Theoretical and Experimental Studies on Alkali Metal Phenoxylacetates

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Abstract. Optimized geometrical structures of alkali metal phenoxylacetates were obtained using B3LYP/6-311++G** method. Geometric and magnetic aromaticity indices, dipole moments, and energies were calculated. Atomic charges on the atoms of phenoxylacetic acid molecule and its alkali metal salts were calculated by Mulliken, APT (atomic polar tensor), NPA (natural population analysis), MK (Merz-Singh-Kollman method), and ChelpG (charges from electrostatic potentials using grid-based method) methods. The theoretical wavenumbers and intensities of IR as well as chemical shifts in NMR spectra were obtained and compared with experimental data. The effect of alkali metals on molecular structure of phenoxylacetic acid appears in the shift of selected bands along the series of alkali metal salts. The correlations between chosen bands and some metal parameters, such as electronegativity, ionization energy, and atomic, and ionic radius, have been noticed.

Keywords: Alkali metal phenoxylacetates, FT-IR, NMR, UV, DFT, molecular structure

1. Introduction

Antimicrobial activity, anticancer, analgesic and anti-inflammatory are some of the important properties of phenoxylacetic acids, which are widely used as plant growth regulators and herbicides. Due to their solubility in water they can move in agricultural ecosystems and cause the pollution of surface and ground waters [1]. It seems to be interesting to study the formation of phenoxylacetate salts with common ions in soil. This paper is a continuation of our reports on the metal effect on the electronic system of carboxylic acids [2, 3]. The influence of lithium, sodium, potassium, rubidium, and cesium on the electronic system of the salt molecules was analyzed in this paper.

2. Experimental

Lithium, sodium, potassium, rubidium, and cesium phenoxylacetates were prepared by dissolving the powder of phenoxylacetic acid in the water solution of the appropriate metal hydroxide in a stoichiometric ratio (1 : 1). All 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 complexes were anhydrous—in the IR spectra of solid state samples the lack of bands characterized for crystallizing water was observed.

Figure 1: Atomic numbers in phenoxyacetate molecule.

The IR spectra were recorded with the Equinox 55, Bruker FT-IR spectrometer within the range $4000\text{--}400\text{ cm}^{-1}$. Samples in the solid state were measured in KBr pellets. The resolution of spectrometer was 1 cm^{-1} . UV/Vis spectra were recorded with the DR/4000 U, HACH spectrophotometer. 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 calculations were performed using the GAUSSIAN 09 [4] program running on a PC computer.

3. Results and Discussion

3.1. Calculated Data

Optimized geometrical structures of lithium (LiPA), sodium (NaPA), and potassium (KPA) phenoxyacetates were calculated using B3LYP/6-311++G** method. The bond lengths and the angles between bonds in studied molecules are presented in Table 1. The changes of almost all bond lengths in aromatic ring are noticed in the order from lithium to sodium phenoxyacetate molecules. The significant increasement of C1–C2 and C6–C1 bond lengths is observed in the series LiPA < NaPA < KPA (atomic numbers are shown in Figure 1). The bond lengths of C3–C4 and C4–C5 insignificantly increase whereas C2–C3 and C5–C6 insignificantly decrease in the above order. The significant decrease of C1–O7, C9–O10, and C9–O11 bond lengths is also observed in the following order: LiPA > NaPA > KPA. But the significant increase is noticed for O7–C8, C8–C9, O10–M, and O11–M bond lengths in the same series. As they might have been expected, the differences between O10–M and O11–M significantly decrease.

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

Atoms	LiPA	NaPA	KPA
Bond lengths (Å) ^a			
C1–C2	1.3981	1.3992	1.3996
C2–C3	1.3978	1.3977	1.3976
C3–C4	1.3899	1.3901	1.3902
C4–C5	1.3982	1.3984	1.3985
C5–C6	1.3875	1.3873	1.3873
C6–C1	1.4013	1.4024	1.4029
C1–O7	1.3649	1.3617	1.3599
O7–C8	1.4121	1.4162	1.4183
C8–C9	1.5222	1.5290	1.5330
C9–O10	1.2601	1.2559	1.2544
C9–O11	1.2727	1.2689	1.2675
O10–M	1.8691	2.2199	2.5286
O11–M	1.8647	2.2169	2.5288
Angles (°)			
C1–C2–C3	119.48	119.55	119.58
C2–C3–C4	120.97	121.01	121.04
C3–C4–C5	119.13	119.07	119.05
C4–C5–C6	120.62	120.63	120.63
C5–C6–C1	120.03	120.14	120.20
C6–C1–C2	119.77	119.59	119.50
C6–C1–O7	115.45	115.55	115.61
C2–C1–O7	124.78	124.87	124.89
C1–O7–C8	118.63	118.64	118.70
O7–C8–C9	111.03	111.45	111.67
C8–C9–O10	121.99	120.84	120.52
C8–C9–O11	115.83	114.37	113.94
C9–O11–M	82.55	87.23	90.75
O10–C9–O11	122.18	124.79	125.54
M–O10–C9	72.85	87.41	91.07
Aromaticity indices			
HOMA ^b	0.979262	0.976809	0.975763
A _J ^c	0.99714	0.99672	0.99656
BAC ^d	0.92688	0.92338	0.92207
I ₆ ^e	95.81867	95.52024	95.41015
NICS ^f	−9.1055	−8.8957	−8.9725
Dipole moment (<i>D</i>)	4.30	6.99	8.67
Energy (hartree) ^g	−542.55	−697.26	−1134.90

^a 1 Å = 10^{−10} m; ^b abbreviation from harmonic oscillator model of aromaticity; ^c normalized function of variance of bond lengths;^d bond alternation coefficient; ^e Bird's index [5]; ^f nuclear independent chemical shifts; ^g 1 hartree = 2625.5 kJ/mol.

Figure 2: Experimental FT-IR spectra registered in KBr pellet (a) and UV spectra (b) for phenoxyacetic acid (PAA) and its salts (LiPA: lithium, NaPA: sodium, KPA: potassium, RbPA: rubidium, and CsPA: cesium phenoxyacetates).

In the case of angles, the increase in the order $\text{LiPA} < \text{NaPA} < \text{KPA}$ was observed for C1–C2–C3, C2–C3–C4, and C5–C6–O1 angles in the aromatic ring, but the decrease in this order was noticed for C3–C4–C5 and C6–C1–C2. The angles between carbon, oxygen, and metal atoms in alkyl chain of molecules increase with exception of C8–C9–O10 and C8–C9–O11 angles.

Geometric and magnetic aromaticity indices [5–7], dipole moments, and energies were calculated and also shown in Table 1. Almost all aromaticity indices decrease in the following order: $\text{LiPA} > \text{NaPA} > \text{KPA}$. Values of energy also decrease in the same series. It might indicate the increase of stability of salt molecules in this order. Mulliken, APT, NPA, MK, and ChelpG atomic charges on the atoms of phenoxyacetic acid molecule and its alkali metal salts are gathered in Table 2. The increase of total charge of carboxylate group (negative values) are observed in the order $\text{LiPA} < \text{NaPA} < \text{KPA}$ when Mulliken and APT methods were used for calculation. In NPA method there are no changes whereas the decrease is observed for MK and ChelpG methods. The total charge in aromatic ring is not changed in above series irrespective of used method.

The theoretical wavenumbers of IR and Raman spectra as well as chemical shifts in NMR spectra were obtained and compared with experimental spectra.

3.2. FT-IR, FT-Raman, and UV Spectra

The vibrational (in KBr) and electronic spectra of synthesized alkali metal phenoxyacetates were recorded and presented in Figure 2. In the UV spectra there were no changes in the wavelengths. The influence of studied metal cations on the vibrational structure of phenoxyacetates appears in the shift of selected bands along the metal series. The wavenumbers of asymmetric stretching vibration bands of carboxylate group in IR spectra decrease in the series $\text{LiPA} \rightarrow \text{CsPA}$; however, for rubidium phenoxyacetate the insignificant increase is noted in comparison to potassium salt. In Raman spectra

Table 2: Calculated (B3LYP/6-311++G**) Mulliken, APT, NPA, MK, and ChelpG atomic charges ($e = 1.6021892 \times 10^{-19}$ C) for lithium, sodium, and potassium phenoxyacetates.

Atom	Mulliken			APT			NPA			MK			ChelpG		
	LiPA	NaPA	KPA	LiPA	NaPA	KPA	LiPA	NaPA	KPA	LiPA	NaPA	KPA	LiPA	NaPA	KPA
C1	-0.20	-0.19	-0.28	0.67	0.68	0.69	0.32	0.33	0.33	0.51	0.55	0.43	0.47	0.47	0.47
C2	0.34	0.32	0.42	-0.19	-0.20	-0.20	-0.29	-0.30	-0.30	-0.31	-0.33	-0.27	-0.29	-0.29	-0.29
H2a	0.16	0.16	0.16	0.06	0.06	0.06	0.21	0.21	0.21	0.12	0.13	0.11	0.12	0.12	0.12
C3	-0.25	-0.27	-0.27	0.06	0.06	0.07	-0.18	-0.19	-0.19	-0.08	-0.07	-0.04	-0.02	-0.02	-0.02
H3a	0.17	0.17	0.17	0.03	0.03	0.02	0.20	0.20	0.20	0.12	0.12	0.09	0.08	0.08	0.08
C4	-0.31	-0.31	-0.26	-0.15	-0.16	-0.16	-0.24	-0.24	-0.24	-0.23	-0.24	-0.15	-0.20	-0.20	-0.20
H4a	0.14	0.14	0.14	0.03	0.03	0.03	0.20	0.20	0.20	0.13	0.13	0.09	0.10	0.10	0.10
C5	-0.11	-0.10	-0.17	0.06	0.07	0.07	-0.19	-0.19	-0.19	-0.04	-0.03	-0.06	-0.03	-0.03	-0.03
H5a	0.16	0.16	0.16	0.03	0.03	0.02	0.20	0.20	0.20	0.11	0.11	0.09	0.08	0.08	0.08
C6	-0.20	-0.19	-0.17	-0.17	-0.18	-0.18	-0.24	-0.24	-0.24	-0.33	-0.36	-0.23	-0.28	-0.28	-0.28
H6a	0.19	0.19	0.19	0.06	0.06	0.06	0.22	0.22	0.22	0.17	0.17	0.13	0.14	0.14	0.14
O7	-0.07	-0.07	-0.07	-0.93	-0.95	-0.96	-0.53	-0.53	-0.53	-0.51	-0.46	-0.49	-0.49	-0.49	-0.49
C8	0.35	0.44	-0.90	0.45	0.47	0.46	-0.12	-0.12	-0.13	0.38	0.19	0.40	0.34	0.34	0.34
H8a	0.19	0.19	0.18	-0.03	-0.04	-0.04	0.20	0.19	0.19	0.02	0.03	-0.03	-0.02	-0.02	-0.02
H8b	0.19	0.19	0.18	-0.03	-0.04	-0.04	0.20	0.19	0.19	0.02	0.03	-0.03	-0.02	-0.02	-0.02
C9	-0.30	-0.32	-0.37	1.23	1.21	1.25	0.76	0.76	0.77	0.77	0.78	0.71	0.77	0.77	0.77
O10	-0.30	-0.43	-0.48	-0.95	-0.95	-0.99	-0.78	-0.78	-0.79	-0.70	-0.77	-0.77	-0.78	-0.78	-0.78
O11	-0.32	-0.45	-0.49	-1.03	-1.03	-1.07	-0.83	-0.83	-0.83	-0.98	-0.84	-0.83	-0.84	-0.84	-0.84
M	0.17	0.38	1.09	0.82	0.85	0.93	0.89	0.92	0.94	0.90	0.87	0.84	0.86	0.86	0.86
Ring	-0.73	-0.74	-0.73	0.28	0.27	0.29	-0.82	-0.83	-0.83	-0.48	-0.48	-0.32	-0.35	-0.35	-0.35
COO	-0.92	-1.20	-1.34	-0.75	-0.77	-0.81	-0.85	-0.85	-0.85	-0.91	-0.83	-0.89	-0.85	-0.85	-0.85

there are no changes in this series. For symmetric stretching vibration bands in Raman spectra the increase of the wavenumbers is noticed from lithium to cesium phenoxyacetate, but in IR spectra the wavenumbers increase to potassium phenoxyacetate and from KPA to CsPA the decrease is observed. The magnitudes of separation between wavenumbers due to asymmetric and symmetric stretching vibration bands $\Delta\nu_{as-s} = \nu_{as}(\text{COO}) - \nu_s(\text{COO})$ in Raman spectra decrease in the series $\text{LiPA} > \text{NaPA} = \text{KPA} > \text{RbPA} > \text{CsPA}$. The corresponding values for lithium, sodium, potassium, rubidium, and cesium phenoxyacetates in IR spectra are equal to 382, 361, 353, 357, and 361, respectively. The wavenumbers of asymmetric in-plane deformations $\beta_{as}(\text{COO})$ decreased in the following series $\text{LiPA} > \text{NaPA} > \text{KPA} > \text{RbPA} > \text{CsPA}$, whereas the magnitudes of separation between wavenumbers due to asymmetric and symmetric in plane deformations of COO^- group increase in this order. The values of $\Delta\beta = \beta_s(\text{COO}) - \beta_{as}(\text{COO})$ are equal to 518, 524, 528, 530, and 536 cm^{-1} . The wavenumbers as well as intensity of the aromatic ring bands did not significantly change.

The correlations between chosen bands and some metal parameters, such as electronegativity, ionization energy, atomic and ionic radius, atomic mass, and inverse of atomic mass [8] have been studied. The best correlation was obtained for ionic radius and ionization energy for band of $\nu(\text{C-O-C})$ etheric group vibration ($R^2 = 0.978$).

3.3. NMR Spectra

Values of the experimental as well as calculated (B3LYP/6-311++G**) chemical shifts in ^1H and ^{13}C NMR spectra of lithium, sodium, potassium, rubidium, and cesium phenoxyacetates are presented in Table 3. Data for the last two salts are only experimentally obtained. Experimental chemical shifts show decreasing tendency in the series $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$ salts for H8a and H8b protons, but for protons connected with the aromatic ring the decrease was observed only for lithium, sodium, and potassium phenoxyacetates, and for rubidium and cesium salts these values increase in comparison to potassium one. The changes in ^{13}C NMR spectra indicated decreasing tendency from lithium to potassium phenoxyacetate, and then the increase from potassium to rubidium, and finally the insignificant decrease for cesium salt were observed for almost all carbon atoms in the aromatic ring (except of C1 and C4) and C9 atom. For C1 and C8 carbon atoms the opposite tendency was observed, whereas an insignificant decreasing tendency was observed for C4 carbon atom in the series $\text{LiPA} = \text{NaPA} > \text{KPA} > \text{RbPA} > \text{CsPA}$.

4. Conclusions

Some regular changes were observed in the calculated values of studied alkali metal phenoxyacetates. Almost all bond lengths decreased in the series $\text{LiPA} > \text{NaPA} > \text{KPA}$. All geometric aromaticity indices decreased in the same order. Values of energy also decreased in the studied series. On the other hand the shift of selected bands in IR, Raman, and NMR spectra along the phenoxyacetate series was also observed.

The calculated parameters were compared to the experimental characteristics of studied compounds. Good correlation between experimental and theoretical IR and Raman spectra was noted. The correlation coefficients (R^2) for IR spectra for lithium, sodium, and potassium phenoxyacetates amount to 0.9986, 0.9990, and 0.9984, respectively. The corresponding values for Raman spectra are 0.9970,

Table 3: Calculated (B3LYP/6-311++G**) as well as experimental chemical shifts (^1H and ^{13}C NMR) of alkali metal phenoxyacetates (ppm).

Atom	LiPA		NaPA		KPA		RbPA	CsPA
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Exp.
H2a	6.848	6.640	6.834	6.650	6.781	6.660	6.828	6.825
H3a	7.211	7.283	7.204	7.297	7.185	7.269	7.194	7.196
H4a	6.835	6.889	6.818	6.923	6.760	6.880	6.786	6.787
H5a	7.211	7.293	7.204	7.321	7.185	7.301	7.194	7.196
H6a	6.848	7.274	6.834	7.209	6.781	7.209	6.828	6.825
H8a	4.210	4.029	4.110	4.237	4.010	4.121	4.080	4.060
H8b	4.210	4.093	4.110	4.236	4.010	4.121	4.080	4.060
C1	158.76	166.94	159.01	166.11	159.30	166.48	159.08	159.18
C2	129.06	113.06	128.93	112.4	128.88	112.26	128.96	128.92
C3	119.80	133.33	119.50	133.58	119.15	133.55	119.40	119.27
C4	114.50	122.86	114.50	123.02	114.41	122.53	114.40	114.39
C5	119.80	134.07	119.50	133.6	119.15	133.39	119.40	119.27
C6	129.06	123.04	128.93	122.74	128.88	122.78	128.96	128.92
C8	67.48	68.15	67.83	67.58	68.11	67.72	67.61	67.96
C9	172.75	178.09	170.85	184.5	169.25	184.05	169.62	169.53

0.9975, and 0.9973. The linear correlation between calculated and experimental data of NMR spectra was also observed. Correlation coefficients for ^{13}C NMR are in the range 0.9002–0.9063 and for ^1H NMR the range is 0.9845–0.9878.

It was interesting to note the linear correlation between wavenumbers of $\nu_s(\text{COO})$ and $\nu_{as}(\text{COO})$ bands and distances between C9–O11 and O10–M. The corresponding correlation coefficients for $\nu_s(\text{COO})$ wavenumbers amount to 0.9951 and 0.9767 and for $\nu_{as}(\text{COO})$ 0.9999 and 0.9469. Good correlation between chemical shifts in ^{13}C NMR spectra and Mulliken atomic charges on C1 and C6 atoms was also found ($R^2 = 0.9718$ and 0.9932, resp.).

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