Ab initio conformational analysis of glutamic acid, chemical shift anisotropy and population studies

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We report on glutamic acid rotation and its stable conformer in gas phase. The calculations were performed by HF/6-31G* and B3lyp/6-31G* levels of theory. There is a pertubation in the population diagram of the C3 that shows nucleophilic or radical attack will probably occur at this site. This fact is confirmed by the charge distribution and CSA (chemical shift anisotropy) diagrams. The energies and the relative energies are given as a function of rotational angle. Also, low and high-energy barriers of N-H rotation computed at various level of theory have been obtained. Vibrational frequencies of the structure were done to verify the minima of the energy.

Keywords: glutamic acid, CSA, conformational analysis

The Gaussian 98 software package[2] was used to perform Hartree–Fock (HF) and density functional theory (DFT) calculations on glutamic acid.

Glutamic acid was first modelled by the semi-empirical AM1 method. After the structure was determined at the HF/6-31G* level of theory, a relaxed scan for every 30° of rotation around the N2-H12 bound was again carried out. The minima obtained by the scan were optimised at the B3LYP/6-31G* level of theory.

Vibrational frequencies were performed by both HF and DFT methods by the 6-31G* basis set at 298.15 K and 1 atm. to verify the minimum energy configuration. Mulliken population was calculated at B3LYP/6-31G* level of theory.

NMR shielding tensors have been computed with the continuous set of the gauge independent atomic orbital (GIAO) method.[3–6] Because of the lack of symmetry in the molecule, only the diagram of chemical shift anisotropy asymmetry (η) *vs* degrees of rotation has been plotted.

Results and discussion

Because of the variable effects of solvent interactions, gas phase studies are much better to show the intrinsic properties of the molecules and to investigate the kinetic and thermodynamic effects of substituents.

The torsional energies computed as a one dimensional (1D)-scan at the B3LYP/6-31G* level of theory for glutamic acid, are shown graphically as a representation of the N2-H12 torsional potential is shown in Fig.1.

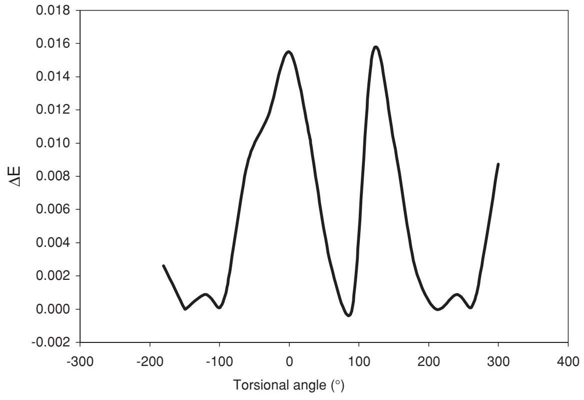
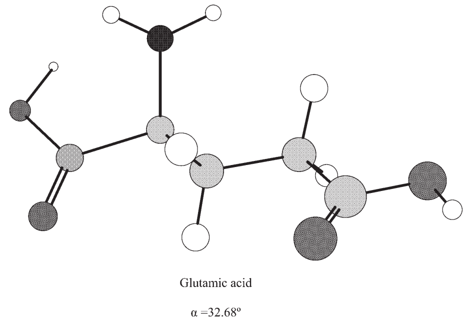


Fig. 1 N-H rotational potential(kcal/mol), D (H12- N2- C1- C3) of Glutamic acid computed at the HF/6-31G* level of theory.

The minima were optimised again by HF and DFT methods at the 6-31G* level of theory. The optimised geometries are given in Table 2. Also, the optimised form of the glutamic acid can be seen in Scheme 1. The α (= 32.68°), which corresponds to coplanarity, has been calculated also.



Scheme 1 B3LYP/6-31G* optimised molecular structure and corresponding dihedral angles

Two transition states can be inferred in Fig.1; the low TS at –120.0° and the high TS at 0°. The relative energies of these transition states have been compared with the minimum energy structure.

As can be seen in population diagrams (Fig.3), there is an unusual form of the population at C3. All the three orbitals have an equivalent population at –30.0° on the other hand, by the use of NBO calculations, the hybridisation of the orbitals of C3 in relation with C3–O9 and C3–O10 bonds at 0.0° and –30.0° are completely different.

The calculation of asymmetric NMR parameters (η) for C3 confirms this matter.

Information about the activity of the molecule is given by the Mulliken charges.

As can be seen in the orbital population diagrams, those orbitals which show little change are the orbitals that make bonds. This is true for C1, C4, C5, C6, O7 and O8, this fact is proven by the NBO calculations. It is interesting to note that in all of the above orbitals, the 2*px* orbital makes the major contribution to the bonds. This is confirmed again by the hybridisation coefficient, calculated by the NBO method. But for N2, C3, O9 and O10, there are some perturbations in population diagrams, especially for C3 and especially at (–30.0°).

These perturbations exist in the charge distributions of these atoms too. From the charge distribution scheme of the molecule it can be inferred that there are just two carbon atoms (except hydrogens) with positive charge. These are carbons of the carboxylic acid parts of the molecule, C3 and C6.

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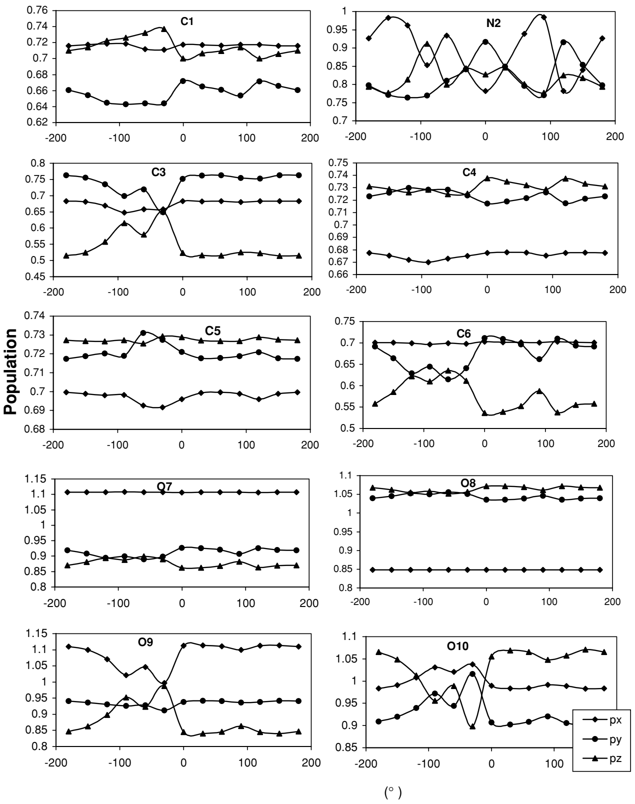

Fig. 3 Population *vs* torsional angle, calculated by B3LYP/6-31G*

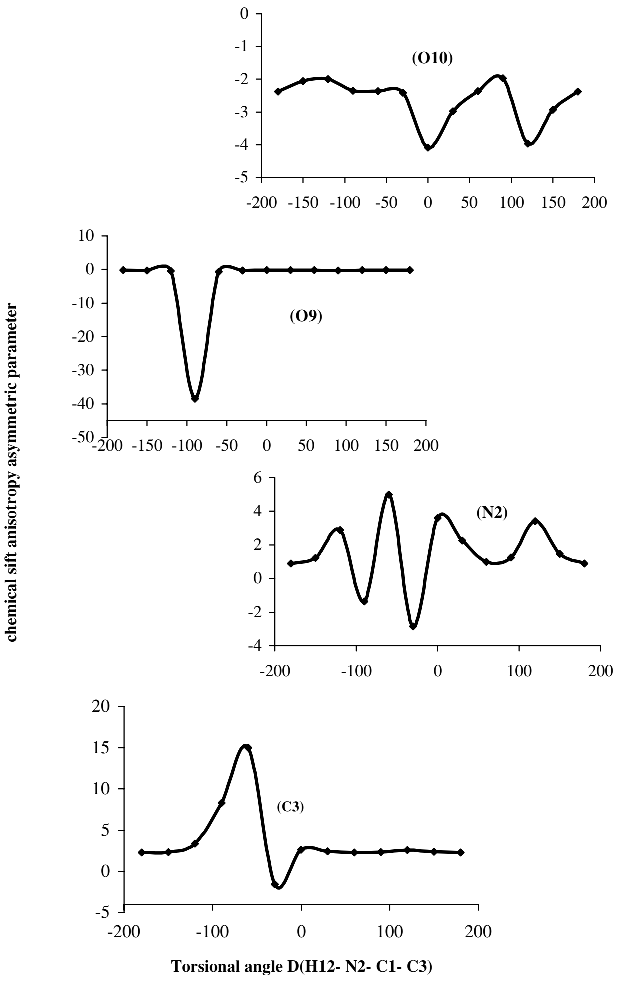

Fig. 5 CSA Asymmetry parameter *vs* torsional angle

Table 2 Optimised geometrical parameters of Glutamic acid as computed at the HF/6-31G* and B3LYP/6-31G* level of theory

	Minimum		Transition state	
	Regular optimisation		Regular optimisation	
			B3LYP/6-31G*	
	HF/6-31G*	B3LYP/6-31G*	At 0°	At – 120°
Bond length (A°)				
N2 – C1	1.4602	1.4768	1.4875	1.4782
C3 – C1	1.5358	1.5496	1.5335	1.5511
C4 – C1	1.5314	1.5345	1.5304	1.5353
C5 – C4	1.5256	1.5293	1.5313	1.5302
C6 – C5	1.5079	1.5149	1.5141	1.5149
O7 – C6	1.1865	1.2102	1.2104	1.2104
O8 – C6	1.3309	1.3565	1.3571	1.3562
O9 – C3	1.1848	1.2084	1.2032	1.2092
O10 – C3	1.3192	1.3406	1.3666	1.3377
H11 – C1	1.0872	1.0990	1.1043	1.0979
H12 – N2	0.9997	1.0161	1.0179	1.0150
H13 – N2	1.0027	1.0194	1.0176	1.0165
H14 – C4	1.0806	1.0934	1.0939	1.0934
H15 – C4	1.0856	1.0972	1.0958	1.0973
H16 – C5	1.0868	1.1000	1.0982	1.0999
H17 – C5	1.0862	1.0969	1.0978	1.0966
H18 – O8	0.9526	0.9760	0.9759	0.9761
H19 – O10	0.9559	0.9906	0.9732	0.9934
Bond length (°)				
C3 – C1 – N2	109.6628	108.8170	110.1802	109.4793
C4 – C1 – N2	115.4779	115.7933	112.9732	113.9757
C5 – C4 – C1	112.3081	112.9132	112.3328	112.9361
C6 – C5 – C4	112.8758	112.7394	112.5820	112.7061
O7 – C6 – C5	125.9093	125.9572	126.0878	125.9251
O8 – C6 – C5	111.5182	111.3247	111.2584	111.3356
O9 – C3 – C1	122.4751	122.9536	125.8036	122.2899
O10 – C3 – C1	114.9995	113.6348	114.0380	113.8559
H11 – C1 – N2	106.8842	106.7683	107.7637	109.1202
H12 – N2 – C1	112.3855	112.1250	110.8439	112.7437
H13 – N2 – C1	111.6780	110.7798	109.4898	112.3652
H14 – C4 – C1	108.8527	108.2306	109.0482	107.9364
H15 – C4 – C1	109.4426	109.5257	109.4316	109.6135
H16 – C5 – C4	111.9898	111.2017	112.2423	111.2902
H17 – C5 – C4	111.3523	111.6269	111.2008	111.4749
H18 – O8 – C6	108.2477	106.0944	106.0444	106.1235
H19 – O10 – C3	108.5548	104.7703	110.1554	104.1390
Dihedral angle (°)				
C4 – C1 – N2 – C3	-125.9995	-125.5459	-125.0908	-123.8019
C5 – C4 – C1 – N2	-65.8732	167.5064	-64.8399	-70.6029
C6 – C5 – C4 – C1	177.4624	173.3496	177.0259	171.9573
O7 – C6 – C5 – C4	-7.2889	-14.5651	-5.0157	-14.8314
O8 – C6 – C5 – C4	173.4459	166.5331	175.3794	166.2903
O9 – C3 – C1 – C4	-164.1972	-166.5052	-125.0458	-178.7354
O10 – C3 – C1 – N2	18.2468	15.3875	53.7869	1.9636
H11 – C1 – N2 – C3	112.4538	112.7168	115.5746	114.4990
H12 – N2 – C1 – C3	-148.8315	-147.3221	0.0000	-120.0000
H13 – N2 – C1 – C3	89.8037	92.6957	115.9740	117.1879
H14 – C4 – C1 – N2	172.1198	170.0055	173.3254	167.3226
H15 – C4 – C1 – N2	56.3455	54.8653	58.1985	52.0114
H16 – C5 – C4 – C1	57.1866	53.5256	55.7461	51.9460
H17 – C5 – C4 – C1	-61.3327	-64.3118	-61.6310	-65.6943
H18 – O8 – C6 – C5	179.4324	178.6821	179.5300	178.6929
H19 – O10 – C3 – C1	-4.0471	-3.2449	6.7020	-1.2344
E_{total} (hartree)	-548.5137051	-551.6181163	-551.6006477	551.6173039

Table 5 Vibrational frequencies (cm^{-1}) of glutamic acid at various methods after optimisation

Method	HF/6-31G*	B3LYP/6-31G*
Number of modes ($3N$-6) = 51		
1	28.4564	23.4024
2	54.1100	52.5855
3	79.3343	73.7056
4	115.2064	103.3185
5	120.1408	112.1722
6	260.7242	245.0096
7	266.9048	248.3125
8	313.2323	298.9275
9	388.0144	361.0909
10	454.6260	422.6735
11	506.6380	465.9502
12	566.6337	527.2431
13	589.0799	547.3501
14	634.1564	584.8787
15	704.3883	652.1610
16	716.7138	685.7635
17	807.1334	735.8155
18	814.7754	784.7611
19	852.4918	841.6966
20	926.9647	862.7668
21	955.8642	895.0766
22	999.7602	924.2282
23	1059.3562	980.0666
24	1134.8374	1054.6874
25	1178.5643	1091.0630
26	1225.1021	1125.9896
27	1262.4749	1151.7478
28	1300.3678	1178.5088
29	1344.0736	1234.4070
30	1365.1539	1249.7161
31	1398.3111	1277.4424
32	1442.8054	1323.4815
33	1453.9767	1335.5591
34	1510.2587	1382.3249
35	1534.0750	1409.7031
36	1564.6000	1438.3895
37	1591.3087	1457.8331
38	1616.4214	1494.5053
39	1637.3158	1518.9480
40	1834.3061	1691.2036
41	2037.1199	1850.3638
42	2055.4156	1873.9568
43	3213.6236	3035.4324
44	3216.4728	3044.0917
45	3234.9143	3067.9013
46	3252.0882	3086.4339
47	3316.7515	3133.8528
48	3739.7125	3398.2568
49	3836.7084	3485.7056
50	3963.9919	3580.6481
51	4051.9380	3684.2866

This suggests that a nucleophilic or a free radical would more likely attack at these sites, most probably at (–30.0°) and for C3. This fact is also shown by the chemical shift anisotropy asymmetry (η) for C3.

The vibrational frequencies of the minima structure are given in Table 5.

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References cited in this synopsis

2 Gaussian 98, Revision A.6, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, and J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

3 R. Ditchfield, *Mol.Phys.* 1974, **27**, 789.

4 J.R. Cheesman, M.J. Frisch, F.J. Devlin and P.J. Stephens, *Chem. Phys. Lett.* 1996, **252**, 211.

5 R. McWeeny, *Phys. Rev.* 1962, **126**, 1028.

6 K. Wolinski, J.F. Hilton and P. Pulay, *J. Am. Chem. Soc.* 1990, **112**, 8251.