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Quantum Chemistry Study of Molecular Structure and Vibrational Spectrum of Dopamine

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ABSTRACT

The purpose of this research was to compare the performance of different DFT methods at different basis sets in predicting geometry and vibrational spectrum of dopamine. The molecular structure and infrared spectrum of dopamine was studied. Quantum chemical calculations using density functional theory (DFT) with functions B3LYP, B3PW91, X3LYP, M06 and M06-2X at various basis set levels (6-311++G(d,p), 6-311++G(2d,2p) and Aug-cc-pVDZ) were performed. The computed result indicates that X3LYP/6-311++G(d,p) level is distinctly superior to all the remaining DFT methods in predicting molecular structure of dopamine. The vibrational spectral analysis indicates the B3LYP/6-311++G(2d,2p) level is better than the other methods at all the remaining basis sets.

1. Introduction

Neurotransmitters are endogenous chemical messenger compounds, which are responsible for signal transmission, enhancement, and modulation in the central and sympathetic nervous systems [1, 2]. Dopamine or 4-(2-aminoethyl) benzene-1, 2-diol is a catecholamine and a fundamental representative of the group of neurotransmitters. As an adrenergic drug, it affects brain processes, which control movement and emotional response. As a hormone in vesicles of the adrenal medulla, it regulates the heart beat rate and the blood pressure [2, 3]. Dopamine receptors are also considered to be the major site of action of antipsychotic and anti-parkinsonism drugs [4]. For example, Parkinsonism is associated with a reduced dopamine level, whereas schizophrenia can be related to an increased dopamine activity [5]. Dopamine may exist in various forms, differing from each other by the arrangements of the ethylamine side chain and catechol hydroxyl groups. Its small size, biological significance, and pharmaceutical relevance have made it attractive target [3-14]. The crystal structure of Dopamine Hydrochloride has been studied by Bergin and Carlstrom [9] and C. L. Klein [10]. A Raman and UV-Vis study of catecholamines oxidized with Mn(III) have been carried out by Barreto et al [11]. Park et al [12] have studied the vibrational analysis of Dopamine Neutral Base based on density functional force field at B3LYP/6-31G (d,p) level. The vibrational spectra and normal coordinate analysis of Dopamine have been carried out by Gunasekaran et al [13]. Recently the vibrational analysis of Dopamine molecule has been made using FTIR and FTRaman spectroscopy by K. Ananddhan and R. Thilak Kumar [14]. DFT method is becoming increasingly popular among chemistry theoreticians and a lot of works have been reported in the field of determination of the molecular structure and computation of chemical properties [9-14]. There are various DFT methods and different basis sets and each of the DFT methods can be combined with various basis sets and applied into a computational method. No work has been reported to compare the performance of them in predicting geometry and vibrational spectrum of dopamine using B3LYP, B3PW91, X3LYP, M06 and M06-2X with three basis sets 6–311++G (d,p), 6–311++G(2d,2p), and Aug-cc-pVDZ. By comparing the calculation results of different DFT methods including B3LYP, B3PW91, X3LYP, M06 and M06-2X with various basis sets 6–311++G (d,p), 6–311++G(2d,2p), and Aug-cc-pVDZ, we can obtain more complete and reliable structural information and the better method to study dopamine. In this paper, we investigated the dopamine in the microscopic view and provided the relative data including the bond lengths and bond angles. The optimized geometry of the dopamine was characterized theoretically for the first time using X3LYP, M06 and M06-2X calculations [17] employing the higher basis sets 6-311++G(d,p).

2. Computational methods

The DFT calculations in this paper were performed using the Gaussian 09 program [16] and the results were analyzed with the Gauss View 5.0 molecular visualization program [16]. The molecular geometry optimizations at the DFT level (B3LYP, B3PW91, X3LYP, M06 and M06-2X functionals) with basis sets 6-311++G(d,p), 6-311++G(2d,2p) and Aug-cc-pVDZ were performed and vibrational frequencies were computed. In this paper, we employed five DFT methods which comprise the gradient-corrected, hybrid functional and newly developed exchange-correlation functional [15, 17-19]. B3LYP is the dynamical functional, Lee–Yang–Parr gradient-corrected correlation functional (LYP) [15, 18], coupled with Becke's three-parameter gradient exchange correction functional (B3) [15, 18]. Perdew–Wang 91 (PW91) is the part of exchanged function which was put forward by Perdew and Wang in 1991, which usually abbreviated as PW91. We also employed B3PW91 method, which provided non-local correlation exactly by Perdew/Wang 91.

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The molecular structure of dopamine was optimized using these five DFT methods at 6-311++G(d,p) basis sets firstly, and then the superior method was employed again with the basis sets respectively, including 6-311++G(d,p), 6-311++G(2d,2p) and Aug-cc-pVDZ. On this basis of optimized molecular structure, the vibrational frequencies of dopamine were calculated and the mean absolute deviations between the calculated and observed vibrational frequencies for each method were compared.

3. Results and discussion

3.1 Geometry optimization with various methods at 6-311++G(d,p) basis set

Geometry optimization was calculated with DFT methods at 6-311++G(d,p) basis set firstly, which determined the most thermodynamically stable dopamine conformer that may be observed. In the basis of optimized molecular structure, the calculated IR spectra will be in better agreement with the experimental IR spectra [13, 14]. The comparison of theoretical molecular structure calculated by B3LYP, B3PW91, X3LYP, M06 and M06-2X methods at 6-311++G(d,p) basis set and the experimental results from X-ray crystal analysis of dopamine [10] are summarized in Table 1. From the comparisons of the theoretical and experimental results, we can reach some conclusion. The calculated C3–C4 bond lengths of dopamine with B3LYP, B3PW91, X3LYP, M06 and M06-2X methods at 6-311++G(d,p) basis set are 1.390, 1.388, 1.389, 1.384, 1.386 Å, respectively. In comparison with the same experimental value of 1.389 Å [10], the error is on average about 0.001 Å for B3LYP, 0.001 Å for B3PW91, 0.000 Å for X3LYP, 0.005 Å for M06, 0.003 Å for M06-2X. Obviously, the X3LYP/6-311++G(d,p) is better than all the remaining methods in predicting the C3–C4 bond lengths of dopamine. The mean absolute deviations between the theoretical and experimental values for each method are also listed in Table 1, so that the performance of each DFT method in predicting the bond length of dopamine could be investigated. The mean absolute deviations between the calculated bond length and experimental value are 0.0080 for B3LYP, 0.0081 for B3PW91, 0.0078 for X3LYP, 0.0102 for M06, 0.0084 for M06-2X, respectively. Synthesizing all the result talked above, we can draw the conclusion that X3LYP method is the best in predicting the bond length of dopamine. We also compared the calculated angles for dopamine with the experimental results.

The error range between the computed angle for dopamine employed different methods with 6-311++G(d,p) basis set and the experimental value is from 0.65° to 0.73° for C1–C2–C3 angle, 0.63-0.84° for C2–C3–C4 angle, 0.18-0.36° for C3–C4–C5 angle, 0.26-0.39° for C4–C5–C6 angle, 0.49-0.83° for C5–C6–C1 angle, 0.04-0.23° for C6–C1–C2 angle, 5.50-5.65° for C1–C2–O17 angle, 3.85-4.16° for C2–C3–O8 angle, 0.28-0.58° for C5–C6–C9 angle, 1.21-2.87° for C6–C9–C10 angle, 0.11-0.62° for C9–C10-N11 angle, respectively.

3.2 Geometry optimization with X3LYP at various basis sets

The comparison of theoretical molecular structure calculated by with X3LYP at 6–311++G(d,p), 6–311++G(2d,2p) and Aug-cc-pVDZ basis sets and the experimental results [10] is summarized in Table 2. In Table 2, we have compared the results calculated by X3LYP method at 6–311++G(d,p), 6–311++G(2d,2p) and Aug-cc-pVDZ basis sets respectively with experimental results. The calculated C3–C4 bond lengths of dopamine with X3LYP methods at 6–311++G(d,p), 6–311++G(2d,2p) and Aug-cc-pVDZ basis sets are 1.389, 1.386, 1.393 Å, respectively. In comparison with the same experimental value of 1.389 Å [10], the error is on average about 0.000 Å for 6-311++G(d,p), 0.003 Å for 6-311++G(2d,2p), 0.004 Å for Aug-cc-pVDZ. The calculated C3–C4 bond lengths of dopamine with X3LYP/6–311++G(d,p) were found to be in better agreement with the experimental value of 1.389 Å [10] than the results calculated at the remaining levels. The mean absolute deviations between the calculated bond length and experimental value are 0.0078 for 6-311++G(d,p), 0.0084 for 6-311++G(2d,2p), 0.0079 for Aug-cc-pVDZ respectively. These results indicate that X3LYP/6-311++G(d,p) level is the best to predict the bond length of dopamine. The optimized molecular structure of dopamine, which calculated at X3LYP/6-311++G(d,p) level, with the label and symbol of atoms is presented in Fig. 1. In the calculated angle values of dopamine, which used X3LYP method at various basis sets, the error range between theoretical and experimental results is also indicate that X3LYP/6-311++G(d,p) is very superior and by contrast, there

Table 1. Comparison of bond lengths (in Å) and bond angles (in °) calculated for dopamine with various DFT methods.

Geometry	Exp.[a]	6-311++G(d,p)				
		B3LYP	B3PW91	X3LYP	M06	M06-2X
R(C1-C2)	1.393	1.389	1.387	1.388	1.384	1.385
R(C2-C3)	1.403	1.400	1.398	1.399	1.395	1.397
R(C3-C4)	1.389	1.390	1.388	1.389	1.384	1.386
R(C4-C5)	1.396	1.394	1.392	1.393	1.388	1.392
R(C5-C6)	1.395	1.398	1.396	1.397	1.392	1.393
R(C6-C1)	1.399	1.401	1.399	1.400	1.394	1.398
R(C2-O7)	1.357	1.379	1.372	1.378	1.367	1.371
R(C3-O8)	1.372	1.365	1.359	1.364	1.354	1.358
RC6-C9)	1.510	1.514	1.508	1.512	1.502	1.509
R(C9-C10)	1.521	1.538	1.533	1.537	1.524	1.532
R(C10-N11)	1.490	1.467	1.460	1.466	1.455	1.462
Mean absolute deviation		0.0080	0.0081	0.0078	0.0102	0.0084
∠C1–C2–C3	119.91	120.64	120.61	120.64	120.56	120.64
∠C2–C3–C4	119.78	118.99	118.94	119.00	119.02	119.15
∠C3–C4–C5	119.93	120.24	120.29	120.23	120.26	120.11
∠C4–C5–C6	120.89	121.28	121.28	121.28	121.16	121.15
∠C5–C6–C1	118.87	118.04	118.05	118.10	118.23	118.38
∠C6–C1–C2	120.60	120.80	120.83	120.78	120.76	120.56
∠C1–C2–O7	118.63	124.13	124.21	124.15	124.25	124.28
∠C2–C3–O8	116.73	120.89	120.76	120.84	120.79	120.58
∠C5–C6–C9	120.73	121.28	121.31	121.28	121.01	121.15
∠C6–C9–C10	110.75	113.62	113.29	113.54	112.24	111.96
∠C9–C10–N11	110.84	111.15	110.95	111.13	110.41	110.22

[a] Experimental X-ray crystal data from Ref. [10].

Table 2. Comparison of bond lengths (in Å) and bond angles (in °) calculated for dopamine with X3LYP method at different basis sets.

Geometry	Exp.[a]	X3LYP		
		6-311++G(d,p)	6-311++G(2d,2p)	Aug-cc-pVDZ
R(C1-C2)	1.393	1.388	1.386	1.393
R(C2-C3)	1.403	1.399	1.396	1.403
R(C3-C4)	1.389	1.389	1.386	1.393
R(C4-C5)	1.396	1.393	1.391	1.398
R(C5-C6)	1.395	1.397	1.395	1.401
R(C6-C1)	1.399	1.400	1.397	1.404
R(C2-O7)	1.357	1.378	1.377	1.380
R(C3-O8)	1.372	1.364	1.364	1.367
RC6-C9)	1.510	1.512	1.511	1.513
R(C9-C10)	1.521	1.537	1.535	1.537
R(C10-N11)	1.490	1.466	1.465	1.467
Mean absolute deviation		0.0078	0.0084	0.0079
∠C1–C2–C3	119.91	120.64	120.56	120.62
∠C2–C3–C4	119.78	119.00	119.01	119.02
∠C3–C4–C5	119.93	120.23	120.26	120.21
∠C4–C5–C6	120.89	121.28	121.27	121.30
∠C5–C6–C1	118.87	118.10	118.00	118.04
∠C6–C1–C2	120.60	120.78	120.89	120.81
∠C1–C2–O7	118.63	124.15	123.95	124.00
∠C2–C3–O8	116.73	120.84	120.92	121.00
∠C5–C6–C9	120.73	121.28	121.27	121.24
∠C6–C9–C10	110.75	113.54	113.61	113.44
∠C9–C10–N11	110.84	111.13	111.17	111.02

[a] Experimental X-ray crystal data from Ref. [10].

would have a obvious deviation if 6-311++G(2d,2p) basis set was used. So we can draw a conclusion that X3LYP level with 6–311++G(d,p) basis set is excellent and reliable in predicting molecular structure of dopamine.

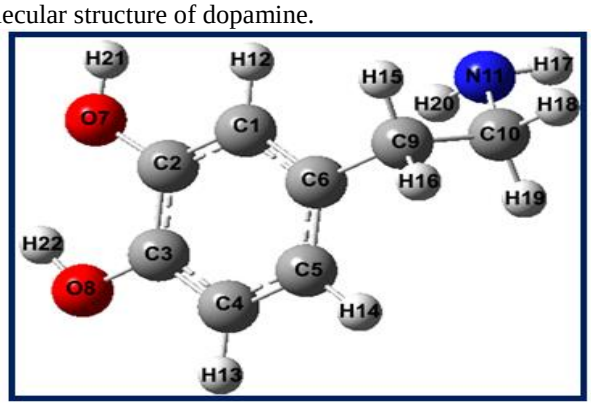

Fig 1. The optimized structure of dopamine at X3LYP/6-311++G(d,p) level.

3.3 Vibrational spectra calculated with various methods at 6-311++G(d,p) basis set

We calculated the IR frequencies and intensities of dopamine at the DFT level. The calculated infrared spectra of dopamine are available with author. The frequencies (in cm^{-1}) and IR intensity (in km/mol) for dopamine with various DFT methods at 6-311++G(d,p) basis set were compared with the observed frequencies and intensities in Table 3.

The calculated O7-H21 stretching vibrational modes of dopamine with B3LYP, B3PW91, X3LYP, M06 and M06-2X level at 6-311++G(d,p) basis set are 3850, 3878, 3857, 3907 and 3920 cm^{-1}, respectively, and in the comparison with the experimental value 3342 cm^{-1}. The error between the theoretical and experimental values are 508 cm^{-1} for B3LYP, 536 cm^{-1} for B3PW91, 515 cm^{-1} for X3LYP, 565 cm^{-1} for M06, 578 cm^{-1} for M06-2X, respectively.

In the same manner, the calculated O8-H22 stretching vibrational modes of dopamine with B3LYP, B3PW91, X3LYP, M06 and M06-2X level at 6-311++G(d,p) basis set are 3795, 3816, 3802, 3842 and 3867 cm^{-1}, respectively, and in the comparison with the experimental value 3317 cm^{-1}. The error between the theoretical and experimental values are 478 cm^{-1} for B3LYP, 499 cm^{-1} for B3PW91, 485 cm^{-1} for X3LYP, 525 cm^{-1} for M06, 550 cm^{-1} for M06-2X, respectively. So, for the purpose of investigating the performance and limits of different DFT methods in predicting the vibrational frequencies, the mean absolute deviation between the calculated and observed fundamental vibrational frequencies for each method are listed in Table 3. The mean absolute deviation between the experimental and the theoretical frequencies are 447.67 cm^{-1} for B3LYP, 471.67 cm^{-1} for B3PW91, 454.67 cm^{-1} for X3LYP, 489.67 cm^{-1} for M06 and 509.67 cm^{-1} for M06-2X, respectively.

Table 3. Theoretical harmoninc frequencies[a] (cm^{-1}) and infrared intensities[b] (km/mol) calculated for dopamine with various DFT methods using 6-311++G(d,p) basis set.

Mode no.	Exp.[c]	6-311++G(d,p)					Assignment
		B3LYP	B3PW91	X3LYP	M06	M06-2X	
Q60	3342	3850 (78)	3878 (81)	3857 (80)	3907 (108)	3920 (98)	O7-H21 str.
Q59	3317	3795 (107)	3816 (110)	3802 110)	3842 (140)	3867 (127)	O8-H22 str.
Q58	3220	3577 (2)	3600 (3)	3584 (3)	3599 (7)	3621 (7)	NH_2 asym. str.
Mean absolute deviation		447.67	471.67	454.67	489.67	509.67	

[a]Frequencies of the modes: Q58 to Q60 no scale. [b]IR intensity: the value in parenthesis; [c]Experimental infrared data from Ref. [13, 14].

Table 4. Theoretical harmoninc frequencies[a] (cm^{-1}) and infrared intensities[b] (km/mol) calculated for dopamine with B3LYP method using different basis sets.

Mode no.	Exp.[c]	B3LYP			Assignment
		6-311++G(d,p)	6-311++G(2d,2p)	Aug-cc-pVDZ	
Q60	3342	3850 (78)	3833 (77)	3858 (75)	O7-H21 str.
Q59	3317	3795 (107)	3781 (103)	3804 (98)	O8-H22 str.
Q58	3220	3577 (2)	3553 (3)	3599 (2)	NH_2 asym. str.
Mean absolute deviation		447.67	429.33	460.67	

[a]Frequencies of the modes: Q58 to Q60 no scale. [b]IR intensity: the value in parenthesis. [c]Experimental infrared data from Ref. [13, 14].

It is clear that B3LYP method is superior to the remaining methods in predicting vibrational spectrum of dopamine.

3.4 Vibrational spectra calculated with B3LYP methods at various basis sets

The calculated infrared spectra of dopamine are depicted in Fig. 2. Both the calculated vibrational frequencies and IR intensity for dopamine with B3LYP method using various basis sets and the corresponding frequencies in the experimental spectra are presented in Table 4. The calculated vibrational frequencies are no scale. The mean deviation between the theoretical and experimental frequencies are 447.67 cm^{-1} for 6-311++G(d,p), 429.33 cm^{-1} for 6-311++G(2d,2p) and 460.67 cm^{-1} for Aug-cc-pVDZ, respectively. As the results shows, 6-311++G(2d,2p) basis sets are the best to predict all frequencies on average for dopamine molecule.

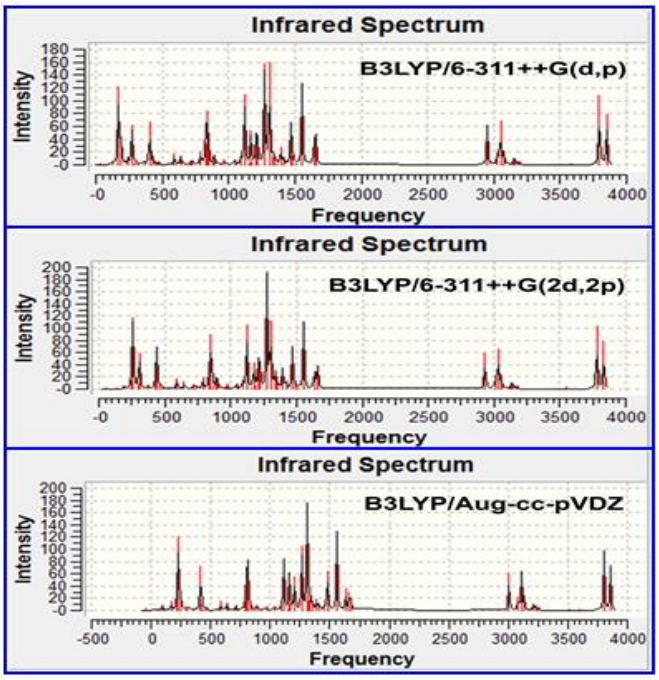

Fig 2. The theoretical frequencies (no scale) and infrared intensities calculated with B3LYP methods using 6-311++G(d,p), 6-311++G(2d,2p) and Aug-cc-pVDZ basis sets for dopamine.

4. Conclusion

The molecular structure and infrared spectrum of dopamine were calculated using various DFT methods including B3LYP, B3PW91, X3LYP, M06 and M06-2X at 6-311++G(d,p), 6-311++G(2d,2p) and Aug-cc-pVDZ basis sets respectively.

Some recent studies have shown that the density functional theory (DFT) is much superior to the conventional methods in computing molecular and chemical properties such as geometries, harmonic frequencies and energies. Therefore, the purpose of this paper is to determine the comparative performance of different DFT methods in predicting molecular structure and vibrational spectra of dopamine. In this study, two most important conclusions can be drawn from the comparisons between the calculated and experimental structural parameters and vibrational frequencies. 1. X3LYP/6-311++G(d,p) method is clearly superior to all of the remaining DFT levels in predicting the structure of dopamine. 2. It is remarkably that the B3LYP/6-311++G(2d,2p) level show better performance in the vibration spectra prediction of dopamine.

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