Vol. 4, No. 2, 2010 Chemistry

Vladimir Babkin[1], Andrei Tsykanov[1], Olga Buzinova[3], Gennady Zaikov[2] and Alexander Rahimov[1]

QUANTUM CHEMICAL CALCULATION OF THE MONOAMINOCARBONIC ACIDS

[1] SF VolgSABU; 21, Michurina str., 403343 Mikhailovka, Volgograd region, sfi@reg.avtlg.ru
[2] Institute of Biochemical Physics, Russian Academy of Sciences; 4 Kosygin str. 117997 Moscow, chembio@sky.chph.ras.ru
[3] Volgograd State Pedagogic University; 27, Lenin Av., 400131 Volgograd

Received: April 21, 2009

Abstract. For the first time quantum chemical MNDO method has been used for the calculation of a classical row of monoaminocarbonic acids of glycines, α-alanines, β-alanines, valines, isoleucines, norvalines and γ–aminobutyric acids, leucines and phenylalanines. The optimized geometrical and electronic structure of these compounds has been received.

Keywords: quantum chemical calculation, MNDO method, aminocarbonic acid, glycine, α-alanine, β-alanine, valine, isoleucine, norvaline, γ–aminobutyric acid, leucine, phenylalanine.

1. Introduction

In spite of the fact that monoaminocarbonic acids have been synthesized in 19th century, their geometrical and electronic structures practically have not been studied by quantum chemical methods till now. Often this fact complicates researches of their properties and mechanisms of reactions with participation of the above-mentioned amino acids.

In this connection the purpose of the present work is quantum chemical calculation of molecules of a classical row of aminocarbonic acids of glycines (Gly), alanines (Ala), valines (Val), isoleucines (Ile), norvalines (Nle) and γ-aminobutyric acids (Abu), leucines (Leu) and phenylalanines (Phe) using MNDO method.

2. Experimental

For quantum chemical calculation of monoaminocarbonic acids molecules the standard MNDO method with geometry optimization by all parameters by the gradient method, was used. It was included in software package PC GAMES [1]. MNDO method has a number of advantages before other quantum chemical methods, *e.g.* in calculations of nonlimiting molecules containing non-divided electron pairs on the adjoined atoms. Moreover, it will give more exact values of valence angels and more correct sequence of molecular orbital levels. This method more correctly reproduces relative stability of isomers containing double bonds [2] that is very important for the investigation of monoaminocarbonic acids. Quantum chemical calculation of molecules of studied amino acids is executed by MNDO method approaching the isolated molecule in a gas phase. For visual representation of molecules models the well-known program MacMolPit [3] was used.

3. Results and Discussion

The optimized geometrical and electronic structures of studied molecules Gly, Ala, Val, Ile, Nle, Abu, Leu, Phe are received by MNDO method presented in Figs. 1-9 and Tables 1-10. For the estimation of acid properties NH_2 and COOH groups are of the greatest interest owing to their amphoteric character. Angles of NHN aminogroup are practically identical and equal to 105–106° in all studied amino acids. OCO and COH angles in COOH group also do not essentially differ in various amino acids. The maximum charges on hydrogen atoms in NH_2 and COOH groups are within the ranges of 0.11–0.12 and 0.188–0.219, correspondingly. This fact testifies that either all of them possess identical acid strength, or the maximum charge on hydrogen atom is not the reactivity index for biomolecules and, in particular, for studied amino acids. The application according to the known formula for the estimation of the acid strength of H-acids pKa = 42.11–$172.18q^{H+}_{max}$ [4] which gives qualitatively non-coordinate results with the experiments testifies it. The search of other correlations pKa (a universal acidity indicator) with the energy of proton separation from NH_2 and COOH groups,

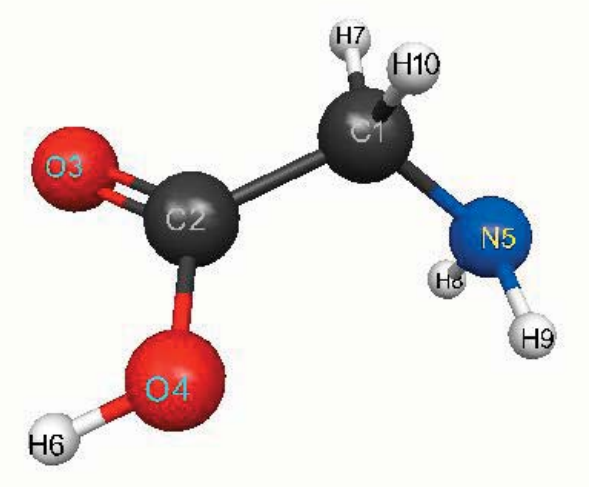

Fig. 1. Geometrical and electronic structure of glycine molecule (E_0 = –113652 kJ/mol, E_{el} = –341272 kJ/mol)

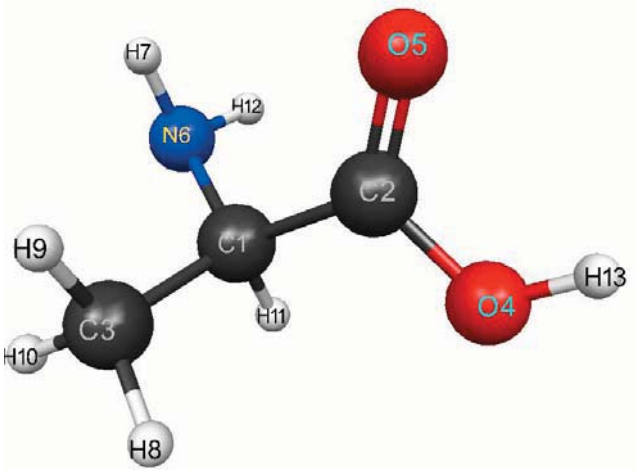

Fig. 2. Geometrical and electronic structure of α-alanine molecule (E_0 = –128734 kJ/mol, E_{el} = –445875 kJ/mol)

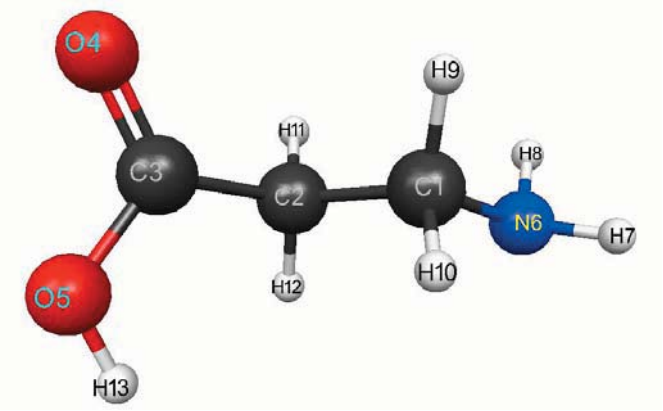

Fig. 3. Geometrical and electronic structure of β-alanine molecule (E_0 = –128708 kJ/mol, E_{el} = –435174 kJ/mol)

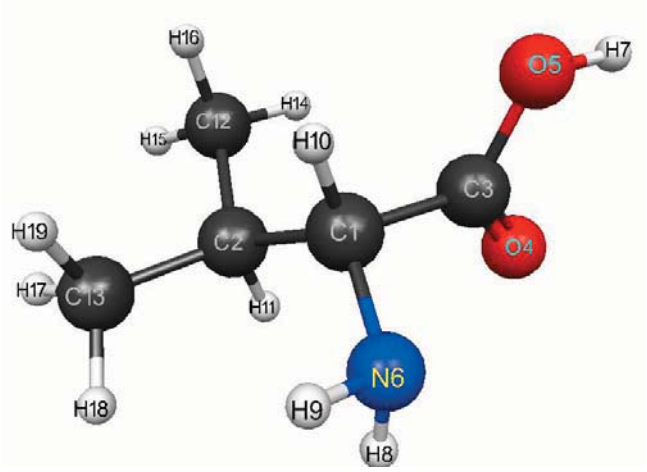

Fig. 4. Geometrical and electronic structure of valine molecule (E_0 = –158872 kJ/mol, E_{el} = –680787 kJ/mol)

Table 1

The optimized bond length, valence angles and atomic charges by Mellikens

Bond length	R, A	Valence angles	Degree	Atom	Charges (by Mellikens)
C(2)-C(1)	1.543			C(1)	0.118
O(3)-C(2)	1.229	O(3)-C(2)-C(1)	126	C(2)	0.291
O(4)-C(2)	1.357	O(4)-C(2)-C(1)	115	O(3)	-0.35
N(5)-C(1)	1.457	N(5)-C(1)-C(2)	117	O(4)	-0.31
H(6)-O(4)	0.949	H(6)-O(4)-C(2)	116	N(5)	-0.27
H(7)-C(1)	1.118	H(7)-C(1)-N(5)	108	H(6)	0.218
H(8)-N(5)	1.007	H(8)-N(5)-C(1)	111	H(7)	0.048
H(9)-N(5)	1.007	H(9)-N(5)-H(8)	106	H(8)	0.108
H(10)-C(1)	1.118	H(10)-C(1)-H(7)	107	H(9)	0.115
				H(10)	0.043

Table 2

The optimized bond length, valence angles and atomic charges by Mellikens

Bond length	R, A	Valence angles	Degree	Atom	Charges (by Mellikens)
C(2)-C(1)	1.551			C(1)	0.076
C(3)-C(1)	1.547	C(3)-C(1)-C(2)	111	C(2)	0.303
O(4)-C(2)	1.355	O(4)-C(2)-C(1)	115	C(3)	0.037
O(5)-C(2)	1.231	O(5)-C(2)-C(1)	127	O(4)	-0.29
N(6)-C(1)	1.466	N(6)-C(1)-C(2)	114	O(5)	-0.37
H(7)-N(6)	1.007	H(7)-N(6)-C(1)	112	N(6)	-0.27
H(8)-C(3)	1.109	H(8)-C(3)-O(5)	101	H(7)	0.115
H(9)-C(3)	1.108	H(9)-C(3)-H(8)	108	H(8)	0.004
H(10)-C(3)	1.108	H(10)-C(3)-H(9)	108	H(9)	0.006
H(11)-C(1)	1.123	H(11)-C(1)-C(3)	108	H(10)	0.019
H(12)-N(6)	1.007	H(12)-N(6)-H(7)	106	H(11)	0.053
H(13)-O(4)	0.949	H(13)-O(4)-C(2)	116	H(12)	0.107
				H(13)	0.217

Table 3

The optimized bond length, valence angles and atomic charges by Mellikens

Bond length	R, A	Valence angles	Degree	Atom	Charges (by Mellikens)
C(2)-C(1)	1.546			C(1)	0.087
C(3)-C(2)	1.536	C(3)-C(2)-C(1)	113	C(2)	-0.02
O(4)-C(3)	1.227	O(4)-C(3)-C(2)	125	C(3)	0.311
O(5)-C(3)	1.361	O(5)-C(3)-C(2)	121	O(4)	-0.30
N(6)-C(1)	1.467	N(6)-C(1)-C(2)	110	O(5)	-0.28
H(7)-N(6)	1.008	H(7)-N(6)-C(1)	109	N(6)	-0.27
H(8)-N(6)	1.008	H(8)-N(6)-H(7)	105	H(7)	0.103
H(9)-C(1)	1.120	H(9)-C(1)-N(6)	113	H(8)	0.101
H(10)-C(1)	1.118	H(10)-C(1)-H(9)	106	H(9)	-0.00
H(11)-C(2)	1.114	H(11)-C(2)-C(1)	110	H(10)	0.016
H(12)-C(2)	1.113	H(12)-C(2)-H(11)	106	H(11)	0.044
H(13)-O(5)	0.946	H(13)-O(5)-C(3)	115	H(12)	0.033
				H(13)	0.202

Table 4

The optimized bond length, valence angles and atomic charges by Mellikens

.Bond length	R, A	Valence angles	Degree	Atom	Charges (by Mellikens)
C(2)-C(1)	1.572			C(1)	0.096
C(3)-C(1)	1.550	C(3)-C(1)-C(2)	113	C(2)	-0.09
O(4)-C(3)	1.229	O(4)-C(3)-C(1)	127	C(3)	0.353
O(5)-C(3)	1.356	O(5)-C(3)-C(1)	114	O(4)	-0.36
N(6)-C(1)	1.470	N(6)-C(1)-C(2)	117	O(5)	-0.30
H(7)-O(5)	0.949	H(7)-O(5)-C(3)	115	N(6)	-0.27
H(8)-N(6)	1.008	H(8)-N(6)-C(1)	112	H(7)	0.215
H(9)-N(6)	1.007	H(9)-N(6)-H(8)	106	H(8)	0.113
H(10)-C(1)	1.122	H(10)-C(1)-N(6)	107	H(9)	0.107
H(11)-C(2)	1.119	H(11)-C(2)-C(1)	108	H(10)	0.048
C(12)-C(2)	1.545	C(12)-C(2)-C(1)	112	H(11)	0.032
C(13)-C(2)	1.544	C(13)-C(2)-C(1)	113	C(12)	0.037
H(14)-C(12)	1.108	H(14)-C(12)-O(5)	60	C(13)	0.034
H(15)-C(12)	1.109	H(15)-C(12)-H(14)	106	H(14)	0.001
H(16)-C(12)	1.108	H(16)-C(12)-H(15)	108	H(15)	0.000
H(17)-C(13)	1.109	H(17)-C(13)-C(2)	111	H(16)	0.000
H(18)-C(13)	1.108	H(18)-C(13)-H(8)	57	H(17)	0.004
H(19)-C(13)	1.108	H(19)-C(13)-H(17)	107	H(18)	-0.00
				H(19)	-0.00

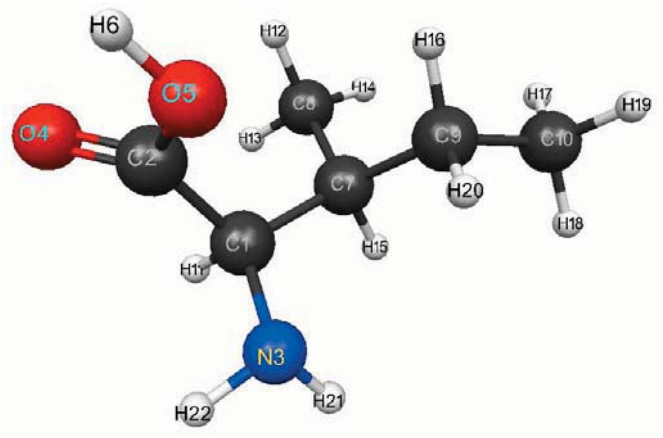

Fig. 5. Geometrical and electronic structure of isoleucine molecule (E_0 = –173928 kJ/mol, E_{el} = –810360 kJ/mol)

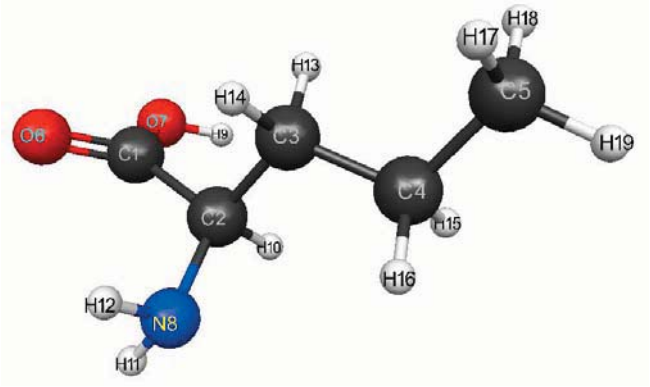

Fig. 6. Geometrical and electronic structure of norvaline molecule (E_0 = –158872 kJ/mol, E_{el} = –663449 kJ/mol)

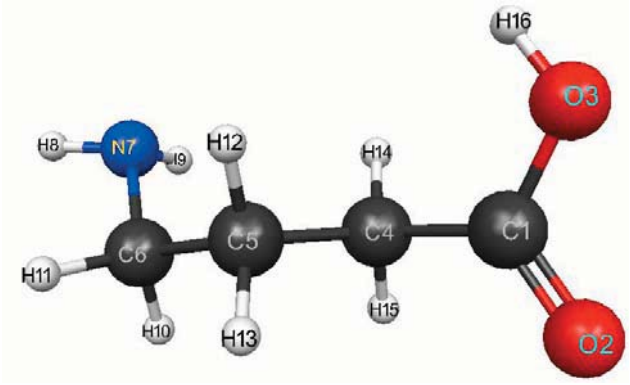

Fig. 7. Geometrical and electronic structure of γ-aminobutyric acid molecule (E_0 = –143790 kJ/mol, E_{el} = –538885 kJ/mol)

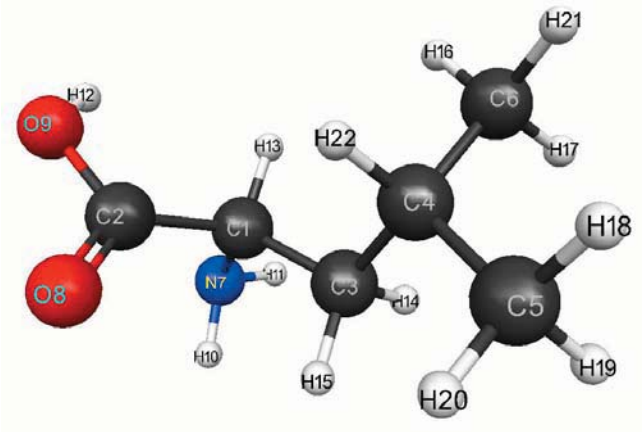

Fig. 8. Geometrical and electronic structure of leucine molecule (E_0 = –173928 kJ/mol, E_{el} = –799528 kJ/mol)

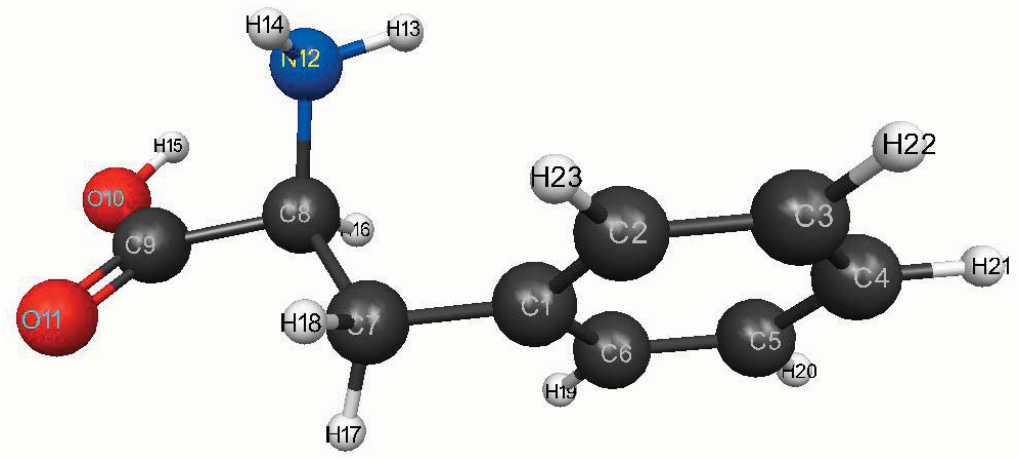

Fig. 9. Geometrical and electronic structure of phenylalanine molecule (E_0 = –208026 kJ/mol, E_{el} = –1023528 kJ/mol)

Table 5

The optimized bond length, valence angles and atomic charges by Mellikens

Bond length	R, A	Valence angles	Degree	Atom	Charges (by Mellikens)
C(2)-C(1)	1.548			C(1)	0.097
N(3)-C(1)	1.472	N(3)-C(1)-C(2)	108	C(2)	0.342
O(4)-C(2)	1.232	O(4)-C(2)-C(1)	124	N(3)	-0.26
O(5)-C(2)	1.352	O(5)-C(2)-C(1)	117	O(4)	-0.37
H(6)-O(5)	0.950	H(6)-O(5)-C(2)	115	O(5)	-0.27
C(7)-C(1)	1.572	C(7)-C(1)-N(3)	113	H(6)	0.214
C(8)-C(7)	1.546	C(8)-C(7)-C(1)	111	C(7)	-0.03
C(9)-C(7)	1.554	C(9)-C(7)-C(1)	116	C(8)	0.029
C(10)-C(9)	1.533	C(10)-C(9)-C(7)	115	C(9)	-0.01
H(11)-C(1)	1.128	H(11)-C(1)-N(3)	110	C(10)	0.027
H(12)-C(8)	1.108	H(12)-C(8)-O(5)	62	H(11)	0.009
H(13)-C(8)	1.109	H(13)-C(8)-H(12)	108	H(12)	0.002
H(14)-C(8)	1.108	H(14)-C(8)-H(12)	107	H(13)	-0.00
H(15)-C(7)	1.122	H(15)-C(7)-C(8)	105	H(14)	0.001
H(16)-C(9)	1.114	H(16)-C(9)-C(7)	110	H(15)	0.011
H(17)-C(10)	1.108	H(17)-C(10)-C(9)	112	H(16)	0.010
H(18)-C(10)	1.108	H(18)-C(10)-N(3)	79	H(17)	-0.00
H(19)-C(10)	1.109	H(19)-C(10)-H(18	107	H(18)	-0.00
H(20)-C(9)	1.112	H(20)-C(9)-H(16)	106	H(19)	-0.00
H(21)-N(3)	1.008	H(21)-N(3)-H(18)	59	H(20)	0.029
H(22)-N(3)	1.009	H(22)-N(3)-H(21)	105	H(21)	0.104
				H(22)	0.102

Table 6

The optimized bond length, valence angles and atomic charges by Mellikens

Bond length	R, A	Valence angles	Degree	Atom	Charges (by Mellikens)
C(2)-C(1)	1.558			C(1)	0.281
C(3)-C(2)	1.558	C(3)-C(2)-C(1)	110	C(2)	0.054
C(4)-C(3)	1.541	C(4)-C(3)-C(2)	115	C(3)	0.007
C(5)-C(4)	1.532	C(5)-C(4)-C(3)	114	C(4)	-0.01
O(6)-C(1)	1.228	O(6)-C(1)-C(2)	125	C(5)	0.026
O(7)-C(1)	1.360	O(7)-C(1)-O(6)	115	O(6)	-0.31
N(8)-C(2)	1.465	N(8)-C(2)-C(1)	113	O(7)	-0.27
H(9)-O(7)	0.946	H(9)-O(7)-C(1)	115	N(8)	-0.26
H(10)-C(2)	1.124	H(10)-C(2)-N(8)	106	H(9)	0.202
H(11)-N(8)	1.008	H(11)-N(8)-C(2)	110	H(10)	0.031
H(12)-N(8)	1.008	H(12)-N(8)-H(11)	106	H(11)	0.108
H(13)-C(3)	1.115	H(13)-C(3)-C(2)	108	H(12)	0.119
H(14)-C(3)	1.113	H(14)-C(3)-H(13)	106	H(13)	0.002
H(15)-C(4)	1.114	H(15)-C(4)-C(3)	109	H(14)	0.023
H(16)-C(4)	1.113	H(16)-C(4)-H(15)	106	H(15)	0.003
H(17)-C(5)	1.108	H(17)-C(5)-C(4)	112	H(16)	0.024
H(18)-C(5)	1.108	H(18)-C(5)-H(17)	108	H(17)	-0.00
H(19)-C(5)	1.109	H(19)-C(5)-H(17)	108	H(18)	-0.00
				H(19)	-0.00

Table 7

The optimized bond length, valence angles and atomic charges by Mellikens

Bond length	R, A	Valence angles	Degree	Atom	Charges (by Mellikens)
O(2)-C(1)	1.227			C(1)	0.314
O(3)-C(1)	1.361	O(3)-C(1)-O(2)	115	O(2)	-0.31
C(4)-C(1)	1.536	C(4)-C(1)-O(2)	125	O(3)	-0.28
C(5)-C(4)	1.540	C(5)-C(4)-C(1)	113	C(4)	-0.02
C(6)-C(5)	1.546	C(6)-C(5)-C(4)	116	C(5)	-0.00
N(7)-C(6)	1.467	N(7)-C(6)-C(5)	112	C(6)	0.084
H(8)-N(7)	1.008	H(8)-N(7)-C(6)	109	N(7)	-0.28
H(9)-N(7)	1.008	H(9)-N(7)-H(8)	105	H(8)	0.100
H(10)-C(6)	1.120	H(10)-C(6)-C(5)	110	H(9)	0.095
H(11)-C(6)	1.119	H(11)-C(6)-H(10)	106	H(10)	-0.01
H(12)-C(5)	1.113	H(12)-C(5)-H(9)	101	H(11)	0.014
H(13)-C(5)	1.115	H(13)-C(5)-H(12)	106	H(12)	0.020
H(14)-C(4)	1.113	H(14)-C(4)-H(10)	101	H(13)	0.017
H(15)-C(4)	1.113	H(15)-C(4)-H(14)	106	H(14)	0.024
H(16)-O(3)	0.946	H(16)-O(3)-C(1)	115	H(15)	0.039
				H(16)	0.202

Table 8

The optimized bond length, valence angles and atomic charges by Mellikens

Bond length	R, A	Valence angles	Degree	Atom	Charges (by Mellikens)
C(2)-C(1)	1.553			C(1)	0.041
C(3)-C(1)	1.559	C(3)-C(1)-C(2)	115	C(2)	0.336
C(4)-C(3)	1.555	C(4)-C(3)-C(1)	116	C(3)	-0.01
C(5)-C(4)	1.544	C(5)-C(4)-C(3)	111	C(4)	-0.06
C(6)-C(4)	1.543	C(6)-C(4)-C(3)	113	C(5)	0.040
N(7)-C(1)	1.472	N(7)-C(1)-C(2)	105	C(6)	0.037
O(8)-C(2)	1.226	O(8)-C(2)-C(1)	126	N(7)	-0.28
O(9)-C(2)	1.359	O(9)-C(2)-C(1)	119	O(8)	-0.31
H(10)-N(7)	1.008	H(10)-N(7)-C(1)	111	O(9)	-0.27
H(11)-N(7)	1.008	H(11)-N(7)-H(10)	106	H(10)	0.114
H(12)-O(9)	0.947	H(12)-O(9)-C(2)	115	H(11)	0.106
H(13)-C(1)	1.123	H(13)-C(1)-N(7)	106	H(12)	0.208
H(14)-C(3)	1.115	H(14)-C(3)-C(1)	108	H(13)	0.032
H(15)-C(3)	1.113	H(15)-C(3)-H(14)	105	H(14)	0.005
H(16)-C(6)	1.108	H(16)-C(6)-C(4)	112	H(15)	0.027
H(17)-C(6)	1.108	H(17)-C(6)-H(16)	108	H(16)	-0.01
H(18)-C(5)	1.109	H(18)-C(5)-C(4)	111	H(17)	-0.00
H(19)-C(5)	1.108	H(19)-C(5)-H(18)	108	H(18)	-0.00
H(20)-C(5)	1.108	H(20)-C(5)-H(18)	107	H(19)	-0.00
H(21)-C(6)	1.109	H(21)-C(6)-H(16)	107	H(20)	0.004
H(22)-C(4)	1.119	H(22)-C(4)-C(5)	106	H(21)	0.000
				H(22)	0.020

Table 9

The optimized bond length, valence angles and atomic charges by Mellikens

Bond length	R, A	Valence angles	Degree	Atom	Charges (by Mellikens)
C(2)-C(1)	1.415			C(1)	-0.10
C(3)-C(2)	1.405	C(3)-C(2)-C(1)	121.0	C(2)	-0.04
C(4)-C(3)	1.404	C(4)-C(3)-C(2)	120.2	C(3)	-0.06
C(5)-C(4)	1.405	C(5)-C(4)-C(3)	119.4	C(4)	-0.04
C(6)-C(5)	1.405	C(6)-C(5)-C(4)	120.2	C(5)	-0.06
C(7)-C(1)	1.515	C(7)-C(1)-C(2)	121.0	C(6)	-0.03
C(8)-C(7)	1.560	C(8)-C(7)-C(1)	114.7	C(7)	0.028
C(9)-C(8)	1.555	C(9)-C(8)-C(7)	113.1	C(8)	0.042
O(10)-C(9)	1.358	O(10)-C(9)-C(8)	119.3	C(9)	0.333
O(11)-C(9)	1.227	O(11)-C(9)-C(8)	125.6	O(10)	-0.27
N(12)-C(8)	1.469	N(12)-C(8)-C(7)	116.5	O(11)	-0.31
H(13)-N(12)	1.007	H(13)-N(12)-C(8)	110.2	N(12)	-0.28
H(14)-N(12)	1.008	H(14)-N(12)-H(13)	105.8	H(13)	0.110
H(15)-O(10)	0.947	H(15)-O(10)-C(9)	114.9	H(14)	0.113
H(16)-C(8)	1.124	H(16)-C(8)-N(12)	107.2	H(15)	0.210
H(17)-C(7)	1.115	H(17)-C(7)-O(11)	76.80	H(16)	0.034
H(18)-C(7)	1.113	H(18)-C(7)-H(17)	105.4	H(17)	0.027
H(19)-C(6)	1.091	H(19)-C(6)-C(5)	118.5	H(18)	0.027
H(20)-C(5)	1.090	H(20)-C(5)-C(6)	119.7	H(19)	0.058
H(21)-C(4)	1.090	H(21)-C(4)-C(3)	120.2	H(20)	0.064
H(22)-C(3)	1.090	H(22)-C(3)-C(4)	120.0	H(21)	0.064
H(23)-C(2)	1.091	H(23)-C(2)-C(1)	120.4	H(22)	0.064
				H(23)	0.058

Table 10

The general energy (E_0), electronic energy (E_{el}), the maximum atomic charge of hydrogen (q^{H+}_{max}), energy of proton separation in COOH group (E^{H+}) and universal acidity indicator pKa (by COOH)

Amino acid	$-E_0$, kJ/mol	$-E_{el}$, kJ/mol	q^{H+}_{max}	$-E^{H+}_{(COOH)}$, kJ/mol	$pKa_{(COOH)}$
Glycine	113652	341272	0.22	1233	2.34
α-Alanine	128655	445508	0.20	1285	2.34
β-Alanine	128708	435174	0.20	1285	3.6
Valine	158872	680787	0.22	1311	2.32
Isoleucine	173928	810360	0.21	1311	2.32
Norvaline	158872	663449	0.20	1285	
γ-Aminobutyric acid	143790	538885	0.20	1285	
Leicine	173928	799528	0.208	1285	
Phenylalanine	208026	1023528	0.210	-	2.2

with the minimum charges on hydrogen atoms in the same groups, by geometrical and other quantum chemical parameters have not given positive results within the MNDO method (see Table 10).

4. Conclusions

Thus, by means of quantum chemical MNDO method we carried out for the first time the calculation of a classical row of monoaminocarbonic acids of Gly, Ala,

Val, Ile, Nle, Abu, Leu, Phe. The optimized geometrical and electronic structures of these compounds have been received. It has been established, that the maximum charge on hydrogen atom for studied amino acids is not the reactivity index as it is shown for common H-acids [4].

References

[1] Shmidt M., Baldrosge K. *et al*.: J.Computchem., 1993, **14**, 1347.
[2] Clark T.: Kompjuternaja Khimiya. Mir, Moskwa 1990.
[3] Bode B. and Gordon M.: Mol. Graphics Mod., 1998, **16**, 133.
[4] Babkin V. *et al*.: Oxidation Commun., 2002, **25**, 21.

ПРО ГЕОМЕТРИЧНУ ТА ЕЛЕКТРОННУ БУДОВУ МОНОАМІНОКАРБОНОВИХ КИСЛОТ

Анотація. *Вперше квантово-хімічним методом MNDO розрахований класичний ряд моноамінокарбонових кислот гліцину, α-аланіну, β-аланіну, валіну, ізолейцину, норваліну та γ-аміномасляної кислоти, лейцину і фенілаланіну. Одержано оптимізовану геометричну та електронну будову цих сполук.*

Ключові слова*: квантово-хімічний розрахунок, метод MNDO, амінокарбонові кислоти, α-аланін, β-аланін, валін, ізолейцин, норвалін, γ-аміномасляна кислота, лейцин, фенілаланін.*