomers have either \( C_{1} \) or \( C_{1} \) point-group symmetry.

We have used two different strategies for the conformation search employing various ab initio methods and basis sets. Strategy I is motivated by chemical intuition suggesting initial geometries by removing different H atoms from the eight known conformers of glycine. Strategy II systematically maps the conformational space of the glycine radicals generating initial structures for geometry optimizations by scanning the most important torsional coordinates with 60° steps as was previously done for the amino acid threonine.\(^{[29]}\) The conclusions of the detailed search using the different strategies and ab initio levels can be summarized as follows:

1. **Strategy I often finds all the conformers.** (\( \text{VIIp}_{\text{NH}} \) is not obtained at UHF/3-21G, UMP2/STO-3G, and UMP2/3-21G; \( \text{In}_{\text{COO}} \) is not found at MCSCF/aug-cc-pVDZ; \( \text{III}_{\text{pCOO}} \) is missing at MRCl-STO-3G.)

2. **The conformational space is usually more structured at the UHF and MCSCF levels than with the UMP2 and MRCl methods.** However, the additional conformers found at the lower levels of theory disappear when further optimizations are performed using higher-level correlation methods.

3. **Strategy II with the UMP2 and MRCl methods provides qualitatively the same conformers with the 3-21G and aug-cc-pVDZ basis sets, whereas the small STO-3G basis predicts additional conformers, which converge to the known minima with larger basis sets.**

4. **Both Strategies I and II give the same conformers at UMP2/aug-cc-pVDZ (\( \text{H}_{2}\text{N}-\text{CH}-\text{COOH} \) and \( \text{HN}-\text{CH}_{2}-\text{COOH} \)) and MRCl/aug-cc-pVDZ (\( \text{H}_{2}\text{N}-\text{CH}_{2}-\text{COO} \)) levels of theory.**

5. **All the conformers found at the UMP2/aug-cc-pVDZ level of theory can be confirmed using the CCSD(T)-F12b method with the aug-cc-pVDZ and aug-cc-pVTZ basis sets.**

6. **For larger systems we recommend the initial conformational search at a computationally cheap low-level of theory using either Strategy I or II, followed by higher-level optimizations where several conformers are likely to disappear.** In the case of Strategy II the MP2 method with the 3-21G basis is an economic choice, for the initial search there is no need for the larger aug-cc-pVDZ basis. Between 3-21G and aug-cc-pVDZ, one may consider using the 6-31G, 6-31G*, and 6-31+G* basis sets as well.

The present study focuses on ab initio methods; however, it is important to note that density functional theory may also become
useful for conformational searches of larger systems. For example, a recent study found excellent performance of the B3LYP-D3BJ and ωB97X-V functionals for the determination of conformational energies of amino acids with N- and C-termination.  

Benchmark MRCI-F12+U(CCSSD(T)-F12b) ZPE-corrected computations show that the four conformers of H2N-CH-COOH have the lowest energies in the 0.00–10.11[0.00–9.72] kcal/mol range, followed by the seven conformers of HN-CH2-COOH in the energy range of 17.32–26.52[20.01–28.88] kcal/mol and the four conformers of H2N-CH2-COO in the range of 31.66–33.87 kcal/mol. We assume that the CCSD(T)-F12b results are more accurate, because CCSD(T)-F12b provides a better description of dynamical electron correlation, whereas static electron correlation is not significant for the H2N-CH-COOH and HN-CH2-COOH conformers as the T1-diagnostic values are only around 0.017. For the H2N-CH2-COO geometries, we have found convergence problems when using single-configuration methods; thus, in this case only multi-reference data could be obtained.

Besides the new benchmark properties and the first comprehensive characterization of the dehydrogenated glycine conformers, the present ab initio investigation opens the door for more detailed studies of the H-abstraction reactions of free radicals with glycine. Future work may consider solvation effects to mimic biological environment. Furthermore, the conformational search strategies could be used to find conformers of similar or even larger complex molecular systems.

ACKNOWLEDGMENTS

We thank the National Research, Development and Innovation Office –NKFIH, K-125317, the Ministry of Human Capacities, Hungary grant 20391-3/2018/FEKUSTRAT, and the Momentum (Lendület) Program of the Hungarian Academy of Sciences for financial support. We acknowledge KIFÜ for awarding us access to computational resource based in Hungary at Szeged.

ORCID

Gábor Czakó ORCID https://orcid.org/0000-0001-5136-4777

REFERENCES

[1] A. G. Császár, J. Am. Chem. Soc. 1992, 114, 9568.
[2] A. G. Császár, J. Mol. Struct. 1995, 346, 141.
[3] V. Kasalová, W. D. Allen, H. F. Schaefer III., E. Czinki, A. G. Császár, J. Comput. Chem. 2007, 28, 1373.
[4] R. M. Balabin, Chem. Phys. Lett. 2009, 479, 195.
[5] R. M. Balabin, J. Phys. Chem. Lett. 2010, 1, 20.
[6] R. M. Balabin, Phys. Chem. Chem. Phys. 2012, 14, 99.
[7] G. Baczó, G. Magyarkalvai, G. Tarczay, J. Mol. Struct. 2012, 1025, 33.
[8] G. Baczó, G. Magyarkalvai, G. Tarczay, J. Phys. Chem. A 2012, 116, 10539.
[9] V. Barone, M. Biczysko, J. Bloino, C. Puzzarini, Phys. Chem. Chem. Phys. 2013, 15, 1358.
[10] V. Barone, M. Biczysko, J. Bloino, C. Puzzarini, Phys. Chem. Chem. Phys. 2013, 15, 10094.
[11] S. Coussan, G. Tarczay, Chem. Phys. Lett. 2016, 644, 189.
[12] F. Gabas, R. Conte, M. Ceotto, J. Chem. Theory Comput. 2017, 13, 2378.
[13] D. Yu, A. Rauk, D. A. Armstrong, J. Am. Chem. Soc. 1995, 117, 1789.
[14] A. Galano, J. R. Alvarez-Idaboy, L. A. Montero, A. Vivier-Bunge, J. Comput. Chem. 2001, 22, 1138.
[15] A. K. Croft, C. J. Easton, L. Radom, J. Am. Chem. Soc. 2003, 125, 4119.
[16] Y. Huang, L. Guler, J. Heidbrink, H. Kenttämaa, J. Am. Chem. Soc. 2005, 127, 3973.
[17] A. Movranonakis, S. C. Farantos, G. E. Froudakis, J. Phys. Chem. B 2006, 110, 6048.
[18] G. Yang, Y. Zu, L. Zhou, J. Phys. Org. Chem. 2008, 21, 34.
[19] P. Carbonniere, A. Dargelos, I. Ciofini, C. Adamo, C. Pouchan, Phys. Chem. Chem. Phys. 2009, 11, 4375.
[20] M. Liessmann, B. Hansmann, P. G. Blachly, J. S. Francisco, B. Abel, J. Phys. Chem. A 2009, 113, 7570.
[21] R.-J. Lin, C.-C. Wu, S. Jang, F.-Y. Li, J. Mol. Model. 2010, 16, 175.
[22] M. C. Owen, M. Szöri, I. G. Csízmadia, B. Viskolcz, J. Phys. Chem. B 2012, 116, 1143.
[23] J. Uranga, O. Lakuntza, E. Ramos-Cordoba, J. M. Matox, J. I. Mujika, Phys. Chem. Chem. Phys. 2016, 18, 30972.
[24] M. C. Owen, I. G. Csízmadia, B. Viskolcz, B. Strodel, Molecules 2017, 22, 655.
[25] T. B. Adler, G. Knizia, H.-J. Werner, J. Chem. Phys. 2007, 127, 221106.
[26] C. Møller, M. S. Plesset, Phys. Rev. 1934, 46, 618.
[27] T. H. Dunning Jr., J. Chem. Phys. 1989, 90, 1007.
[28] J. A. Pople, R. K. Nesbet, J. Chem. Phys. 1954, 22, 571.
[29] R. D. Amos, J. S. Andrews, N. C. Handy, P. J. Knowles, Chem. Phys. Lett. 1991, 185, 256.
[30] W. J. Hehre, R. F. Stewart, J. A. Pople, J. Chem. Phys. 1969, 51, 2657.
[31] J. S. Binkley, J. A. Pople, W. J. Hehre, J. Am. Chem. Soc. 1980, 102, 939.
[32] W. J. Hehre, L. Radom, P. R. Schleyer, J. A. Pople, Molecular Orbital Theory, Wiley, New York 1986.
[33] H.-J. Werner, P. J. Knowles, J. Chem. Phys. 1985, 82, 5053.
[34] H.-J. Werner, P. J. Knowles, J. Chem. Phys. 1988, 89, 5803.
[35] G. Knizia, T. B. Adler, H.-J. Werner, J. Chem. Phys. 2009, 130, 054104.
[36] S. R. Langhoff, E. R. Davidson, Int. J. Quantum Chem. 1974, 8, 61.
[37] T. Shiozaki, G. Knizia, H.-J. Werner, J. Chem. Phys. 2011, 134, 034113.
[38] Mâzcu, version 2015.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz and others, see http://www.molpro.net.
[39] T. Szidarovszky, G. Czakó, A. G. Császár, Mol. Phys. 2009, 107, 761.
[40] M. K. Kesharwani, A. Karton, J. M. L. Martin, J. Chem. Theory Comput. 2016, 12, 444.
[41] T. J. Lee, P. R. Taylor, Int. J. Quant. Chem. 1989, 323, 199.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Orján EM, Nacs A B, Czakó G. Conformers of dehydrogenated glycine isomers. J Comput. Chem. 2020;41:2001–2014. https://doi.org/10.1002/jcc.26375