Spectroscopic (FT-IR, Raman, NMR) and DFT Quantum Chemical Studies on Phenoxyacetic Acid and Its Sodium Salt

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Abstract. FT-IR, Raman, and NMR spectra of phenoxyacetic acid and its sodium salt were recorded and analyzed. Optimized geometrical structures of studied compounds were calculated by B3LYP/6-311++G** method. The atomic charges were calculated by Mulliken, NPA (natural population analysis), APT (atomic polar tensor), MK (Merz-Singh-Kollman method), and ChelpG (charges from electrostatic potentials using grid-based method) methods. Geometric as well as magnetic aromaticity indices, dipole moments, and energies were also calculated. The theoretical wavenumbers and intensities of IR spectra as well as chemical shifts in ^1H and ^{13}C NMR spectra were obtained. The calculated parameters were compared with experimental characteristics of these molecules.

Keywords: Phenoxyacetic acid, sodium phenoxyacetate, FT-IR, Raman, DFT, molecular structure

1. Introduction

Phenoxyacetic acid has been investigated by various researches because of its biological activities. It is useful in the treatment of insulin resistance and hyperglycemia [1]. Derivatives of phenoxyacetic acid are widely used in herbicide and pesticide formulations. The molecular basis of their mode of action is not fully understood. The estimation of the electronic charge distribution in metal complexes and salts allows to predict what kind of deformation of the electronic system of ligand would undergo during complexation [2]. It also permits to make more precise interpretation of mechanism by which metals affect the biochemical properties of ligands. In this paper the influence of sodium cation on the electronic system of phenoxyacetic acid was studied.

2. Experimental

Sodium phenoxyacetate was prepared by dissolving the powder of phenoxyacetic acid in the water solution of the appropriate sodium hydroxide in a stoichiometric ratio (1 : 1). Both reagents were

obtained from Aldrich Chemical Company. The solution was left at the room temperature for 24 h until the sample crystallized in the solid-state. Precipitants were filtered, washed by water, and dried under reduced pressure at 110°C. Obtained complex was anhydrous—in the IR spectra of solid-state sample the lack of bands characterized for crystallizing water was observed.

The IR spectra were recorded with the Equinox 55, Bruker FT-IR spectrometer within the range 4000–400 cm^{-1} . Samples in the solid state were measured in KBr pellets. The resolution of spectrometer was 1 cm^{-1} . Raman spectra of solid samples in capillary tubes were recorded in the range of 4000–400 cm^{-1} with a FT-Raman accessory of the Perkin Elmer System 2000. The resolution of spectrometer was 1 cm^{-1} . The NMR spectra of DMSO solution were recorded with the NMR AC 200 F, Bruker unit. TMS was used as an internal reference.

The density functional (DFT) hybrid method B3LYP/6-311++G** was used to calculate optimized geometrical structures of studied compounds (Figure 1). All theoretical calculation were performed using the Gaussian'09 [3] of programs running on a PC computer.

3. Results and Discussion

3.1. Vibrational Spectra

Experimental and theoretical bands together with their relative intensities and band assignments for phenoxyacetic acid and its sodium salt in FT-IR and Raman spectra were obtained. Complete assignments of all bands require application of both IR and Raman methods supported by theoretical calculations and literature data [4]. The calculated wavenumbers were obtained by B3LYP method and 6-311++G** basis set. The correlation between calculated and experimentally obtained wavenumbers in IR and Raman spectra of phenoxyacetic acid and sodium phenoxyacetate was studied and good agreement was found. The correlation coefficient R^2 for phenoxyacetic acid spectra is amount 0.9972 and for its sodium salt $R^2 = 0.9990$. The corresponding values for Raman spectra amount to 0.9969 and 0.9975.

IR and Raman spectra for phenoxyacetic acid and its sodium salt are presented in Figure 1. Comparing results obtained for sodium phenoxyacetate to the, respectively, values of phenoxyacetic acid, certain changes of intensities and wavenumbers of the bands of aromatic system and carboxylic group can be noticed.

The changes of intensities and wavenumbers of the bands of aromatic system and carboxylate group in the case of sodium salt were discussed comparing to the free ligand. The characteristic bands occurring in the IR spectra of sodium phenoxyacetate, which do not exist in the spectra of free acid, for example: symmetric or asymmetric stretching vibrations $\nu(\text{COO})$ and in plane $\beta(\text{COO})$ and out of plane $\gamma(\text{COO})$ deformations of carboxylic group were noticed. On the other hand, the lack of bands, which are characteristic for phenoxyacetic acid (the C=O band, 1736 and 1703 cm^{-1} ; $\beta(\text{OH})$ band, 1300 cm^{-1} , broad band of $\nu(\text{OH})$, e.g.) were observed in the sodium salt spectra. The wavenumbers of aromatic bands numbered as 20b, 9b, 17a, and 5 in IR as well as in Raman spectra increase in comparison to free acid. For 2, 3, and 17b bands the increase of wavenumbers was noticed only in IR spectra. In the case of 8a and 6a bands the decrease in comparison to phenoxyacetic acid was observed in IR spectra, whereas for 2, 3, 17b, and 19a bands in Raman the decrease of wavenumbers was noticed. There are also some changes of alky chain part of studied molecules. The wavenumbers of $\nu_{\text{as}}(\text{CH}_2)$ and $\nu(\text{O}-\text{CH}_2)$ bands shift to higher values in IR spectra of sodium phenoxyacetate, while $\nu_{\text{s}}(\text{CH}_2)$ band shifts to lower values.

Figure 1: Raman (a) and IR (b) spectra for phenoxyacetic acid (PAA) and its sodium salt (NaPA).

Figure 2: Calculated (B3LYP/6-311++G**) as well as experimental chemical shifts: (a) ¹H NMR, (b) ¹³C NMR of phenoxyacetic acid (PAA) and its sodium salt (NaPA).

3.2. NMR Spectra

Theoretically as well as experimentally obtained ¹H NMR and ¹³C NMR chemical shifts of phenoxyacetic acid and its sodium salt are presented in Figure 2. The linear correlation between proton as well as carbon NMR shieldings of studied compounds and experimental data is observed. The correlation coefficient (R^2) for ¹H NMR spectra are amount to 0.9739 for phenoxyacetic acid (PAA) and 0.9868 for sodium phenoxyacetate (NaPA). For ¹³C NMR spectra corresponding values are 0.8945 and 0.9035. All protons in sodium phenoxyacetate are shifted diamagnetically in comparison to PAA. This tendency suggests that introduction of sodium atom causes the decrease in ring current intensity. Some changes in ¹³C NMR spectra were also observed. The chemical shifts of almost all carbon atoms in sodium phenoxyacetate molecule, except of C1, C8, and C9 atoms, are lower than those in free acid.

3.3. Calculated Molecular Structure

Optimized geometrical structures of phenoxyacetic acid as well as of sodium phenoxyacetate molecule were obtained using B3LYP/6-311++G** method. The bond lengths and the angles between bonds in sodium salt molecule in comparison to free acid were presented in Table 1. The increase of almost all bond lengths in aromatic ring except of C2–C3 and C5–C6 bonds in sodium salt molecule in comparison to acid was observed. The increase of O7–C8, C8–C9, C9–O10, and O10–O11a bond lengths was also noticed, whereas bond lengths of C1–O7, C9–O11, and O11–O11a decreased in NaPA in comparison to PAA molecule. The differences between C9–O10 and C9–O11 as well as O10–O11a and O11–O11a bond lengths almost disappeared. In the case of angles, the increase was observed for almost all angles in the aromatic ring, except of C3–C4–C5 and C6–C1–C2 angles in NPA molecule. For C2–C1–O7 and O7–C8–C9 angles the increase was observed, but decrease was noticed only for C8–C9–O10, C9–O11–O11a, and C9–O10–O11a angles.

Table 1: The bond lengths, angles, aromatic indices, values of dipole moment, and energy calculated (B3LYP/6-311++G**) for alkali metal phenoxyacetates.

Atoms	PAA	NaPA	Atomic numbers of PAA and NaPA molecules
Bond lengths (Å) ^a
C1–C2	1.3963	1.3992	
C2–C3	1.3981	1.3977	
C3–C4	1.3897	1.3901	
C4–C5	1.3980	1.3984	
C5–C6	1.3877	1.3873	
C6–C1	1.3995	1.4024	
C1–O7	1.3706	1.3617	
O7–C8	1.4038	1.4162	
C8–C9	1.5174	1.5290	
C9–O10	1.1977	1.2559	
C9–O11	1.3576	1.2689	
O10–H(Na)11a	0.9689	2.2169	
O11–H(Na)11a	2.3148	2.2199	
Angles (°)
C1–C2–C3	119.34	119.55	
C2–C3–C4	120.89	121.01	
C3–C4–C5	119.24	119.07	
C4–C5–C6	120.61	120.63	
C5–C6–C1	119.84	120.14	
C6–C1–C2	120.10	119.59	
C6–C1–O7	115.28	115.55	
C2–C1–O7	124.62	124.87	
C1–O7–C8	118.49	118.64	
O7–C8–C9	108.85	111.45	
C8–C9–O10	127.23	120.84	
C8–C9–O11	109.00	114.37	
C9–O11–H(Na)11a	107.43	87.23	
O10–C9–O11	123.78	124.79	
H(Na)11a–O10–C9	107.43	87.41	
Geometric aromaticity indices			
HOMA ^b	0.982557	0.976809	
A _J ^c	0.99765	0.99672	
BAC ^d	0.93095	0.92338	
I ₆ ^e	96.21196	95.52024	
Magnetic aromaticity indices			
NICS ^f	–11.0192	–8.8957	
Dipole moment (<i>D</i>)	2.48	6.99	
Energy (hartree) ^g	–535.5	–542.55	

^a1 Å = 10^{–10} m; ^babbreviation from Harmonic Oscillator Model of Aromaticity; ^cnormalized function of variance of bond lengths; ^dbond alternation coefficient; ^eBird's index [5]; ^fnuclear independent chemical shifts; ^g1 hartree = 2625.5 kJ/mol.

Figure 3: Electronic charge distribution (NPA method) calculated for molecules of phenoxyacetic acid (a) and its sodium salt (b).

Geometric and magnetic aromaticity indices [5–7], dipole moments, and energies were calculated and also shown in Table 1. All geometric aromaticity indices calculated for sodium phenoxyacetate in comparison to acid molecule decreased. It indicates that aromaticity of salt molecule decreased in comparison to free acid. This conclusion was confirmed by values of magnetic aromaticity indices NICS.

Mulliken, NPA, APT, MK, and ChelpG methods were used to calculate atomic charges on the atoms of phenoxyacetic acid molecule and its sodium salt. One of them, exemplary, is presented in Figure 3. The highest changes irrespective of used method are observed for carboxylate group. Total charges calculated for COO significantly decrease in comparison to free acid, for example, the values calculated by the Mulliken method for PAA amount to -0.766 , but for NaPA molecule -1.194 . In the case of other methods corresponding values are -0.473 and -0.852 (NPA); -0.292 and -0.763 (APT); -0.473 and 0.835 (MK); -0.341 and -0.851 (ChelpG method).

4. Conclusions

Replacement of hydrogen by sodium in molecule causes significant changes in geometrical structure of studied molecules. The highest changes are noticed for carboxylate group, as may be expected. However almost all bond lengths in aromatic ring insignificantly increase, the decrease of aromaticity of studied molecules are observed. The displacements of bands in FT-IR, Raman, as well as in NMR spectra are also noticed. In IR and Raman spectra, different changes of bands are observed, some of them shift to higher, other to lower, wavenumbers. In ^1H and ^{13}C NMR spectra almost all bands shift to lower values in sodium phenoxyacetate spectra in comparison to free acid. It is characteristic tendency for molecules, in which the decrease of aromaticity is noticed.

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References

- [1] N. Sundaraganesan, C. Meganathan, B. Anand, and C. Lapouge, "FT-IR, FT-Raman spectra and ab initio DFT vibrational analysis of p-bromophenoxyacetic acid," *Spectrochimica Acta Part A*, vol. 66, no. 3, pp. 773–780, 2007.
- [2] W. Lewandowski, M. Kalinowska, and H. Lewandowska, "The influence of metals on the electronic system of biologically important ligands. Spectroscopic study of benzoates, salicylates, nicotines and isoorotates," *Journal of Inorganic Biochemistry*, vol. 99, no. 7, pp. 1407–1423, 2005.
- [3] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., *Gaussian 09 (Revision A.1)*, Gaussian, Inc., Wallingford, Conn, USA, 2009.
- [4] G. Varsányi, *Assignments for Vibrational Spectra of 700 Benzene Derivatives*, Akademiai Kiado, Budapest, Hungary, 1973.
- [5] T. M. Krygowski and M. Cyrański, "Separation of the energetic and geometric contributions to the aromaticity of π -electron carbocyclics," *Tetrahedron*, vol. 52, no. 5, pp. 1713–1722, 1996.
- [6] E. Regulska, M. Samsonowicz, R. Świsłocka, and W. Lewandowski, "Molecular structure of alkali metal 4-nitrobenzoates," *Journal of Physical Organic Chemistry*, vol. 20, no. 2, pp. 93–108, 2007.
- [7] P. Von Ragué Schleyer, M. Manoharan, Z. X. Wang et al., "Dissected nucleus-independent chemical shift analysis of π -aromaticity and antiaromaticity," *Organic Letters*, vol. 3, no. 16, pp. 2465–2468, 2001.