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PHYSICAL CHEMISTRY 2016

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CONFORMATIONAL AND VIBRATIONAL ANALYSIS OF 3-METHOXYTYRAMINE

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ABSTRACT
Conformations and vibrational spectra of 3-methoxytyramine (3-MT), a metabolite of dopamine, have been investigated by density functional theory, at B3LYP/6-311++G(d,p) level, implemented in Gaussian Program package. From crystallographic data, by the conformational search, the most stable conformations were determined in gas phase. The most stable conformer, with emphasis on the specific interactions (hydrogen bonds and N–H···π) stabilizing the structure, is discussed. Experimental IR and Raman spectra, recorded in the region 4000-400 cm⁻¹, have been assigned based on the potential energy distribution (PED).

INTRODUCTION
3-methoxytyramine (3-MT) is a major extracellular metabolite of dopamine, produced via catechol-O-methyltransferase from parent molecule. This molecule acts as neuromodulator that can be involved in movement control. Its elevated concentrations may indicate mental disorders, brain and carcinoid tumors’ development [1]. Unlike the other metabolites of dopamine, for example homovanillic acid and 3,4-dihydroxyphenylacetic acid, 3-MT has not been investigated by the means of theoretical methods and results of those being compared to experimental spectra and crystallographic data. In present study, the theoretical vibrational spectra are compared to experimental (IR and Raman), after the detailed conformational analysis.

THEORETICAL AND EXPERIMENTAL METHODS
All of the calculations have been performed with the Gaussian 09 program package [2]. Density functional theory (DFT) with B3LYP functional in conjunction with 6-311++G(d,p) basis set, has been employed for the conformational search of the most stable conformer of 3-MT. Vibrational
frequencies, computed in harmonic approximation, verified that the minimum of potential energy surface was found. The calculated frequencies were scaled based on the least square method, with scaling factor of 0.9800 in order to obtain better reproduction of experimental spectra. The assignation of vibrational modes was done based on PED analysis implemented in VEDA [3] software. Natural bond Orbital analysis was performed in order to investigate possible stabilization interactions.

RESULTS AND DISCUSSION
Conformational analysis
3-methoxtyramine 3-MT (Figure 1.) consists of aliphatic 2-aminoethyl chain and aromatic ring with hydroxyl and methoxy substituents. For the present study the protonated form of molecule was chosen, because 3-MT hydrochloride was used for experiments. The conformational search was as following: three possible orientations of substituents were selected – hydroxyl and methoxy substituents oriented in the same direction with methoxy group pointing to hydroxyl (a), with hydroxyl group pointing to methoxy (b), and with substituents pointing in opposite directions (c). For these orientations, the rotation around dihedral angles $\alpha$ and $\beta$ was performed and minima of the potential energy curve taken as starting structures for optimization.

There was the total of 12 structures. Based on differences in energy and enthalpy, two conformers, that were the most stable, were chosen (Figure 2), and named 1-I and 2-I. In the most stable conformers hydroxyl and methoxy substituents are oriented in the same direction, leading to the formation of an intramolecular OH···O–CH$_3$ hydrogen bond. The energy difference was 20.51 kJ/mol with 1-I being more stable, but when enthalpy is concerned structure
2-l is more stable for 13.86 kJ/mol, which is very ambiguous about the real conformation of 3-MT. Structure 1-l resembles the most stable conformer of dopamine from reference of Lagutschewkov[4] and this structure is additionally stabilized by the presence of weak intermolecular bond between N-H group of aliphatic chain and aromatic ring π system. The stabilization energy for this conformer is only 2 kJ/mol as predicted by NBO. These interactions are broken if solvent model for water is used, and more stable conformer is l-l for only 0.29 kJ/mol. Structure 2-l is found in crystallographic structure of some salts of 3-MT, due to strong interactions with surrounding molecules through amino group.

Vibrational analysis
The total of 72 vibrational modes were calculated and scaled, in the region between 4000 and 400 cm$^{-1}$, of which 60 are assigned based on PED analysis. As this is a low symmetry molecule, the most of modes are present in both spectra. The correlation between experimental and theoretical spectra was higher than 0.99. The comparative representation of experimental and theoretical IR and Raman spectra (R) are shown in Figure 3.

In high frequency region (4000-2000 cm$^{-1}$) the most prominent peak is assigned to N-H stretching vibration of aliphatic chain, along with C-H stretching mode of aromatic ring and aliphatic chain (3440-2940 cm$^{-1}$). The mid frequency region (1700-100 cm$^{-1}$) comprises of medium to strong and very strong bands at 1603, 1279, 1249, 1160, 1032 cm$^{-1}$ (IR) and 1616, 1593, 1279 and 1025 cm$^{-1}$ (R) assigned to C–C and C–O stretching vibrations of aromatic ring and aliphatic chain, along with weak vibrations.
of the same type at 1433, 1385, 1085 cm\(^{-1}\) (IR) and 1150 and 1083 cm\(^{-1}\) (R). In the region between 1500 and 1000 cm\(^{-1}\) there are bending H–C–C, C–C–C, H–C–H, H–C–N and H–O–C modes appearing as weak intensity bands at 1623, 1506, 1471, 1458, 1304 cm\(^{-1}\) (IR) and 1508, 1303, 1206 and 1131 cm\(^{-1}\) (R). Below 1000 cm\(^{-1}\), the observed bands go from strong to medium, and are assigned to OC, CC and NC stretching modes (1032 and 799 cm\(^{-1}\) (IR) and 1025 and 803 cm\(^{-1}\) (R)). The torsion modes, composed of mixed vibrations of type C–C–C–C, H–C–C–C, C–C–C–O, H–O–C–C and C–C–O–C are positioned at 816, 724, 571, 460 and 457 cm\(^{-1}\) (IR) and 821, 725, 571 and 454 cm\(^{-1}\) (R) mostly as low intensity bands.

**CONCLUSION**

The conformational search for the most stable structure of 3-MT was performed at B3LYP/6-311++G(d, p) level. Formation of hydrogen bond between O–H and O–CH\(_3\) additionally stabilizes structure\(1\)-l, along with N–H interactions with π system, thus making the discussed structure the most stable in gas phase, although these interactions are broken in polar solvent. For the comparison, structure \(2\)-l was chosen because it resembles structure from crystallographic data. Experimental vibrational spectra were assigned based on the best-fit comparison between experimental and theoretical spectra, with correlation of higher than 0.99, thus proving that structure of 3-MT describes well structure in solid state and solution.

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**REFERENCES**


