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Spectroscopic and theoretical study on alkali metal phenylacetates

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1. Introduction

It is well known that molecular structure and electronic charge distribution determine micro- and macro-properties as well as the changes in physical, chemical and biological activity of chemical compounds decide about their effects on biological systems. Relationship between molecular structure and biological activity of chemical compound was intensively studied [1-3]. Phenylacetic acid is one of biological active ligand from the series $C_6H_5COO^-$, C_{6-} H₅CH₂COO⁻, C₆H₅C₂H₂COO⁻. Benzoate, phenylacetate and phenylpropionate are intermediates in the methanogenic degradation of rice straw [4]. There are some papers about antioxidative and antiradical properties of phenylacetic acid [5,6]. Phenylacetic acid and its sodium salt exhibited a high antifungal activity [5]. Antimicrobial activity of Chungkook-Jang (traditional Korean fermentedsoyabean food) is due to phenylacetic acid, which is produced during fermentation process [7]. Sodium phenylacetate was used for the treatment of hyperammonemia in patients with urea cycle disorders [8,9]. Castro et al. [10] presented the vibrational study of Raman spectra of phenylacetic acid (solid) and its sodium salt (aqueous solution) as well as SERS spectra, where studied molecules adsorbed on silver colloids link to the metal through carboxylic group. Hong et al. [11] reported the syntheses and structural characterization of silver(I) complex with mixed bis(diphenylphosphino)-methane and phenylacetate ligands. Johnston et al. [12] obtained divalent cobalt coordination polymer as result of hydrothermal reaction of cobalt nitrate(V), 4,4'-dipyridylamine (dpa) and phenylmalonic acid. Phenylacetate ligand (generated

ABSTRACT

The influence of lithium, sodium, potassium, rubidium and cesium cations on the electronic system of phenylacetic acid was studied. The FT-IR, FT-Raman and ¹H and ¹³C NMR spectra were recorded for studied compounds. Characteristic shifts in IR and NMR spectra along alkali metal phenylacetates were observed. Good correlations between the wavenumbers of the vibrational bands in the IR spectra of phenylacetates and some alkali metal parameters such as ionic potential, electronegativity, inverse of atomic mass, atomic radius and ionization energy were found. The density functional hybrid method B3LYP with 6-311++G^{**} basis set was used to calculate optimized geometrical structures of studied compounds. Aromaticity indices, atomic charges, dipole moments and energies were calculated as well as the wavenumbers and intensities of IR spectra and chemical shifts in NMR spectra. The theoretical parameters were compared to experimental characteristic of alkali metal phenylacetates.

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in situ from decomposition of phenylmalonic acid) formed binuclear hydrated cobalt phenylacetate units with both bridging and monodentate benzenecarboxylate ligands. Each unit is connected to four others through the dpa ligands and form two-dimensional rhomboid grid coordination polymer motifs. Particular structure and magnetic properties of studied compounds is described in cited paper [12]. Tsaryuk et al. [13,14] reported about the blocking influence of the methylene $-CH_2$ — bridge in phenylacetate ligand (dividing the conjugated π -electron system of the ligand in two parts) on the luminescence excitation of europium and terbium aromatic carboxylates.

In our works spectroscopic methods as well as quantum chemical calculations were used to determine the effect of various metals as well as substituents in aromatic ring on the electronic system of some benzoic acid derivatives [15–17]. In this paper the spectroscopic and theoretical study of series of alkali metal phenylacetates is presented and the influence of lithium, sodium, potassium, rubidium and cesium cations on the electronic system of phenylacetic acid was discussed.

2. Experimental

Lithium, sodium, potassium, rubidium and cesium phenylacetate were prepared by dissolving the powder of phenylacetic acid in the water solution of the appropriate alkali metal hydroxide in a stoichiometric ratio. The hydroxides were Aldrich analytical chemicals, except of LiOH and CsOH (Sigma Chemical Company). Phenylacetic acid was produced by Fluka Analytical. The mixed solution was slowly condensed at 70 °C to about 30% of starting volume. The solution was then left at the room temperature for 48–72 h until the sample crystallized in the solid-state. Then, the

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remaining solvent was removed by drying under reduced pressure at 110 °C. Obtained complexes were anhydrous – in the IR spectra of solid state samples the lack of bands characteristic 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 matrix. Pellets were obtained with a hydraulic press under 739 MPa pressure. 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 saturated solution were recorded with the NMR AC 200 F, Bruker unit at room temperature. TMS was used as an internal reference.

To calculate optimized geometrical structures of phenylacetic acid and its alkali metal salts the DFT hybrid method B3LYP/ $6-311++G^{**}$ was used. All theoretical calculations were performed using the GAUSSIAN 09 package of programs [18] running on a PC computer.

3. Results and discussion

3.1. Calculated geometrical structure

The distances between atoms in alkali metal phenylacetate molecules and the angles between bonds were calculated and the

values of them are presented in Tables 1 and 2. The atoms of molecule are numbered as Fig. 1. Experimental data for potassium phenylacetate were found in literature [19] and also are gathered in Tables 1 and 2. Quite good correlation was found between calculated and experimental data, the correlation coefficient exemplary for angles amounts to R = 0.900. The values of the bonds lengths are almost the same in studied molecules except of those in carboxylate group. The increase of O2—H9/M and O1—M/H9 bond lengths as well as for distance of C8—M/H9 are observed in the series: PNA < LiPN < NaPN < KPN. The bond lengths of C8—O1 and C8—O2 do not change in the series of salts, although they are different from the corresponding values calculated for phenylacetic acid molecule.

In the case of angles in studied molecules the changes are observed for those in aromatic ring as well as in CH_2 and carboxylate groups. The highest changes are noticed for C8-O1-M and C8-O2-M angles, the values of them increase in order LiPN < NaPN < KPN.

Geometric and magnetic aromaticity indices [20,21] as well as the values of the largest differences of distances between atoms and of angles between bonds in aromatic ring of lithium, sodium and potassium phenylacetates in comparison with acid are also presented in Table 1. Geometric indices are almost the same for studied molecules except of sodium salt, for which the decrease of aromaticity is observed. Only the highest differences between angles in aromatic ring increase in following order: phenylacetic

Table 1

The distances (Å)^a between atoms in phenylacetate (MPN) molecules in comparison with phenylacetic acid (PNA) and aromaticity indices calculated based of the values of aromatic ring.

Bonds between atoms ^b	Distances (Å ^a)				
	Calculated data (B3LYP/6-311++G**)			Experimental data [19]
	PNA	LiPN	NaPN	KPN	KPN
C1—C2	1.40	1.40	1.40	1.40	1.35
C2–C3	1.39	1.39	1.39	1.39	1.44
C3–C4	1.39	1.39	1.40	1.39	1.41
C4–C5	1.39	1.39	1.39	1.39	1.39
C5–C6	1.39	1.39	1.39	1.39	1.41
C6-C1	1.40	1.40	1.40	1.40	1.41
C1C7	1.51	1.52	1.52	1.51	1.53
C2—H2	1.08	1.08	1.08	1.08	1.09
С3—Н3	1.08	1.08	1.08	1.08	1.11
C4—H4	1.08	1.08	1.08	1.08	1.07
C5—H5	1.08	1.08	1.08	1.08	1.13
С6—Н6	1.09	1.08	1.08	1.08	1.12
С7—Н7	1.10	1.09	1.09	1.09	1.06
С7—Н8	1.09	1.09	1.09	1.09	1.13
С7—С8	1.52	1.53	1.54	1.54	1.53
C8-01	1.20	1.27	1.27	1.26	1.29
C8–02	1.36	1.27	1.27	1.26	1.24
O2—H9/M	0.97	1.86	2.21	2.52	-
01—H9/M	1.26	1.86	2.21	2.52	-
C8—H9/M	0.96	2.12	2.50	2.84	-
Geometric aromaticity indices					
A _j ^c	0.999	0.999	0.997	0.999	0.914
BAC ^d	0.974	0.974	0.931	0.974	0.599
I ₆ ^e	98.185	98.185	95.810	98.185	76.531
HOMA ^f	0.987	0.987	0.981	0.987	0.759
$\Delta(C-C)^{g}$	0.01	0.01	0.01	0.01	0.06
$\Delta(C-C-C)^h$	1.91	2.10	2.29	2.53	3.65
Magnetic aromaticity indice					
NICS ⁱ	-8.3179	-8.2060	-8.0606	-7.9779	

^a 1 Å = 10^{-10} m.

^b Atom numbers according to Fig. 1.

^c Normalized function of variance of bond lengths.

^d Bond alternation coefficient.

e Bird's indice.

^f Abbreviation from harmonic oscillator model of aromaticity.

^g The highest difference between length of the bonds in the aromatic ring.

^h The highest difference between angles in the aromatic ring.

ⁱ Nuclear independent chemical shifts.

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Table 2 The angles (°) between bonds in phenylacetate molecules in comparison with phenylacetic acid.

Angles between bonds	The angles (°)									
	Calculated (B3L)	(P/6-311++G**)			Experimental data [19]					
	PNA	LiPN	NaPN	KPN	KPN					
C1—C2—C3	120.65	120.69	120.77	120.89	121.78					
C2-C3-C4	120.18	120.22	120.26	120.23	118.13					
C3–C4–C5	119.62	119.52	119.45	119.41	119.33					
C4—C5—C6	120.03	120.16	120.16	120.23	121.52					
C5-C6-C1	120.78	120.75	120.87	120.89	119.1					
C6-C1-C2	118.74	118.65	118.48	118.36	120.15					
C6-C1-C7	120.33	120.67	120.79	120.81	118.13					
C2-C1-C7	120.94	120.67	120.72	120.81	121.72					
H8—C7—H7	105.68	109.18	109.11	109.22	107.57					
H8–C7–C8	111.26	110.11	108.55	108.36	107.37					
H7–C7–C8	110.93	109.99	108.03	108.36	106.66					
C1-C7-H7	110.93	109.99	109.82	110.02	112.22					
С1—С7—Н8	111.26	110.11	110.03	110.02	112.84					
C1-C2-H2	119.67	119.31	119.13	119.18	120.19					
H2-C2-C3	119.68	120.00	120.09	119.93	117.95					
С2—С3—Н3	119.75	119.73	119.73	119.74	119.55					
H3-C3-C4	120.06	120.05	120.01	120.03	122.32					
C3-C4-H4	120.17	120.24	120.27	120.30	118.92					
H4-C4-C5	120.20	120.24	120.28	120.30	121.46					
C4—C5—H5	120.17	120.09	120.09	120.03	120.71					
H5-C5-C6	119.80	119.74	119.75	119.74	117.95					
C5-C6-H6	119.61	119.84	119.82	119.93	123.91					
H6-C6-C1	119.61	119.41	119.32	119.17	116.86					
C7–C8–O2	110.49	119.46	118.21	117.68	119.73					
C7–C8–O1	127.02	110.49	117.90	117.68	112.7					
02	122.48	122.48	122.48	124.62	-					
C8-01-H9/M	53.43	82.76	87.67	91.17	-					
C8—O2—H9/M	107.07	82.75	87.68	91.16	-					



Fig. 1. Atom numbers in phenylacetic acid molecule.

acid < lithium < sodium < potassium salts, which may indicate that aromaticity of studied molecules in this series decrease. The magnetic aromaticity indices NICS (Nuclear Independent Chemical Shift) shifting to low negative values confirm decreasing tendency of aromaticity in the series PNA > LiPN > NaPN > KPN.

Mulliken (M), APT and NPA total atomic charges were calculated for studied molecules using B3LYP/6-311++G^{**} method and gathered in Table 3. Obtained values indicate changes in electronic charge distribution in studied molecule. The highest changes of total charge independently on used method are observed on carboxylate anion (Fig. 2). However insignificant decrease of total charge with increasing positive charge of metal ion is noticed on CH_2 group as well as on aromatic ring (Fig. 3).

Values of dipole moment and energy were also calculated for lithium, sodium and potassium phenylacetates and they are presented in Table 4 in comparison with those of phenylacetic acid molecule. The increase is observed for values of dipole moment in following order PNA \rightarrow LiPN \rightarrow NaPN \rightarrow KPN. Values of energy decrease in above series.

3.2. Vibrational spectra

FT-IR and Raman spectra of phenylacetic acid and lithium, sodium, potassium, rubidium and cesium phenylacetaes were recorded. Data of wavenumbers, intensities and assignments of selected bands occurring in the experimental as well as calculated (B3LYP/6-311++G^{**}) spectra are gathered in Table 5. The bands are numbered along with the notation used by Varsányi [22]. The bands assignments were made by using both the animation option of GaussView 5.0.8 graphical interface for Gaussian programs [23] and VEDA 4 program [24]. The calculated spectra were interpreted in terms of potential energy distributions (PEDs). The exemplary results of PED analysis obtained for phenylacetic acid and its sodium salt were presented in Table 5. The literature data of Raman spectra of phenylacetic acid are also included in Table 5 [10]. Exemplary FT-IR and FT-Raman spectra of phenylacetic acid and its sodium salt are presented in Fig. 4. A good correlation between experimental and theoretical wavenumbers in those spectra of studied compounds were obtained. The correlation coefficients R were calculated and for PNA they equal 0.9972 and 0.9998, respectively for IR and Raman spectra; the corresponding values for LiPN are 0.9995 and 0.9990; for NaPN 0.9995 and 0.9992; and for KPN R equal 0.9993 (IR) and 0.9994 (Raman spectra).

Vibrational spectra of studied compounds contain the bands connected with vibrations, which are characteristic for carboxylic and methylene groups as well as for the aromatic ring. Particular analysis of the infrared and Raman spectra of phenylacetic acid was presented by Badawi and Förner [25] basing on the experimental as well as on calculated (B3LYP/6-311G^{*+}) data. Very strong band of vC=0 stretching vibrations appears at 1699 cm⁻¹ in IR and 1657 cm⁻¹ in Raman spectra. The calculated wavenumber is higher

Table 3

Mulliken (M), APT and NPA atomic charges (e^a) on the atoms in lithium, sodium and potassium phenylacetates calculated using B3LYP/6-311++G** method.

Atoms ^b	Charge (e ^a)													
	PNA		LiPN			NaPN			KPN					
	М	APT	NPA	М	APT	NPA	М	APT	NPA	М	APT	NPA		
C1	0.832	0.054	-0.037	0.857	0.101	-0.026	0.957	0.110	-0.021	0.959	0.122	-0.018		
C2	0.084	-0.047	-0.183	-0.192	-0.074	-0.198	-0.178	-0.077	-0.197	-0.263	-0.082	-0.199		
C3	-0.237	-0.021	-0.194	-0.274	-0.014	-0.200	-0.276	-0.011	-0.202	-0.294	-0.007	-0.204		
C4	-0.264	-0.040	-0.202	-0.364	-0.056	-0.211	-0.364	-0.065	-0.215	-0.352	-0.071	-0.219		
C5	-0.309	-0.023	-0.197	-0.297	-0.012	-0.199	-0.307	-0.008	-0.202	-0.294	-0.007	-0.204		
C6	-0.642	-0.061	-0.195	-0.339	-0.077	-0.197	-0.382	-0.081	-0.200	-0.264	-0.082	-0.199		
C7	-0.275	0.023	-0.498	-0.240	-0.056	-0.480	-0.364	-0.046	-0.481	-0.647	-0.081	-0.484		
C8	-0.265	1.180	0.812	0.098	1.137	0.787	0.134	1.118	0.786	0.043	1.157	0.793		
H2	0.177	0.034	0.205	0.176	0.036	0.206	0.184	0.033	0.212	0.162	0.038	0.207		
H3	0.167	0.030	0.205	0.171	0.025	0.202	0.166	0.021	0.200	0.165	0.019	0.199		
H4	0.149	0.033	0.205	0.140	0.028	0.202	0.136	-0.065	0.200	0.134	0.023	0.199		
H5	0.171	0.029	0.205	0.172	0.024	0.202	0.167	0.020	0.200	0.165	0.019	0.199		
H6	0.143	0.029	0.201	0.158	0.044	0.211	0.153	0.046	0.204	0.162	0.038	0.207		
H7	0.182	0.003	0.241	0.176	-0.007	0.224	0.166	-0.016	0.219	0.160	-0.019	0.215		
H8	0.229	0.010	0.235	0.169	-0.007	0.222	0.163	-0.017	0.216	0.160	-0.019	0.215		
H9/M	0.280	0.283	0.483	0.270	0.793	0.889	0.550	0.826	0.917	0.947	0.909	0.939		
01	-0.259	-0.738	-0.587	-0.337	-0.943	-0.819	-0.455	-0.936	-0.821	-0.472	-0.979	-0.824		
02	-0.161	-0.777	-0.695	-0.347	-0.940	-0.815	-0.452	-0.941	-0.815	-0.472	-0.979	-0.824		
CO0	-0.685	-0.336	-0.470	-0.586	-0.746	-0.847	-0.773	-0.759	-0.850	-0.901	-0.801	-0.855		
CH ₂	0.136	0.036	-0.022	0.105	-0.07	-0.034	-0.035	-0.079	-0.046	-0.327	-0.119	-0.054		
C ₆ H ₅	0.271	0.017	0.013	0.208	0.025	-0.008	0.256	-0.077	-0.014	0.280	0.017	-0.032		

^a 1 e = 1,6021892 \times 10⁻¹⁹

^b Atom numbers according to Fig. 1.



Fig. 2. The changes in Mulliken (M), APT and NPA total charges on carboxylate group in alkali metal phenylacetate molecules in comparison with phenylacetic acid.



Fig. 3. NPA total atomic charges calculated for COO, CH₂ groups as well as for aromatic ring of phenylacetate molecules.

than this experimentally obtained and equals 1820 cm⁻¹. The appropriate literature [25] values (1698 and 1828 cm⁻¹, respec-

Table 4

Values of dipole moment and energy calculated for phenylacetate molecules in comparison with phenylacetic acid.

	Phenylacetic	Lithium	Sodium	Potassium
	acid	salt	salt	salt
Dipole moment (Debye)	1.387	3.732	6.303	7.8288
Energy (Hartree ^a)	-460.3	-467.3	-622.0	1059.7

^a 1 Hartree = 2625.5 kJ/mol.

tively for IR and calculated spectra) confirm this high difference between theoretical and experimental data. Other bands of $\beta C=0$ in plane and γ C=O out of plane deformations occur in lower wavenumbers: 839 cm⁻¹ in IR and 842 cm⁻¹ in Raman spectra for first band and for second 602 cm⁻¹ (IR and Raman). Appropriate literature values are 839 cm⁻¹ (IR) and 840 cm⁻¹ (Raman) – for band of β C=O and 601 cm⁻¹ (IR) and 596 cm⁻¹ (R) – for γ C=O out of plane deformations band. Calculated wavenumbers are 846 cm⁻¹ (β C=O) and 516 cm⁻¹ (γ C=O), while literature [25] data 853 and 596 cm⁻¹, respectively. The bands of v(C-OH) vibrations are found at 1289 cm⁻¹ (IR) and at 1312 cm⁻¹ (Raman spectra), while in literature 1235 cm⁻¹ and 1230 cm⁻¹, respectively. The bands of β OH in-plane deformations appear at 1408 cm^{-1} (IR) and 1409 cm^{-1} (Raman), calculated value is lower than experimental, it amounts to 1384 cm⁻¹. The last result is confirmed by appropriate value published by Badawi and Förner [25] (1374 cm⁻¹). The above mentioned bands occurring in the acid spectra disappeared in the spectra of alkali metal phenylacetates.

In phenylacetic acid vibration spectra some bands of methylene group are found. Exemplary there are asymmetric $v_{as}(CH_2)$ and symmetric stretching vibrations $v_s(CH_2)$, which occur at 2974 and 2942 cm⁻¹ in IR spectra, 2985 and 2943 cm⁻¹ in Raman spectra of acid and the calculated values are 3114 and 3060 cm⁻¹. Literature data [25] are properly: 2962 and 2916 cm⁻¹ (IR); 2955 and 2924 cm⁻¹ (R); 3123 and 3070 cm⁻¹ (calculated).

Table 5	
Wavenumbers (cm ⁻¹), intensities and assignments of selected bands in the IR and Raman spectra of alkali metal phenylacetates (MPN) in comparison with phenylacetates	ate acid (PNA).

Assi	gnment [*]	PNA						LiPN				NaPN					KPN				RbPN		CsPN	
		FT-IR	Calc.	Int.	PED	FT-R	R [10]	FT-IR	Calc.	Int.	FT-R	FT-IR	Calc.	Int.	PED	FT-R	FT-IR	Calc.	Int.	FT-R	FT-IR	FT-R	FT-IR	FT-R
	vOH		3758	71.18	100%																			
2	vCH	3092 vw	3190	11.74	41%			3084 w	3187	12.32		3086 w	3186	12.29	64%	3074 s	3086 vw	3184	13.09	3072 vs	3088 vw	3069 vs		3069 s
20b	vCH	3065 w	3180	29.23	38%	3066 s	3069	3063 w	3179	28.05	3064 s	3061 w	3178	28.28	81%	3057 m	3063 vw	3176	33.62	3055 s	3061 w		3058 w	3051 s
20a	vCH	3032 w	3171	10.03	37%	3039 w		3034 w	3172	16.42		3030 w	3171	22.14			3030 w	3171	19.62	3042 w	3030 w	3040 w	3028 w	3041 w
	vasCH2	2967 w	3088	4.63	100%	2954 w		2974 w	3114	8.36	2985 w	2945 w	3112	11.26	96%	2945 w	2943 w	3108	12.31	2956 m	2943 w	2947 w	2941 w	2940 w
	v _s CH ₂	2922 w	3033	11.20	100%	2925 m	2930	2942 m	3060	16.56	2943 w	2920 w	3057	21.28	96%	2924 w		3056	25.16	2898 m	2913 w	2892 s	2914 w	2893 m
	vC=0	1699 vs	1820	269.76	86%	1657 w	1660																	
8a	v(CC)	1603 m	1647	2.48	30%	1605 m	1608	1587 s	1642	5.60	1601 m	1580 sh	1641	8.39	51%	1599 m		1641	9.40	1597 m		1596 m		1602 m
	v _{as} COO							1578 vs	1562	468.26	1590 s	1564 vs	1579	499.27	84%	1588 m	1572 vs	1589	448.82	1587 s	1568 vs	1586 s	1570 vs	1586 s
8b	v(CC)	1570 vw	1626	0.56	28%	1588 m	1590	1562 s	1623	0.78			1622	2.67	27%			1621	5.50					
19a	v(CC)	1499 m	1529	9.90		1501 w		1493 m	1525	10.41	1499 w	1495 m	1524	12.55		1494 w	1497 m	1523	11.88	1496 vw	1497 m	1502 vw	1495 m	1488 vw
19b	v(CC)	1454 m	1485	7.50		1440 w		1443 s	1484	11.49	1443 w	1452 s	1485	6.47	11%	1440 m	1452 w	1483	7.23	1436 sh	1452 m	1457 w	1452 m	1458 vw
	δCH_2		1461	17.00	76%		1410		1482	5.95		1425 m	1480	2.35	53%		1420 sh	1481	1.64	1429 s	1420 m	1427 s	1422 m	1422 m
	v _s COO							1416 s	1430	309.07	1429 m	1412 vs	1402	289.55	70%	1419 w	1385 s	1393	373.77	1415 w	1381 vs	1394 w	1376 vs	1409 w
	βΟΗ	1408 s	1384	59.31		1409 m																		
3	β(CH)		1358	5.83	27%				1360	0.19			1359	0.58	72%			1358	0.01					
14	v(CC)	1341 m	1338	2.14		1343 w		1335 w	1337	2.31	1341 w	1331 w	1337	1.58	55%	1345 m		1336	1.03	1340 m		1339 m		1338 m
	γCH_2							1292 w	1306	2.70	1295 w	1296 m	1301	3.48	79%	1298 m	1283 m	1296	8.64	1296 w	1281 m	1294 m	1285 m	1293 m
	vC—OH	1289 m	1131	368.10	52%	1312 vw																		
13	v(CH)	1242 s	1225	4.58	30%	1231 w	1195				1246 w					1242 m				1244 m		1254 m		1252 m
9a	β(CH)	1186 s	1204	0.12	21%	1191 w	1180	1196 w	1203	0.12	1179 m	1194 w	1202	0.11	74%	1179 m	1204 w	1201	0.14	1204 vw	1204 w		1202 w	1202 vw
9b	β(CH)	1153 sh	1182	0.10	37%	1155 w		1161 w	1181	0.54	1157 m	1163 m	1179	0.40	79%	1157 m	1177 vw	1178	0.15	1179 s	1175 w	1178 s	1178 w	1179 m
	δCH_2								1168	24.60		1150 sh	1168	20.00	49%		1155 w	1164	18.50	1158 w	1152 vw	1157 m		1157 m
18a	β(CH)	1074 w	1103	3.36	16%			1074 w	1050	5.85	1066 w	1074 w	1050	6.42	45%	1086 w	1074 w	1049	6.48	1087 w	1074 w	1087 w	1074 w	1086 w
18b	β(CH)	1030 w	1050	13.48	13%	1032 m		1030 w	1099	0.65	1030 s	1030 w	1098	1.06	35%	1029 m	1030 vw	1097	0.75	1027 m	1028 w	1026 m	1029 w	1025 m
12	α(CCC)	1003 w	1019	1.02	60%	1005 vs	1005	1005 w	1018	0.02		1005 vw	1017	0.13	54%		1005 vw	1017	0.33		1005 vw		1003 w	
5	γ(CH)	986 w	999	0.03	73%	994 w			995	0.03	998 vs	993 vw	992	0.04	41%	997 vs	988 vw	991	0.06	996 vs	989 vw	995 vs	985 w	994 vs
17a	γ(CH)	964 sh	980	0.04	91%			959 w	981	0.18	961 w	970 vw	980	0.28	83%	978 vw	974 vw	978	0.35	986 vw	972 w	984 w	948 w	984 sh
	$\beta_{as}CH_2$		948	4.78	45%			945 w	952	7.59	947 vw	939 w	948	7.48		938 w	930 w	949	8.69	938 m	930 m	937 m	930 m	935 m
	<i>v</i> С—СООН	926 m	878	2.18	13%	958 w	931	908 w	921	1.67		914 w	916	2.24	21%		908 w	909	9.22		907 w	911 vw	907 w	
	γОН	905 m	646	85.84	38%	898 w																		
	βsCOO							861 w	870	4.35	845 m	863 w	868	3.29	26%	842 m	842 w	867	4.25	844 m	843 w	843 m	842 w	842 m
	βC=0	839 m	846	13.98		842 m																		
11	γ(CH)	752 m	709	46.74	42%	752 m		772 w	708	21.05	789 m	764 m	708	32.33	85%	766 vw	760 w	708	32.12	766 w	760 m	765 w	765 w	759 w
	γ _s COO							721 s	691	121.99	722 w	729 s	668	39.86	37%	714 w	730 sh	658	53.22	711 w	728 sh	710 w	729 sh	706 w
4	$\varphi(CC)$	700 vs				703 vw		694 m			694 vw	708 s				710 vw	708 m				708 s		707 s	
1	$\alpha(CCC)$	677 s	586	44.40	11%	674 w	752	662 m	586	81.46	666 vw	650 m				663 vw	646 w				650 w	646 vw	650 w	
	γ C= 0	602 m	516	17.79	32%	602 vw																		
16b	$\varphi(CC)$	554 w				562 vw			478	15.89	582 w	565 w	487	0.49	45%	586 vw	577 w	487	0.28	576 w	581 w	575 w	579 vw	574 vw
	$\beta_{as}COO$							530 m	487	6.68	529 w	530 m	456	0.62	57%	532 w	550 w	454	0.65	542 vw	551 vw		534 vw	
6b	$\alpha(CCC)$	478 w	481	6.60	40%	481 W	622	463 m	44.0	0.01		463 W	44.0	0.01			478 w	44.0	0.01		480 w		480 w	
16a	$\varphi(CC)$		412	0.04		436 vw		436 w	413	0.01		446 w	413	0.01	77%		442 w	413	0.01		440 vw		442 vw	

s – strong; m – medium; w – weak; v – very; sh – shoulder; v: stretching; β: in plane deformations; γ: out of plane deformations; δ: scissoring; α: the aromatic ring in-plane bending modes, φ: the aromatic ring out-of-plane ones; * Fundamental modes of the phenyl ring are numbered according to Varsányi [22], mono- "light".



Fig. 4. Experimental FT-IR and FT-Raman spectra of phenylacetic acid (a and c) and its sodium salt (b and d).

The position of the bands of ring vibrations are also in agreement with theoretical results as well as literature data. For example ring deformation band occurs in acid spectra at 1030 cm⁻¹ (IR), 1032 cm⁻¹ (R) and 1050 cm⁻¹ (calculated); according to literature [25] appropriate values are 1028, 1031 and 1050 cm⁻¹.

In our knowledge there are no vibrational assignments in literature for phenylacetates. The influence of metals on the vibrational



Fig. 5. Relationship between calculated charges on the aromatic ring carbon atoms and chemical shifts in experimental ¹³C NMR spectra obtained for lithium phenylacetate.

structure of phenylacetic acid expresses in the shift of selected bands along the series of alkali metal salts. The wavenumbers of $v_{as}(CH_2)$ band increase in spectra of lithium phenylacetate in comparison to acid spectra and then decrease in the following series: LiPN > NaPN > KPN = RbPN > CsPN in IR spectra and LiPN > NaPN < KPN > RbPN > CsPN in IR and Raman. The symmetric stretching vibrations $v_s(CH_2)$ band shifts to lower wavenumbers as following: LiPN > NaPN > RbPN < CsPN in IR as well as in Raman spectra. The decreasing tendency is also observed for $\beta_{as}CH_2$ band in IR spectra: LiPN > NaPN > KPN = RbPN = CsPN; in Raman the order is LiPN > NaPN = KPN = RbPN > CsPN.

In the case of ring vibration bands the decrease of wavenumbers is observed for 8a- ν (CC) in IR and Raman spectra; 14- ν (CC) in IR spectra and in Raman (with exception of sodium salt), 5- γ (CH) in Raman: LiPN > NaPN > KPN > RbPN > CsPN and in IR spectra: NaPN > KPN > RbPN > CsPN; 18b- β (CH) in Raman decreased in the series LiPN > NaPN > KPN > RbPN > CsPN, in IR spectra no changes are noticed. Wavenumbers of 11- γ (CH) band changes as following order PNA \ll LiPN > NaPN > KPN = RbPN < CsPN in IR and in Raman spectra: PNA \ll LiPN > NaPN = KPN > RbPN > CsPN. The wavenumbers of 1- α (CCC) band decrease in the series PNA > LiPN > NaPN > RbPN in Raman spectra, the order in IR spectra is PNA > LiPN > NaPN > KPN < RbPN = CsPN. The increase is noticed for 9a- β (CH) in comparison to acid in IR spectra and in Raman with

Table 6

Calculated (B3LYP/6-311++G**) and experimental chemical shifts [ppm] in ¹H and ¹³C NMR spectra of alkali metal phenylacetates in comparison with phenylacetic acid (PNA).

Atoms ^a	Chemical shifts [ppm]													
	PNA			LiPN		NaPN		KPN		RbPN	CsPN			
	Calc.	Exp.	[25]	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Exp.	Exp.			
C1	139.449	135.221	140.02	145.684	139.527	147.307	139.804	148.261	140.401	140.516	140.720			
C2	136.419	129.552	131.82	134.374	129.328	134.112	129.190	134.045	129.175	129.184	129.166			
C3	132.944	128.431	131.30	132.565	127.491	132.003	127.468	131.622	127.372	127.374	127.312			
C4	131.650	126.773	131.82	130.329	124.949	129.389	124.846	128.533	124.596	124.568	124.449			
C5	132.665	128.431	131.30	132.540	127.491	131.956	127.468	131.625	127.372	127.374	127.312			
C6	133.822	129.552	131.82	134.305	129.328	134.050	129.190	134.059	129.175	129.184	129.166			
C7	41.040	40.960	41.12	48.998	45.763	48.991	46.003	51.134	46.719	46.886	47.135			
C8	176.598	172.933	183.58	197.144	174.922	189.965	174.919	189.183	173.624	173.296	172.585			
H2	7.455	7.243	7.29	7.767	7.100	7.851	7.096	7.626	7.077	7.073	7.067			
H3	7.480	7.315	7.36	7.381	7.213	7.395	7.212	7.267	7.192	7.185	7.174			
H4	7.399	7.243	7.29	7.201	7.100	7.200	7.096	7.206	7.077	7.073	7.067			
H5	7.419	7.315	7.36	7.354	7.213	7.230	7.212	7.264	7.192	7.185	7.174			
H6	7.171	7.243	7.29	7.540	7.100	7.492	7.096	7.627	7.077	7.073	7.067			
H7	3.607	3.565	3.53	3.538	3.257	3.574	3.244	3.384	3.192	3.179	3.132			
H8	3.461	3.565	3.53	3.328	3.257	3.266	3.244	3.383	3.192	3.179	3.132			
H9	5.579	12.353		-	-	-	-	-	-	-	-			

^a Atom numbers according to Fig. 1.

the exception of lithium and sodium salt; for 9b- β (CH) in IR with exception of rubidium salt and in Raman but not regularly; 18a- β (CH) band do not change in IR spectra but in Raman the order is Li < Na < K = Rb > Cs. The order of changes noticed for 16b- φ (CC) band in Raman spectra is PNA < LiPN < NaPN > KPN > RbPN > CsPN and in IR PNA > NaPN > KPN > RbPN \ll CsPN. Wavenumbers of 17a- γ (CH) band changes as following series LiPN < KPN > Rb > CsPN in IR and LiPN < NaPN < KPN > RbPN = CsPN in Raman spectra.

Moreover there are other bands characteristic only for salt spectra concerning asymmetric v_{as}COO and symmetric v_sCOO stretching vibrations and in plane deformations β_{as} COO and β_{s} COO as well as out-of-plane bending γ_s COO of carboxylate anion. The regular decrease in the wavenumbers of symmetric and asymmetric stretching vibration bands of carboxylate group along the series: Li > Na > K > Rb > Cs phenylacetates must be caused by the influence of certain metal parameters, which change regularly while going down the first group of the Periodic Table. Good correlations between the wavenumbers of vibrational bands in the IR spectra of phenylacetates and some alkali metal parameters such as ionic potential, electronegativity, inverse of atomic mass, atomic and ionic radii, affinity, ionization potential and ionization energy were found for alkali metal phenylacetates. The most bands correlate well (R > 0.900) with ionic radius, ionization potential and ionization energy. Such bands as v_s COO and β_{as} CH₂ correlate well with the most of studied parameters.

The increase of difference between bands of asymmetric and symmetric stretching vibrations of the carboxylate anion $\Delta v_{as-s} = v_{as}COO - v_sCOO$ is observed in the series: NaPN < LiPN < KPN < RbPN < CsPN (152, 162, 187, 187 and 194 cm⁻¹) in FT-IR spectra, in Raman the order is LiPN < NaPN < KPN < CsPN < RbPN (161, 169, 172, 178, 187 cm⁻¹). The increasing tendency of the values of $\Delta v_{as-s}(COO)$ while going down a group of the Periodic Table may indicate the higher degree of the ionic bond [26]. The values of $\Delta \beta_{s-as}$ were also calculated and decrease tendency were noticed for Raman spectra from lithium to potassium phenylacetates, in the case of IR the order is: NaPN > LiPN > CsPN > KPN = RbPN.

It is interesting to notice that some of bands in IR or Raman spectra correlate with angles or distances between atoms in carboxylate group. For example well correlation is observed between band of v_s COO vibration and M-O distance (R equals 0.9050 for band in IR and 0.9788 in Raman spectra), while for correlation between band of v_{as} COO asymmetric stretching vibration in Raman spectra and M—O bond R = 0.9879 is obtained. However lower correlation is between C8—O1—M angle and v_s COO band, R equals 0.8769.

3.3. NMR spectra

Experimental and calculated (B3LYP/6-311++G^{**}) data of chemical shifts in ¹H and ¹³C NMR spectra obtained for phenylacetates are gathered in Table 6. For comparison our results with literature data published by Chang et al. [27] for phenylacetic acid the last one were also included in Table 6. A good correlation between experimental and theoretical chemical shifts is obtained. Values of correlation coefficient *R* for carbon NMR are in the range of 0.9935–0.9995. The corresponding range for ¹H NMR is 0.9915– 0.9985. The values of correlation coefficients for correlation between literature and calculated data are 0.9967 and 0.9986, respectively for ¹³C and ¹H NMR. The appropriated values for correlation between experimental and literature results equal 0.9987 and 1.000.

The chemical shifts of protons and carbons express the effect of alkali metal on the electronic charge density around those atoms. The highest changes in chemical shifts are observed on C1 and C7 carbon atoms in experimental as well as theoretical ¹³C NMR spectra. In experimental spectra the increase of chemical shifts in

comparison with benzoic acid spectra equals 5.499 and 6.175 ppm, respectively for C1 and C7. In both cases chemical shifts significant increase from acid to lithium salt and then from lithium to cesium phenylacetates the increase is lower. Chemical shifts on C2, C3, C4, C5 and C6 carbon atoms decrease in the series: PNA > LiPN > NaPN > KPN > RbPN > CsPN (Fig. 4), but in the case of C3, C4 and C5 atoms the decrease from acid to lithium salt is higher than for C2 and C6 carbon atoms. Whereas for C8 carbon atom significant increase is observed from phenylacetic acid to lithium salt, then chemical shifts insignificantly decrease to cesium salts.

Taking into account ¹H NMR spectra the decrease in chemical shifts of all protons in phenylacetates in comparison with free acid is observed (PNA > LiPN > NaPN > KPN > RbPN > CsPN). Appreciable decrease is noticed from acid to lithium salt, then chemical shifts decrease slightly. It points at an increase in the screening of the protons as a consequence of decrease of the circular current.

In NMR, as like in vibration spectra, you could observe some interesting correlation. For example the correlation between APT atomic charge on C1 (C8) atom and experimental chemical shifts on these atoms are examined for studied compounds, *R* equals 0.9899 (0.9508). In the case of correlation between NPA atomic charge and chemical shifts on C1 and C8 carbon atoms the lower values of correlation coefficient is obtained, 0.9649 and 0.9170, respectively. On the other hand, taking into consideration all aromatic ring carbon atoms for one compound and calculate correlation coefficient between experimental chemical shifts on those atoms and corresponding values of calculated atomic charges, the best correlation is obtained for NPA charges (Fig. 5).

4. Conclusions

The influence of lithium, sodium, potassium, rubidium and cesium cations on the electronic system of phenylacetic acid is analyzed in this report. Characteristic shifts in FT-IR, FT-Raman as well as ¹H and ¹³C NMR spectra of studied compounds are noticed along alkali metal phenylacetates series. Some calculated parameters of structure of studied molecules (bond lengths, angles between bonds, atomic charge) well correlate with chosen experimentally obtained spectroscopic data, such as NMR chemical shifts or wavenumbers of characteristic bands. For example, APT as well as NPA total charge on carboxylate group well correlate with $\Delta\beta_{s-as}$ difference between band of symmetric and asymmetric in-plane deformations. The correlation coefficients *R* are amount to 0.9633 (IR) and 0.9772 (Raman) for APT and 0.9116 (IR) and 0.9980 (Raman) for NPA charges.

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