Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 8 (3) 161-173: Fall 2011
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Theoretical Analysis on the Conformational Features of the HCO–Gly–L–Leu–NH_2 Protected Dipeptide Motif: *Ab initio* and DFT Exploratory

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Received June 2011; Accepted September 2011

ABSTRACT

For better understanding of conformational stability of the dipeptide model HCO–Gly–L–Leu–NH_2, *ab initio* and DFT computations at HF/6-31G(*d*), 6-311++G(*d,p*) and B3LYP/6-31G(*d*) levels of theory were carried out. Geometry optimization of the dipeptide within the leucine (Leu) side chain angles (χ_1,χ_2) resulted in three stable conformations as followings: anti-anti, the most stable one, (χ_1 = 180°, χ_2 = 180°), Gauche (+)-*trans* (χ_1 = 60°, χ_2 = 210°) and 270°-Gauche (-)(χ_1 = 270°, χ_2 = 300°). The thermodynamic properties E, H, G, and S by changing dihedral angles Ψ_1 (D_1) and Φ_1 (D_{11}) of glycine (Gly), Ψ_2 (D_6), and Φ_2 (D_4) of Leu and keeping the SC dihedral angles of the anti-anti conformer were obtained by frequency calculations at the same levels. The calculations indicate that the BB has the highest stability bearing Ψ_1 (D_1) = 180°, Φ_1 (D_{11}) = 180°, Ψ_2 (D_6) = 150°, and Φ_2 (D_4) = 210°.

Keywords: Dipeptide structures; *Ab initio*; DFT calculations; Conformational stability

INTRODUCTION

Structures of proteins as a key factor of their function are built of 20 naturally of amino acids [1, 2]. The number of the amino acid residues of a protein is typically range 100-1800 [3]. Since physical and chemical properties of the all 20 amino acids residues of proteins are different, they have different structure than each other [3, 4]. Their properties are controlled by the 3D dimensional structure which is dependent to amino acids linear sequence [3]. Peptides are formed by highly controlled polymerization reaction bearing amide bond so called the peptide bond. Two amino acids joined by a peptide bond form a dipeptide (Fig. 1) [2]. The entire 20 amino acids can naturally bonded together with both L- and D-enantiomeric configurations. The D isomers are often found in the cell walls of bacteria and in their antibiotics, while L-amino acids are using for protein synthesis in human body organisms [5]. The Leu is an amino acid hasing two dihedral SCs that show important affect on energy and thermodynamic functions. Peptide structures were almost investigated employing the *ab initio* calculations for nine decades [1]. [For more information see ref. 6]. Related initial studies [7–8] due to restriction of technology limited to insufficient ones about diamides and dipeptides until 1980s [9–10]. Recently, the potential energies of diamides, dipeptides, and other short chain peptides

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structures have been studied [11-15].These conclude that the related potential energies are just functions of the torsional angles of respective amino acid. However, not more geometrical parameters affected the energy and structure of peptides has been considered [1]. Considering the dipole moment, the planar geometry, and the relatively high rotational barrier around C–N bond, the conformation of polypeptides and proteins have been determined [16]. Plenty work on dipeptide models Ac–Ala–Ala–HN–Me [17], Por–Ala–Ala–NH_2 [18], and Ac–Pro–Ala–NH_2 [19] elucidated the mechanism of protein folding [20]. Herein, we report the most stable structure of dipeptide with respect to dihedral angles of BB and SC. For this purpose, here, the HF/6-31G (*d*), HF/6-311++G (*d, p*) and B3LYP/6-31G (*d*) optimized geometries of the HCO–Gly–L–Leu–NH_2 within protected dipeptide with rotation around the Cα and the dihedral angles of the amide plane have been investigated. General structure and numbering scheme of the HCO–Gly–L–Leu–NH_2 within protected dipeptide is shown in Fig. 2. The 3D dimensional structure of HCO–Gly–L–Leu–NH_2 can be predicted - using an empirical energy function, $E = f(\chi)$, defined in terms of a set of BB and SC dihedral angles where $\chi = [(\Phi_i, \Psi_i, \omega_i, \chi_i^1, \ldots \chi_i^2)]$ associated with the constituent amino acid (Fig. 2). All peptide bonds are in the *trans* isomeric state, and chiral Cα is in the L- enantiomeric state. With aid of dipeptide angles (ω_0, Φ_1, Ψ_1, ω_1, Φ_2, Ψ_2, and ω_2), and χ_1 & χ_2 the most stable BB and SC conformations have been determine.

THEORETICAL METHODS

The structure of HCO–Gly–L–Leu–NH_2 was numbered according to the standardized modular numbering system in Fig. 2. The dipeptide was divided four to sections that numbered separately as the N-terminal protecting group, the Gly residue, the Leu residue and the C-terminal protecting group. The optimization and frequency calculations at HF/6-31G (*d*), HF/6-311++G (*d, p*), and B3LYP/6-31G (*d*) levels on the SC angles ($\chi_1$and χ_2) of Leu from 0.0° to 360.0° with 30.0° intervals have been performed. The torsion angles are defined as follows: $\omega_0 = \angle H_{32}–C_{14}–N_1–C_2$, $\Phi_1 = \angle C_{14}–N_1–C_2–C_3$, $\Psi_1 = \angle N_4–C_3–C_2–N_1$, $\omega_1 = \angle C_2–C_3–N_4–C_6$, $\Phi_2 = \angle C_7–C_6–N4–C_3$, $\Psi_2 = \angle N_9–C_7–C_6–N_4$, $\omega_2 = \angle H_{23}–N_9–C_7–C_6$, $\chi_1 = \angle C_{11}–C_8–C_6–N_4$, $\chi_2 = \angle C_{12}–C_{11}–C_8–C_6$ (Fig. 2). All of calculations were carried out by employing the Gaussian 03 package with using HF/6-31G(*d*), HF/6-311++G(*d,p*), and B3LYP/6-31G(*d*) for all atoms.

RESULTS AND DISCUSSION

Side chain conformers

The rotation angles of the N–Cα, the Cα–CO of HCO–Gly–L–Leu–NH_2 have been defined as: ω_0, Φ_1, χ_1, χ_2, Ψ_1, ω_1, Φ_2, Ψ_2, and ω_2 (Fig. 2) which six of them, Φ_1, Ψ_1, χ_1, χ_2, Φ_2, and Ψ_2, relevant mostly to the shape and stability of the dipeptide model. For determining the effect of SC angles on stability of dipeptide, the SC dihedral angles (χ_1 and χ_2) from 0° to 360° with 30° intervals have been changed. At first, the χ_1 was changed and each conformer was optimized at the HF/6-31G (*d*), HF/6-311++G (*d, p*), and B3LYP/6-31G (*d*) levels. The dihedral angles and energies that obtained from χ_1 optimization summarized in Table1. Three minima for χ_1 in the: 180° (anti), 60° (g^+) and 270° states, were obtained respectively, which the anti conformer has the lowest energy (Table 1).Then for χ_1=180° (anti), 60° (g^+), and 270° the χ_2 angle was rotated around $C_{12}–C_{11}–C_8–C_6$ atoms from 0° to 360° with 30° intervals and optimization of each state carried out at HF/6-31G(*d*), HF/6-31G(*d,p*), and B3LYP/6-31G(*d*) levels of theory. From changing of χ_1 and χ_2, three minima anti-anti (χ_1 and χ_2 = 180°), g (+)-*trans* (χ_1 = 60° and χ_2 = 210°), and 270°-g (-) (χ_1 = 270° and χ_2 = 300°) with the most stable anti-anti conformation and the best SC angles has been found (Table 2). Based on our calculation results the most favored SC angles for HCO–Gly–L–Leu–NH_2 dipeptide are χ_1 and χ_2 = 180°.

Dihedral angles

Investigating of dihedral angles in the dipeptide can provide valuable information regarding the peptide bond and the planarity of the amide plane. Specifically the dihedral angle between atoms 4 and 3 (peptide bond), 14 and 1, 7 and 9, 2 and 3, 1 and 2, 6 and 7, and 4 and 6 of the amide plane referred to D_3, D_{29}, D_{20}, D_1, D_{11}, D_6, and D_4, respectively. The planar amide plane bearing the dihedral angles, D_{29}, D_3, and D_{20}, equal to 180° (Fig. 2). D_{29}, D_{11}, D_8, D_9, D_1, D_3, D_4, D_6, and D_{20} are equal to ω_0, Φ_1, χ_1, χ_2, Ψ_1, ω_1, Φ_2, Ψ_2, and ω_2, respectively.

Energy and thermodynamic properties

With performing optimization and frequency calculations of the BB angles between 0° to 360° with intervals 30°, their effect on the shape and stability of the dipeptide has been investigated. From the frequency calculations on BB angles, the thermodynamic properties, ΔE, ΔH, ΔG, and ΔS, relative to most stable conformer, anti-anti, were obtained (Tables 3-6). For this purpose, at the first part of calculations for D_1 the SC was fixed at anti-anti conformer and D_{11}, D_6 and D_4 dihedral angles kept at 180°, by 30.0° intervals from 0.0° to 360.0°. The most stable conformer by optimization - and frequency calculations at HF/6-31G (*d*), HF/6-311++G (*d,p*), and B3LYP/6-31G(*d*) levels has been determined (Table 3). We found that at HF/6-31G(*d*) level the lowest values of the energy, enthalpy, and Gibbs free energy are at the state of D_1, D_{29}, D_3, and D_{20} are equal to 180°, -179.6°, -174.4°, and -172.3°, respectively. The same calculations at the HF/6-311++G(*d,p*) level showed that minimum energy values gain for D_1, D29, D_3, and D_{20} are equal to 180°, -179.5°, -174.2°, and -172.1°, respectively. According to the B3LYP/6-31G(*d*) calculations, the most stable conformer has been found within D_1, D_{29}, D_3, and D_{20} are equal to 180°, 179.7°, 195.6°, and 173.3°, respectively (Fig. 3). Followings, the energy values of conformers with keeping D_1, D_6, and D_4 at 180.0° and changing the D_{11} from 0.0° to 360.0° along with 30.0° intervals have been determined (Table 4). The most stable optimized conformers at the HF/6-31G (*d*), HF/6-311++G (*d, p*), and B3LYP/6-31G (*d*) bearing the dihedral angle D_{11} = 180.0° (Table 4). At the HF/6-31G(*d*), HF/6-311++G(*d, p*), and B3LYP/6-31G(*d*) levels dihedral angles D_{29}, D_3, and D_{20} are equal to (-179.6°,-174.4° and -172.3°), (-179.5°, -174.2°, and -172.1°), and (-179.7°, -175.58°, and -173.3°), respectively. The calculations indicate that the lowest stable conformers at the HF/6-31G (*d*), HF/6-311++G (*d, p*), and B3LYP/6-31G (*d*) levels was turned out in the D_{11} = 0° or 360°. Their relative energies (ΔE) to the respective most stable conformers are 20.969, 21.032, and 18.833 kcal mol^{-1}, respectively. One can conclude that while D_1 and D_{11} are both equal to 180° the E, H, and G have the minimum values for the Gly conformer (Tables 3, 4 and Figs. 3, 4). The third part of calculations carried out at all previous mentioned levels show while D_6 dihedral angle is 150° the dipeptide has the highest stability (Table 5), and other dihedral angles (D_{29}, D_3, and D_{20}) are (-179.3°, -170.0°, and 178.8°), (-179.3°, -169.5°, and 179.8°), and (-179.4°, -171.5°, and 175.7°), respectively (Fig. 5). Finally, the D_4 dihedral angle has been changed from 0.0° to 360.0° with 30.0° intervals while D_1, D_{11}, and D_6 kept at 180°.

The results show that while D_4 is equal to 210° the HCO–Gly–L–Leu–NH_2 within dipeptide has the most stable conformer bearing the D_{29}, D_3, and D_{20} dihedral angles equal to (179.9°, 173.2°, and -172.1°), (180.0°, 173.5°, and -172.0°), and (179.8°, 171.5°, and -173.1°), respectively. For this part of calculations, the conformer with the lowest stability was turned out that its D_4 dihedral angle is either equal to 0° or 360°, and the relative energies (ΔE) are 25.376, 24.994, and 22.624 kcal mol^{-1}, respectively (Fig. 6). For L-Leu amino acid while the D_6 and D_4 dihedral angles are equal to 150° and 210°, respectively the conformer has minimum values for E, H, and G (Figs. 5 and 6).

CONCLUSION

The results of the present work obtained using *ab initio* and DFT optimization and frequency calculations at the HF/6-31G (*d*) , HF/6-311++G (*d, p*), and B3LYP/6-31G (*d*) levels of theory indicating that:

1. Three minima anti-anti (χ_1 and χ_2 = 180°), g (+) - *trans* (χ_1 = 60° and χ_2 = 210°), and 270°-g (-) (χ_1 = 270° and χ_2 = 300°) found for SC.
2. The most stable anti-anti conformer, within both SC dihedral angles χ_1 and χ_2 are 180° obtained.
3. For Gly amino acid, the relative conformer within both D_1 and D_{11} dihedral angles equal to 180° has the minimum values of E, H, and G.
4. For L-Leu amino acid, the relative conformer has minimum values of E, H, and G while the D_6 and D_4 dihedral angles are equal to 150° and 210°, respectively.
5. The most stable conformer of HCO – Gly–L–Leu–NH_2 within protected dipeptide bearing the D1, D_{11}, D_6, and D_4 dihedral angles equal to 180°, 180°, 150°, and 210°, respectively.

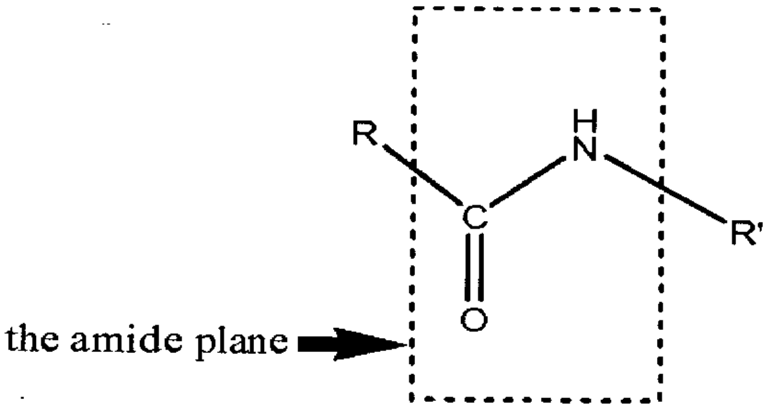

Fig. 1. General Structure of an amino plane.

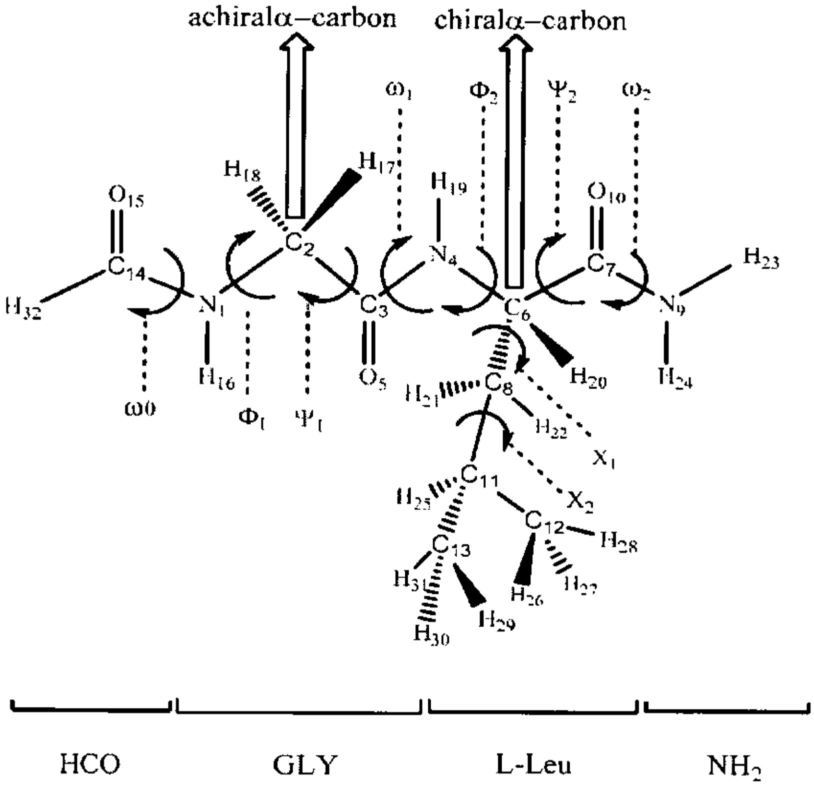

Fig. 2. HCO-Gly-L-Leu-NH_2 within dipeptide model. The dipeptide was divided into four sections: the N-terminal protecting group, the Gly residue, the Leu residue and the C-terminal protecting group and showing all backbone torsional angles.

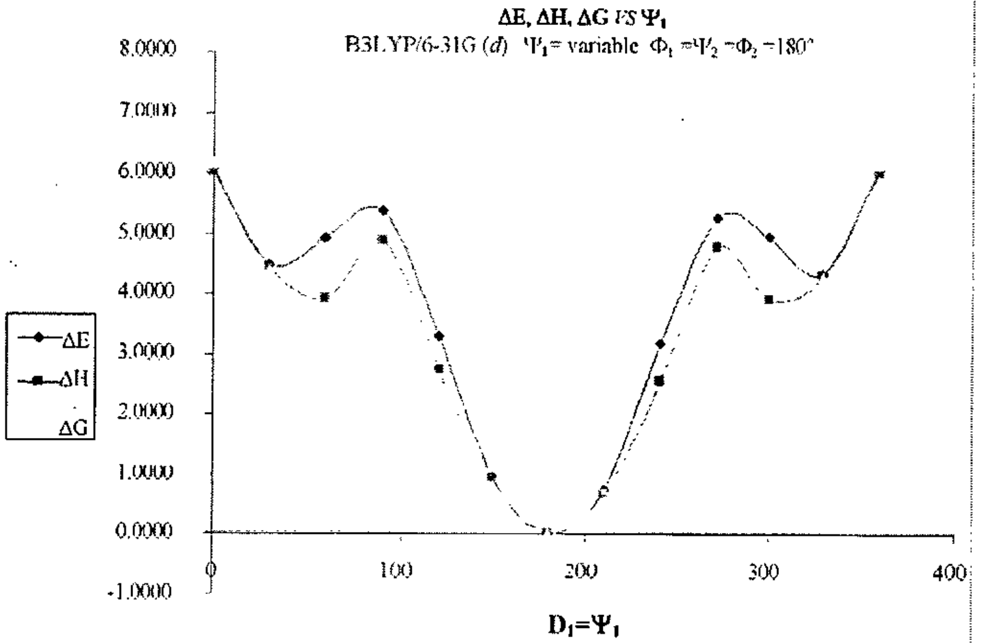

Fig. 3. Relative energies, enthalpies and Gibbs free energies for various amount of Ψ_1 at the B3LYP/6-31G (*d*) level of theory.

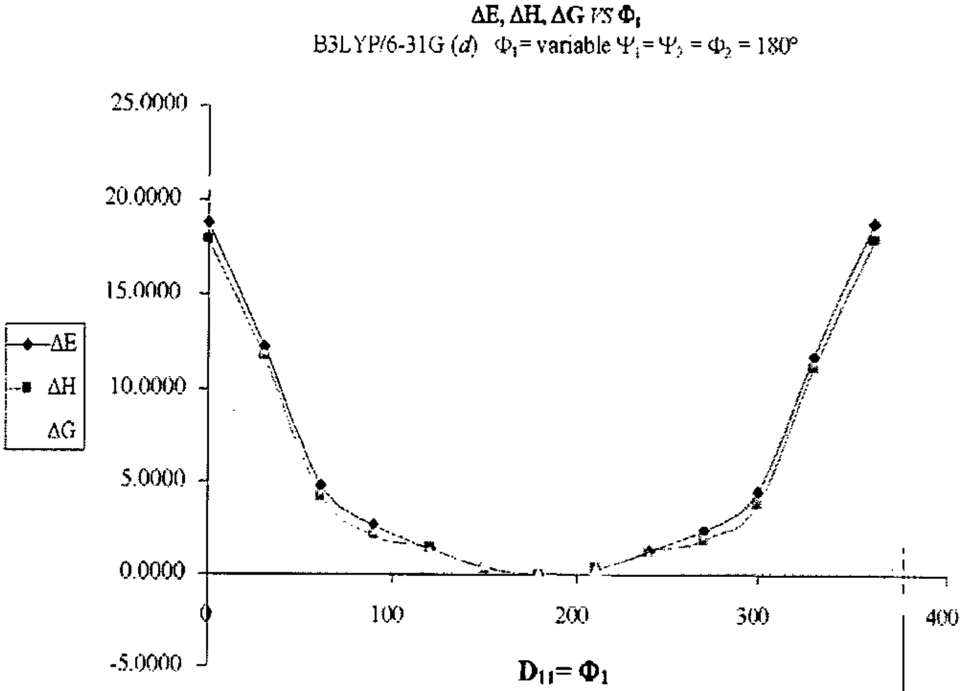

Fig. 4. Relative energies, enthalpies and Gibbs free energies for various amount of Φ_1 at the B3LYP/6-31G (*d*) level of theory.

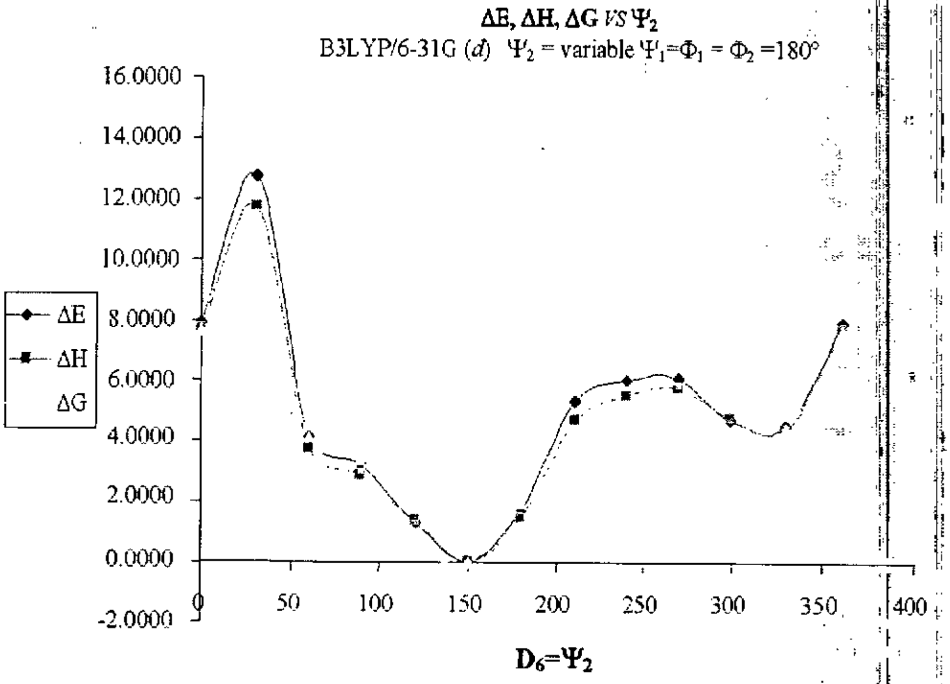

Fig. 5. Relative energies, enthalpies and Gibbs free energies for various amount of Ψ_2 at the B3LYP/6-31G (*d*) level of theory.

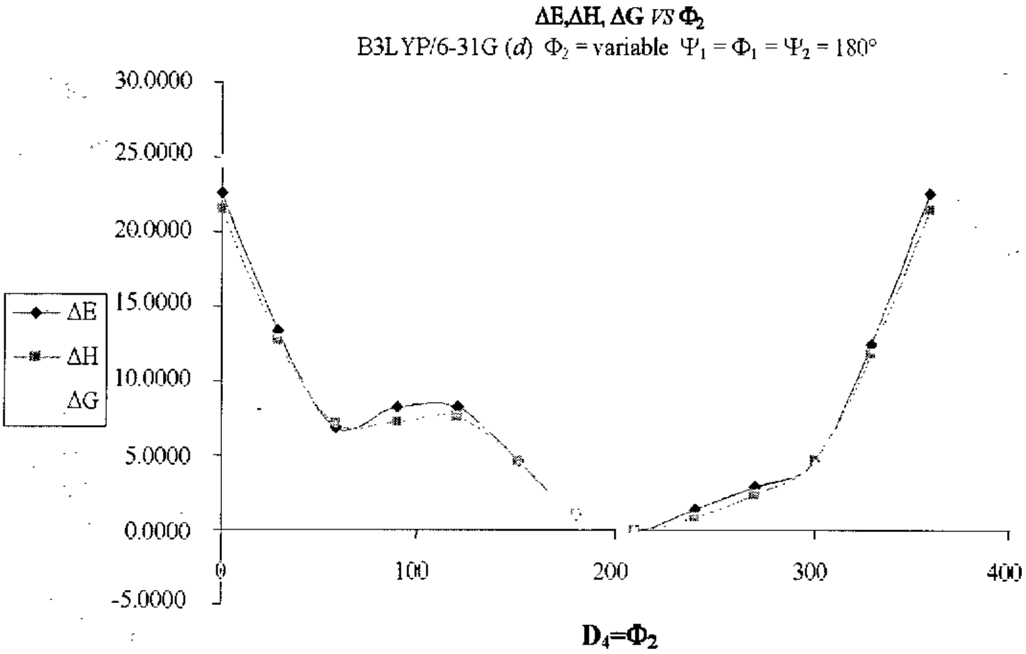

Fig. 6. Relative energies, enthalpies and Gibbs free energies for various amount of Φ_2 at the B3LYP/6-31G (*d*) level of theory.

Table1. Optimized energies for HCO-Gly-L-Leu-NH$_2$ varying the SC dihedral angle χ_1 at the HF/6-31(*d*), HF/6-311++G (*d, p*), and B3LYP/6-31G (*d*) levels of the theory.

χ_1	**HF/6-31G(*d*)**	**HF/6-311++G(*d,p*)**	**B3LYP/6-31G(*d*)**
0	-738.6962478	-738.9058139	-743.1634749
30	-738.7004776	-738.9094260	-743.1674221
60	**-738.7023251**	**-738.9114036**	**-743.1691305**
90	-738.6968324	-738.9060905	-743.1641187
120	-738.6921353	-738.9013249	-743.1600897
150	-738.6980965	-738.9074587	-743.1645556
180	**-738.7033790**	**-738.9128561**	**-743.1694293**
210	-738.7016777	-738.9111489	-743.1682850
240	-738.6992196	-738.9088330	-743.1664941
270	**-738.7010425**	**-738.9106395**	**-743.1674876**
300	-738.7008885	-738.9102700	-743.1674858
330	-738.6978902	-738.9074165	-743.1651200
360	-738.6962478	-738.9058139	-743.1634749

Table 2. Optimized energies (in hartree) for HCO-Gly-L-Leu-NH_2 varying the SC dihedral angle χ_2 at the HF/6-31G(*d*), HF/6-311++G(*d,p*), and B3LYP/6-31G(*d*) levels of the theory while χ_1 is 60°, 180° and 270°

60- χ_2	**HF/6-31G(*d*)**	**HF/6-311++G(*d,p*)**	**B3LYP/6-31G(*d*)**	**180- χ_2**	**HF/6-31G(*d*)**	**HF/6-311++G(*d,p*)**	**B3LYP/6-31G(*d*)**	**270- χ_2**	**HF/6-31G(*d*)**	**HF/6-311++G(*d,p*)**	**B3LYP/6-31G(*d*)**
60-0	-738.6921681	-738.9011593	-743.1600842	180-0	-738.6949013	-738.9038500	-743.1625145	270-0	-738.6915828	-738.9018313	-743.1585925
60-30	-738.694972	-738.9038828	-743.1624601	180-30	-738.6975056	-738.9062894	-743.1650252	270-30	-738.6949954	-738.9049433	-743.1614419
60-60	-738.6981446	-738.9068328	-743.1654686	180-60	-738.6990705	-738.9081233	-743.1655153	270-60	-738.6999061	-738.9094603	-743.1665183
60-90	-738.6963794	-738.9051305	-743.1636772	180-90	-738.6958461	-738.9046784	-743.1632265	270-90	-738.6972055	-738.906574	-743.1648055
60-120	-738.6919537	-738.9006847	-743.1600906	180-120	-738.6937771	-738.9029925	-743.1612697	270-120	-738.6915873	-738.9016377	-743.1588657
60-150	-738.6960726	-738.9050549	-743.1634295	180-150	-738.7003116	-738.9094332	-743.1673252	270-150	-738.6950706	-738.9050444	-743.1615201
60-180	-738.701401	-738.9102070	-743.1684480	**180-180**	**-738.7030704**	**-738.9124622**	**-743.1691628**	270-180	-738.7009064	-738.910502	-743.1672486
60-210	**-738.7021263**	**-738.9115099**	**-743.1686666**	180-210	-738.7015657	-738.9112374	-743.1676072	270-210	-738.6990796	-738.9088652	-743.1659116
60-240	-738.7010535	-738.9100437	-743.1673676	180-240	-738.6991674	-738.9086200	-743.1653438	270-240	-738.6970251	-738.9067425	-743.1641145
60-270	-738.7014055	-738.9105366	-743.1679109	180-270	-738.7005416	-738.9099808	-743.1668731	270-270	-738.7004415	-738.9101652	-743.1671127
60-300	-738.7007973	-738.9099607	-743.1674567	180-300	-738.6985736	-738.9079312	-743.1650183	**270-300**	**-738.7018736**	**-738.9113904**	**-743.1685871**
60-330	-738.6971949	-738.9059936	-743.1645422	180-330	-738.6966298	-738.9054740	-743.1639891	270-330	-738.6969991	-738.9066486	-743.1646156
60-360	-738.6921669	-738.9011593	-743.1600842	180-360	-738.6949013	-738.9038500	-743.1625145	270-360	-738.6915828	-738.9018313	-743.1585925

Table 3. Relative energies and thermodynamic properties for HCO-Gly-L-Leu-NH_2 varying the backbone dihedral angle Ψ_1 (D_1) at the HF/6-31G (*d*), HF/6-311++G (*d, p*), and B3LYP/6-31(*d*) levels of theory

Ψ_1	ΔE			ΔH			ΔG			ΔS		
(D_1)	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-31G(*d*)	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-31G(*d*)	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-31G(*d*)	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-31G(*d*)
0	6.053	5.992	6.093	5.989	5.960	6.043	6.145	5.858	6.170	-0.520	0.337	-0.429
30	4.457	4.596	4.484	4.408	4.559	4.452	4.458	4.509	4.390	-0.164	0.166	0.208
60	5.046	5.006	4.941	4.569	3.965	3.918	5.491	7.144	7.153	-3.094	-10.670	-10.852
90	5.579	5.230	5.375	5.029	4.706	4.887	6.355	5.996	5.684	-4.445	-4.327	-2.671
120	3.566	3.388	3.314	2.939	2.762	2.732	4.808	4.663	4.539	-6.266	-6.381	-6.062
130	1.124	1.105	0.977	1.063	1.045	0.930	1.231	1.216	1.129	-0.560	-0.571	-0.668
180	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
210	0.823	0.741	0.749	0.761	0.674	0.690	0.996	0.963	0.961	-0.788	-0.969	-0.908
240	3.271	3.066	3.204	2.652	2.450	2.579	4.562	4.389	4.621	-6.404	-6.507	-6.848
270	5.438	5.107	5.274	4.903	4.576	4.796	6.288	5.911	5.933	-4.613	-4.478	-3.812
300	4.934	4.868	4.961	4.477	4.421	3.926	5.455	5.276	7.285	-3.281	-2.871	-11.266
330	4.293	4.413	4.349	4.227	4.360	4.307	4.412	4.440	4.301	-0.619	-0.269	0.022
360	6.053	5.992	6.093	5.989	5.960	6.043	6.145	5.858	6.170	-0.520	0.337	-0.429

ΔE, ΔG, ΔH are Kcal/mol and ΔS is cal/mol K

Table 4. Relative energies and thermodynamic properties for HCO-Gly-L-Leu-NH_2 varying the backbone dihedral angle $\Phi_1(D_{11})$ at the HF/6-31G (*d*), HF/6-311++G (*d, p*), and B3LYP/6-31G (*d*) levels of theory

Φ_1	ΔE			ΔH			ΔG			ΔS		
(D_{11})	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-33G(*d*)	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-31G(*d*)	HF/6-31G(*d*)	HF/6-333++G(*d,p*)	B3LYP/6-31G(*d*)	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-31G(*d*)
0	20.968	21.032	18.833	20.043	20.099	17.889	22.804	22.895	20.901	-9.259	-9.382	-10.106
30	12.971	12.804	12.288	12.444	12.253	11.743	14.167	14.110	13.671	-5.777	-6.228	-6.465
60	4.224	4.267	4.743	4.084	4.127	4.127	4.511	4.572	6.344	-1.429	-1.497	-7.434
90	2.214	2.171	2.647	2.154	2.114	2.055	1.882	1.925	3.711	0.915	0.635	-5.557
120	1.593	1.564	1.403	0.982	0.954	1.335	2.748	2.757	1.229	-5.919	-6.047	0.355
150	0.563	0.547	0.350	0.534	0.518	0.288	0.375	0.404	0.548	0.535	0.382	-0.861
180	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
210	0.483	0.458	0.310	0.457	0.432	0.257	0.275	0.291	0.309	0.613	0.472	-0.173
240	1.405	1.354	1.245	0.796	0.747	1.194	2.580	2.563	0.885	-5.980	-6.091	1.034
270	1.921	1.822	2.408	1.869	1.780	1.846	1.485	1.433	3.009	1.290	1.163	-3.902
300	3.668	3.652	4.466	3.534	3.512	3.816	3.953	3.980	6.221	-1.402	-1.573	-8.066
330	12.218	11.987	11.718	11.666	11.409	11.172	13.532	13.422	13.124	-6.256	-6.754	-6.547
360	20.969	21.032	18.833	20.043	20.099	17.888	22.804	22.895	20.901	-9.259	-9.382	-10.106

ΔE, ΔG, ΔH are Kcal/mol and ΔS is cal/mol K.

Table 5. Relative energies and thermodynamic properties for HCO-Gly-L-Leu-NH_2 varying the backbone dihedral angle Ψ_2 (D_6) at the HF/6-31G (*d*), HF/6-311++G (*d, p*), and B3LYP/6-31G (*d*) levels of theory

Ψ_2	ΔE			ΔH			ΔG			ΔS		
(D_6)	**HF/6-31G(*d*)**	**HF/6-311++G(*d,p*)**	**B3LYP/6-31G(*d*)**	**HF/6-31G(*d*)**	**HF/6-311++G(*d,p*)**	**B3LYP/6-31G(*d*)**	**HF/6-31G(*d*)**	**HF/6-311++G(*d,p*)**	**B3LYP/6-31G(*d*)**	**HF/6-31G(*d*)**	**HF/6-311++G(*d,p*)**	**B3LYP/6-31G(*d*)**
0	8.422	8.697	7.893	8.244	8.545	7.701	8.151	8.338	7.646	0.311	0.694	0.185
30	13.750	5.740	12.764	12.672	5.059	11.751	15.280	6.598	14.154	-8.756	-5.161	-8.059
60	3.928	3.828	4.154	3.529	3.405	3.800	4.217	4.226	4.163	-2.307	-2.752	-1.219
90	2.693	2.248	3.274	2.259	1.819	2.910	3.154	2.745	3.416	-3.000	-3.107	-1.699
120	0.685	0.470	1.308	0.755	0.531	1.399	0.248	0.124	0.557	1.699	1.365	2.821
150	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
180	2.736	2.765	1.684	2.568	2.613	1.506	2.845	2.826	1.970	-0.930	-0.712	-1.558
210	7.250	7.044	5.307	6.675	6.500	4.712	7.228	7.085	5.867	-1.855	-1.962	-3.876
240	6.838	6.606	6.059	6.261	6.043	5.519	7.322	7.088	6.664	-3.561	-3.507	-3.841
270	5.958	5.286	6.099	5.116	4.413	5.755	7.236	6.674	4.834	-7.111	-7.582	3.087
300	4.204	3.862	4.689	4.309	3.971	4.790	3.309	3.106	3.622	3.355	2.900	3.917
330	4.305	4.482	4.526	4.179	4.381	4.393	4.258	4.399	4.478	-0.269	-0.062	-0.284
360	8.422	8.697	7.893	8.244	8.545	7.701	8.151	8.338	7.646	0.311	0.694	0.185

ΔE, ΔG, ΔH are Kcal/ mol and ΔS is cal/mol K.

Table 6. Relative energies and thermodynamic properties for HCO-Gly-L-Leu-NH_2 varying the backbone dihedral angle $\Phi_2(D_4)$ at the HF/6-31G (*d*), HF/6-311++G (*d, p*), and B3LYP/6-31G (*d*) levels of theory

Φ_2	ΔE			ΔH			ΔG			ΔS		
(D_4)	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-31G(*d*)	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-31G(*d*)	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-31G(*d*)	HF/6-31G(*d*)	HF/6-311++G(*d,p*)	B3LYP/6-31G(*d*)
0	25.376	24.994	22.624	24.258	23.874	21.520	27.309	25.735	24.718	-10.240	-6.239	-10.727
30	13.874	13.805	13.314	13.285	13.234	12.764	15.275	15.198	14.639	-6.674	-6.587	-6.287
60	6.443	6.539	6.884	6.113	6.181	7.155	7.1492	7.469	5.998	-3.475	-4.323	3.880
90	8.601	8.483	8.251	7.625	7.526	7.306	10.488	10.374	10.167	-9.604	-9.553	-9.593
120	9.481	9.503	8.192	8.399	8.418	7.680	11.626	11.699	9.191	-10.820	-11.000	-5.067
150	6.367	6.456	4.608	5.784	5.879	4.613	7.493	7.553	3.871	-5.733	-5.610	2.491
180	1.675	1.815	1.032	1.649	1.799	1.019	1.736	1.818	1.179	-0.296	-0.059	-0.536
210	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
240	1.243	1.0473	1.383	0.722	0.524	0.822	2.098	1.951	2.479	-4.620	-4.786	-5.554
270	1.905	1.723	2.856	1.398	1.216	2.331	2.606	2.454	3.738	-4.053	-4.148	-4.720
300	3.586	3.477	4.647	3.510	3.402	4.664	3.7105	3.552	4.421	-0.673	-0.504	0.815
330	13.175	12.822	12.485	12.482	12.122	11.849	14.605	14.306	13.713	-7.124	-7.326	-6.253
360	25.376	24.994	22.624	24.258	23.874	21.520	27.309	25.735	24.718	-10.240	-6.239	-10.727

ΔE, ΔG, ΔH ore Kcal/mol and ΔS is cal/mol K.

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