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Molecular structure of alkali metal 4-nitrobenzoates

E. Regulska, M. Samsonowicz, R. Świsłocka and W. Lewandowski*

Department of Chemistry, Białystok Technical University, Zamenhofa 29, 15-435 Białystok, Poland

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ABSTRACT: The influence of lithium, sodium, potassium, rubidium, and cesium on the electronic system of the 4-nitrobenzoic acid molecule was studied. The vibrational (FT-IR, FT-Raman) and NMR (^{1}H and ^{13}C) spectra for 4-nitrobenzoic acid salts of alkali metals were recorded. The assignment of vibrational spectra was done. Characteristic shifts of band wavenumbers and change in band intensities along the metal series were observed. Good correlation between the wavenumbers of the vibrational bands in the IR and Raman spectra for 4-nitrobenzoates and ionic potential, electronegativity, atomic mass, and affinity of metals were found. The chemical shifts of protons and carbons (^{1}H, ^{13}C NMR) in the series of studied alkali metal 4-nitrobenzoates were observed too.

Optimized geometrical structures of studied compounds were calculated by HF, B3PW91, B3LYP methods using 6-311++G** basis set. The theoretical IR, Raman, and NMR spectra were obtained. The theoretical vibrational spectra were interpreted by means of potential energy distributions (PEDs) using VEDA 3 program. The calculated parameters were compared to experimental characteristic of studied compounds. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: 4-nitrobenzoates; FT-IR; FT-Raman; NMR; geometrical structure

INTRODUCTION

The aims of our works are to investigate: (i) specific effect of various metals on the electronic system of biologically important ligands, (ii) the effect of various substituents on the electronic system of carboxylic acids, their salts and complexes, (iii) the correlation between electronic charge distribution and microbial activity of studied molecules, (iv) search for new antimicrobial active substances, which may be applied in medicine, preserving technology and environment protection as preservatives or new conservants and disinfectants.

Benzoic, salicylic, nicotinic acids, and their derivatives are regarded as model systems representing a wide group of aromatic ligands, which are incorporated into enzymes and other biologically important molecules. The influence of metals on the electronic system was examined through comparison of the changes in so called 'logical series.' The exemplary series are following: Li → Na → K → Rb → Cs; Mg → Ca → Sr → Ba and Zn → Cd → Hg(II) (where ionic radii increase in group) or Na(I) → Ca(II) → La(III) → Th(IV) (ionic radii of these cations do not differ significantly, while their charges increase along series). Our previous works[1,2] have shown that there is a correlation between the perturbation of the electronic system of the investigated ligands and the position of metals in the periodic table. Heavy metals, such as Ag(I), Hg(I), Hg(II), Pb(II), Cd(II) and alkali elements destabilize the electronic system of benzoic, salicylic, and nicotinic acids, while transition metals (3d and 4f), Al and Mg stabilize it. In the case of 3- and 4-aminobenzoic acids, the increase of aromaticity was observed under the influence of alkali metals.[3,4] The influence of substituents in different position in the aromatic ring on the electronic system of ligands was also examined. The substituents in an extremely different manner influence the electronic system of ligand namely: strongly activate (NH_2, OH, OCH_3), weakly deactivate (Cl, Br, I), and strongly deactivate the aromatic ring on an electrophilic substitution (NO_2). The influence of amino and hydroxyl groups, and various halogens on the electronic system of benzoic acid were analyzed earlier.[5–8] The effect of nitro group substituted at 2-, 3-, and 4-position in the ring has been studied recently.[9] For that purpose, experimental and theoretical FT-IR, Raman, NMR spectra, and calculated geometrical structure of the nitrobenzoic acids have been studied. Our team has also examined picolinic, nicotinic, and isonicotinic acids vibrational spectra and the influence of nitrogen atom position in the aromatic ring on aromaticity of molecules.[10,11]

The aim of this paper was to determine the geometry and theoretical molecular spectra of alkali metal 4-nitrobenzoates and to compare them with the

**Correspondence to:* W. Lewandowski, Department of Chemistry, Białystok Technical University, Zamenhofa 29, 15-435 Białystok, Poland.
E-mail: wlewando@pb.edu.pl

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experimental data obtained by various molecular spectroscopic methods in order to characterize the aromaticity and electronic charge distribution in 4-nitrobenzoates. In view of different electronic nature of the $-NO_2$ (electron withdrawing) and $-NH_2$ (electron donating) groups, it is of interest to study the effect of nitro group substitution instead of the amino group. We are looking for correlation between molecular structure and macroscopic properties of studied compounds. The main topic of our spectroscopic investigation was the evaluation of change of aromaticity in studied benzene derivatives.

Aromaticity is associated with enhanced electron delocalization resulting in increased stability, characteristic reactivity, and equalization of inter-atomic bond lengths, and ring currents evidenced by magnetic consequence.[12] To make quantity evaluation of aromaticity, various indices[13] have been defined, which described the distribution of electronic density in the molecule. Electronic charge distribution was also examined by molecular spectroscopic study, which may be the source of quality criterion of aromaticity.

EXPERIMENTAL

Lithium, sodium, potassium, rubidium, and cesium 4-nitrobenzoates were prepared by dissolving the powder of 4-nitrobenzoic acid in the water solution of the appropriate metal hydroxide in a stoichiometric ratio. All reagents were Aldrich analytical chemicals. 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 remaining solvent was removed by drying under reduced pressure at 110 °C. Obtained salts were anhydrous, in the IR spectra of solid state samples, the lack of bands characterized for crystallizing water was observed.

The IR spectra were recorded with an 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 a Perkin Elmer System 2000. The resolution of spectrometer was 1 cm^{-1}.

The NMR spectra of DMSO saturated solution were recorded with a NMR AC 200 F, Bruker unit at room temperature. TMS was used as an internal reference.

To calculate optimized geometrical structures, a few quantum-mechanical methods were used: (i) Hartree-Fock (HF), (ii) density functional (DFT) hybrid method B3PW91, which uses the Becke's three-parameter functional with nonlocal correlation provided by Perdew-Wang 91 expression, (iii) the DFT hybrid method B3LYP with nonlocal correlation provided by Lee-Yang-Parr expression. The 6-311++G** basis set was used as the standard basis set available for all atoms.

The theoretical IR and Raman spectra were obtained. The theoretical vibrational spectra were interpreted by means of potential energy distributions (PEDs) using VEDA 3 program.[14]

NMR properties of 4-nitrobenzoates and 4-nitrobenzoic acid were predicted using B3LYP/6-311+G* and B3LYP/6-311++G** basis sets with respect to TMS. B3LYP/6-311++G** method was used to obtain the optimized structures. The chemical shifts were calculated by Gaussian 98 and Gauss View 3.09 molecular visualization program[15,16] subtracting the appropriate isotropic part of the shielding tensor q from that nitrobenzoates (isotropic shielding).

All theoretical calculations were performed using the GAUSSIAN 98W (v.5.4) package of program[16] running on a PC computer. The calculated parameters were compared to experimental characteristic of studied compounds.

RESULTS AND DISCUSSION

Calculated geometrical structure

To calculate optimized geometrical structures, a few quantum chemical methods were used: HF/6-311++G**, B3PW91/6-311++G**, B3LYP/6-311++G**. The distances between atoms and the angles between bonds were calculated. The atoms of molecule are numbered as Fig. 1. Geometric[17] and magnetic[18,19] aromaticity indices, dipole moments, and energies for 4-nitrobenzoates were calculated too. The results obtained by three methods for lithium, sodium, and potassium 4-nitrobenzoates are presented in Table 1.

The results show that the bond distances of seven carbon atom and 9, 10 oxygen atoms vary in free 4-nitrobenzoic acid molecule,[9] in which they are 1.206 Å and 1.348 Å (B3PW91), respectively, but in the salts, they

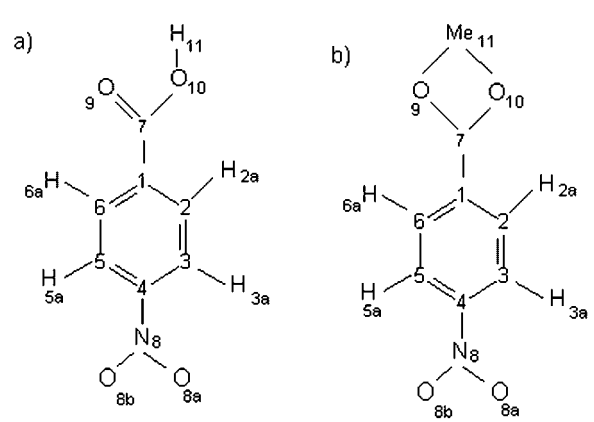

Figure 1. Structures of: (a) 4-nitrobenzoic acid and (b) 4-nitrobenzoate of alkali metal (Me)

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Table 1. The values of distances (Å[a]) between atoms, bonds angles, and aromaticity indices calculated for 4-nitrobenzoates using three methods

Methods	HF/6-311++G**			B3PW91/6311++G**			B3LYP/6-311++G**		
Metals	Li	Na	K	Li	Na	K	Li	Na	K
				Distance					
1–2	1.388	1.388	1.388	1.396	1.396	1.396	1.399	1.400	1.399
2–3	1.383	1.383	1.383	1.387	1.387	1.387	1.389	1.390	1.390
3–4	1.382	1.382	1.382	1.390	1.390	1.390	1.392	1.392	1.393
4–5	1.382	1.382	1.382	1.390	1.390	1.390	1.392	1.392	1.393
5–6	1.383	1.383	1.383	1.387	1.387	1.387	1.390	1.390	1.390
1–6	1.388	1.388	1.388	1.396	1.396	1.396	1.399	1.400	1.399
1–7	1.502	1.512	1.518	1.499	1.509	1.514	1.502	1.512	1.518
7–9	1.244	1.240	1.238	1.267	1.263	1.261	1.270	1.266	1.264
7–10	1.244	1.240	1.238	1.267	1.263	1.261	1.270	1.266	1.264
10–11	1.859	2.214	2.561	1.872	2.224	2.526	1.868	2.221	2.534
4–8	1.469	1.468	1.467	1.475	1.473	1.472	1.481	1.479	1.478
8–8a	1.187	1.188	1.188	1.219	1.220	1.220	1.225	1.226	1.226
8–8b	1.187	1.188	1.188	1.219	1.220	1.220	1.225	1.226	1.226
2–2a	1.073	1.072	1.072	1.084	1.084	1.084	1.082	1.082	1.082
3–3a	1.071	1.071	1.071	1.082	1.083	1.083	1.081	1.081	1.081
5–5a	1.071	1.071	1.071	1.082	1.083	1.083	1.081	1.081	1.081
6–6a	1.073	1.072	1.072	1.084	1.084	1.084	1.082	1.082	1.082
				Angles					
1–2–3	122.2	120.4	120.5	120.3	120.5	120.5	120.3	120.5	120.6
2–3–4	118.4	118.4	118.4	118.5	118.5	118.5	118.5	118.5	118.6
3–4–5	122.6	122.4	122.3	122.4	122.2	122.2	122.3	122.2	122.1
4–5–6	118.4	118.4	118.5	118.5	118.5	118.5	118.5	118.5	118.6
5–6–1	120.2	120.4	120.5	120.3	120.4	120.5	120.3	120.5	120.6
2–1–6	120.3	120.0	119.8	120.1	119.8	119.7	120.1	119.8	119.6
1–7–9	119.4	118.1	117.6	119.1	117.9	117.5	119.3	118.0	117.6
1–7–10	119.3	118.1	117.5	119.2	117.9	117.5	119.3	118.0	117.6
7–9–11	83.7	88.4	92.2	82.9	87.8	91.2	82.9	87.8	91.4
7–10–11	121.3	123.9	124.9	121.7	124.2	124.9	121.4	124.0	124.8
9–11–10	119.8	120.0	120.1	119.9	120.1	120.1	120.0	120.1	120.2
2–1–7	119.9	120.0	120.1	119.9	120.1	120.1	120.0	120.1	120.2
6–1–7	118.7	118.8	118.8	117.6	118.9	118.9	118.8	118.9	118.9
1–2–2a	119.2	119.0	118.9	118.7	118.5	118.4	118.8	118.6	118.5
2–3–3a	121.4	121.4	121.4	121.9	121.9	121.9	121.8	121.8	121.8
3–4–8	120.2	120.2	120.1	119.6	119.6	119.5	119.7	119.7	119.6
4–8–8a	120.6	120.6	120.6	121.0	121.1	121.1	120.9	120.9	120.9
4–8–8b	117.6	117.7	117.8	117.6	117.7	117.8	117.7	117.8	117.8
8a–8–8b	117.6	117.7	117.8	117.6	117.7	117.8	117.7	117.8	117.8
4–5–5a	124.7	124.6	124.5	124.8	124.6	124.5	124.6	124.4	124.3
				Geometric aromaticity indices					
Aj	0.999	0.999	0.999	0.998	0.998	0.998	0.998	0.998	0.998
BAC	0.975	0.975	0.975	0.954	0.954	0.954	0.952	0.950	0.954
HOMA	0.995	0.995	0.995	0.994	0.994	0.994	0.988	0.986	0.987
GEO	0.002	0.002	0.002	0.004	0.004	0.004	0.004	0.005	0.004
EN	0.003	0.003	0.003	0.002	0.002	0.002	0.008	0.009	0.009
I_6	97.819	97.819	97.819	96.877	96.877	96.877	96.632	96.391	96.871
				Magnetic aromaticity indices					
NICS	−10.954	−10.923	−10.859	−9.167	−9.186	−6.734	−8.974	−9.003	−8.943
				Dipole moment					
D	8.870	11.949	13.922	8.752	11.759	13.413	8.705	11.659	13.471
				Energy					
Hartree[b]	−628.9	−783.3	−1220.6	−632.2	−787.0	−1224.6	−632.5	−787.3	−1224.9

[a] 1Å=10^{-10} m.
[b] 1 hartree = 2625.500 kJ/mol.

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are equal. It indicates a symmetric structure of carboxylic ion. The lengths of C7–O9 and C7–O10 bonds slightly decrease in the series from lithium to potassium 4-nitrobenzoate, but in the case of O10–Me11 bond, the distance, inversely, increase in this series. The O10-Me11 bond length is about two times longer than O10-H11 bond in free acid (0.946-HF; 0.967-B3PW91; 0.969-B3LYP).

In sodium and potassium salts, the bond lengths are longer. The bond distances between 1 and 7 carbon atoms distinctly increase from 4-nitrobenzoic acid (1.495 Å-HF; 1.489 Å-B3PW91; 1.492 Å-B3LYP) through lithium and sodium to potassium 4-nitrobenzoates. Comparing the bond lengths of aromatic ring of studied 4-nitrobenzoates and free acid, one can observe that the differences between the largest and the least bond in the ring decrease in the case of salts. Exemplary, for lithium, sodium, and potassium salts, it amounts to 0.009 Å but for 4-nitrobenzoic acid 0.011 Å (B3PW91). In the case of B3LYP method, the values of difference amount to 0.010 Å for lithium and sodium 4-nitrobenzoates and 0.009 Å for potassium 4-nitrobenzoate (K 4-NB) while 0.012 Å for 4-nitrobenzoic acid (4-NBA). This simple parameter indicates that aromaticity of salt molecule insignificantly increases in comparing to acid molecule. In alkali metal aminobenzoates, which have been studied previously, the changes are clearer.[3,4]

Equalization of angles in aromatic ring is another of the criteria of aromaticity of molecule. The values of angles between C−C bonds in aromatic ring become equalized along the series: lithium → sodium → potassium salt. These results suggest that the perturbation of aromatic system of investigated molecules decrease from potassium to lithium salt. Taking into consideration data obtained for free 4-nitrobenzoic acid,[9] the values of angles become equalized when nitrobenzoates are created. The largest value of differences of angles is observed for free acid (3.9°-B3LYP) and the smallest one for potassium salt (3.5°-B3LYP). Comparing the values of differences of angles, the following conclusion could be drawn: aromaticity insignificantly increases in the order 4-NBA → Li 4-NB → Na 4-NB → K 4-NB.

The energy shows significantly decreasing tendency along the series: 4-nitrobenzoic acid > Li > Na > K 4-nitrobenzoates. The values of energy calculated by B3LYP method are −625.5; −632.5; −787.3; −1224.9 hartree (1 hartree = 2625.5 kJ/mol), respectively. It indicates that stability of studied molecules increase in the series. Values of total energy for 4-aminobenzoates (previously obtained) are higher than for 4-nitrobenzoates,[4] so 4-nitrobenzoates are more stable than 4-aminobenzoates.

Comparing values of dipole moment for molecules of lithium, sodium, and potassium salts of 4-nitrobenzoic acid increasing tendency along the series: free acid → lithium → sodium → potassium 4-nitrobenzoates is observed. The values of dipole moment calculated by B3LYP method are 3.770; 8.705; 11.659; 13.471 D, respectively. The value obtained for 4-nitrobenzoic acid is considerably smaller than for lithium salt.

To make quantitative evaluation of aromaticity of studied molecules, the geometric aromaticity indices were calculated. Obtained values of such indices as: A_j – normalized function of variance of bond lengths; BAC – Bond Alternation Coefficient; HOMA – abbreviation from Harmonic Oscillator Model of Aromaticity, and I_6-Bird's indices are presented in Table 1. These indices were detailed described in our previous work.[20]

Distribution of electronic density in the molecule determines the forces acting on the nuclei. Thus, geometry may be a source of reliable information on the electron distribution and may be used for description of π-electron delocalization. Thus aromaticity index HOMA may be used for estimation of π-electron delocalization. The extended form of HOMA allows one to get information about the nature of dearomatization. If dearomatization is due to an increase of bond alternation, then the GEO index is large; if dearomatization is due to bond elongation, then the EN term is large (HOMA = 1-EN-GEO).

Geometric aromaticity indices for free 4-nitrobenzoic acid (calculated exemplary by B3PW91 method: 0.998; 0.950; 0.993; 0.005; 0.002; 96.29, respectively) are insignificantly smaller then those obtained for alkali salts. It indicates a higher aromaticity of salt molecules than of 4-nitrobenzoic acid. Comparing values of the aromaticity indices in the series lithium, sodium, and potassium salts, no differences were noticed. It arises from these criteria that aromaticity in this series do not change. In previously studied 4-aminbenzoates,[4] the values of aromaticity indices significantly increase along series 4-ABA → Li 4-AB → Na 4-AB → K 4-aminobenzoates.

The aromaticity indices based on magnetism NICS were also calculated. The negative values of the absolute shielding estimated in the center of the ring and 1 Å above it were obtained and presented in Table 1. They are bigger then those obtained for 4-nitrobenzoic acid −11.143 (HF), −9.338 (B3PW91), and −9.148 (B3LYP).[9] It indicates that aromaticity of salt molecule decreases in comparison with acid one. This conclusion is opposite to this based on geometry. According to Schleyer,[18] magnetic aromaticity indices are more representatively indices because they depend on electronic structure of molecule.

The charges on the atoms in lithium, sodium, and potassium 4-nitrobenzoates molecules calculated by HF/6-311++G**, B3PW91/6311++G**, and B3PLYP/6311++G** methods are presented in Table 2. The Mulliken Population (M) and Natural Population Analysis phase of Natural Bond Orbital (NBO) analysis[21] were used.

The charges on 9 and 10 oxygen atoms in 4-nitrobenzoic acid calculated by B3LYP method are: −0.275 and −0.177 according to Mulliken, and according

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Table 2. Atomic charges (e^a) on the atoms in lithium, sodium, and potassium 4-nitrobenzoates

Atom position	HF/6-311++G**						B3PW91/6-311++G**						B3LYP/6-311++G**					
	Lithium		Sodium		Potassium		Lithium		Sodium		Potassium		Lithium		Sodium		Potassium	
	M	NBO	M	NBO	M	NBO	M	NBO	M	NBO	M	NBO	M	NBO	M	NBO	M	NBO
C1	1.834	−0.138	1.743	−0.124	1.495	−0.117	2.499	−0.123	2.579	−0.113	1.630	−0.110	2.085	−0.120	2.184	−0.110	1.279	−0.106
C2, C6	−1.457	−0.145	−1.304	−0.154	−1.320	−0.159	−1.593	−0.163	−1.497	−0.170	−1.494	−0.173	−1.289	−0.158	−1.199	−0.165	−1.204	−0.168
C3, C5	1.008	−0.170	0.875	−0.169	0.880	−0.168	1.168	−0.195	1.089	−0.196	1.056	−0.197	0.914	−0.190	0.848	−0.191	0.825	−0.191
C4	−1.370	0.070	−1.329	0.061	−1.289	0.056	−1.763	0.075	−1.745	0.069	−1.717	0.066	−1.329	0.081	−1.312	0.075	−1.290	0.071
C7	−0.059	0.930	−0.040	0.929	−0.085	0.930	−0.522	0.748	−0.630	0.747	−0.122	0.750	−0.387	0.757	−0.516	0.756	−0.097	0.758
H2a, H6a	0.260	0.225	0.267	0.224	0.258	0.224	0.241	0.242	0.245	0.241	0.234	0.240	0.211	0.237	0.215	0.236	0.204	0.235
H3a, H5a	0.320	0.232	0.313	0.229	0.314	0.228	0.316	0.248	0.311	0.245	0.311	0.244	0.274	0.243	0.270	0.241	0.270	0.239
N8	−0.107	0.629	−0.115	0.630	−0.112	0.631	−0.165	0.489	−0.174	0.489	−0.171	0.489	−0.173	0.486	−0.182	0.486	−0.180	0.486
O8a, O8b	−0.046	0.453	−0.048	−0.456	−0.052	−0.459	0.023	−0.377	0.021	−0.382	0.016	−0.384	0.003	−0.380	−0.000	−0.384	0.004	−0.387
O9, O10	−0.443	−0.915	−0.572	−0.907	−0.600	−0.906	−0.290	−0.822	−0.421	−0.810	−0.456	−0.809	−0.313	−0.826	−0.439	−0.813	−0.479	−0.814
M11	0.419	0.957	0.679	0.970	1.032	0.982	0.220	0.947	0.475	0.951	1.046	0.964	0.207	0.944	0.437	0.945	1.062	0.962

[a] $e = 1.6021892 \times 10^{-19}$ C.

to NBO: −0.585; −0.688, respectively. These values are different but those obtained for alkali salts by both Mulliken and NBO analyses are equal. The absolute values of Mulliken charges increase in series 4-NBA < Li 4-NB < Na 4-NB < K 4-NB. They change similarly according to HF and B3PW91 methods.

In the case of NBO analysis, the values of charges on those oxygen atoms are also negative. The absolute values of them obtained for acid are also smaller than those obtained for salt molecules but they decrease in the series of alkali metals. These values for sodium and potassium salts are almost equal.

The Mulliken charges on C1 atom in 4-nitrobenzoates are positive and they are larger then that in free acid (1.053 B3LYP). NBO charges on C1 atom for 4-nitrobenzoates as well as for acid (−0.138 B3LYP) are negative. These values increase in the series from acid to potassium salt. The Mulliken charge on C7 atom in 4-nitrobenzoic acid is positive (0.238 B3LYP), but it is negative in salts. These changes are the same as those previously obtained for 4-aminobenzoates.[4] It means that the influence of metal on the atomic charges independents on the kind of substituent in benzoate ring. According to NBO analysis, the decrease of charge value on C7 atom is also observed in comparison with free acid (0.792 B3LYP). The polarity of bonds was calculated by HF, B3PW91, and B3LYP methods. The results obtained for Mulliken as well as NBO analysis are presented in Table 3. From Mulliken's one follows that polarity insignificantly decrease along the series Li 4-NB → Na 4-NB → K 4-nitrobenzoates. However, polarity for salt molecules is significantly bigger than for free acid, for which they are 20.679-HF; 25.090-B3PW91; 20.089-B3LYP. The same conclusion is for HF, B3PW91 as well as B3LYP method. It arises that electronic system was disturbed and aromaticity of salts is smaller than for acid, whereas it increases along series from lithium to potassium 4-nitrobenzoates. NBO analysis shows that polarity insignificantly increases for salts in the series Li 4-NB → Na 4-NB → K 4-nitrobenzoates for HF method, but for two others the series is Na 4-NB → Li 4-NB → K 4-nitrobenzoates. The polarity for free acid is also smaller then for salts in B3PW91 and B3LYP methods (9.389, 9.601) and in HF method, it varies between lithium and sodium 4-nitrobenzoates.

NMR spectra

^{1}H NMR and ^{13}C NMR spectra of lithium, sodium, potassium, rubidium, and cesium 4-nitrobenzoates were recorded and obtained data are gathered in Table 4. Differences of chemical shifts in ^{1}H and ^{13}C NMR spectra of alkali metal 4-nitrobenzoates in comparison to those of 4-nitrobenzoic acid are shown in Table 5. The atom positions are numbered as in Fig. 1. The chemical shifts of

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Table 3. Polarity of lithium, sodium, and potassium 4-nitrobenzoates

	HF						B3PW 91						B3LYP					
	Lithium		Sodium		Potassium		Lithium		Sodium		Potassium		Lithium		Sodium		Potassium	
	M	NBO	M	NBO	M	NBO	M	NBO	M	NBO	M	NBO	M	NBO	M	NBO	M	NBO
C1–C2	3.291	0.007	3.047	0.03	2.815	0.042	4.092	0.04	4.076	0.057	3.124	0.063	3.374	0.038	3.383	0.055	2.483	0.062
C2–C3	2.465	0.025	2.179	0.015	2.2	0.009	2.761	0.032	2.586	0.026	2.55	0.024	2.203	0.032	2.047	0.026	2.029	0.023
C3–C4	2.378	0.24	2.204	0.23	2.169	0.224	2.931	0.27	2.834	0.265	2.773	0.263	2.243	0.271	2.16	0.266	2.115	0.262
C4–C5	2.378	0.24	2.204	0.23	2.169	0.224	2.931	0.27	2.834	0.265	2.773	0.263	2.243	0.271	2.16	0.266	2.115	0.262
C5–C6	2.465	0.025	2.179	0.015	2.2	0.009	2.761	0.032	2.586	0.026	2.55	0.024	2.203	0.032	2.047	0.026	2.029	0.023
C6–C1	3.291	0.007	3.047	0.03	2.815	0.042	4.092	0.04	4.076	0.057	3.124	0.063	3.374	0.038	3.383	0.055	2.483	0.062
C1–C7	1.893	1.068	1.783	1.053	1.58	1.047	3.021	0.871	3.209	0.86	1.752	0.86	2.472	0.877	2.7	0.866	1.376	0.864
C2–H2a	1.717	0.37	1.571	0.378	1.578	0.383	1.834	0.405	1.742	0.411	1.728	0.413	1.5	0.395	1.199	0.165	1.204	0.168
C3–H3a	0.688	0.402	0.562	0.398	0.566	0.396	0.852	0.443	0.778	0.441	0.745	0.441	0.64	0.433	0.633	0.427	0.621	0.426
C5–H5a	1.008	0.17	0.875	0.169	0.88	0.168	1.168	0.195	1.089	0.196	1.056	0.197	0.914	0.19	0.848	0.191	0.825	0.191
C6–H6a	1.717	0.37	1.571	0.378	1.578	0.383	1.834	0.405	1.742	0.411	1.728	0.413	1.5	0.395	1.199	0.165	1.204	0.168
N8–O8a	0.061	0.176	0.067	1.086	0.06	1.09	0.188	0.866	0.195	0.871	0.187	0.873	0.176	0.866	0.182	0.87	0.184	0.873
N8–O8b	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.061
C2–N8	1.35	0.774	1.189	0.784	1.208	0.79	1.428	0.652	1.323	0.659	1.323	0.662	1.116	0.644	1.017	0.651	1.024	0.654
C7–O9	0.384	1.845	0.532	1.836	0.515	1.836	0.232	1.57	0.209	1.557	0.334	1.559	0.074	1.583	0.077	1.569	0.382	1.572
C7–O10	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384	0.384
O10–H11	0.862	1.872	1.251	1.877	1.632	1.888	0.51	1.769	0.896	1.761	1.502	1.773	0.52	1.77	0.876	1.758	1.541	1.776
Σ	26.393	8.036	24.706	8.954	24.41	8.976	31.08	8.305	30.62	8.308	27.694	8.336	24.997	8.28	24.356	7.801	22.06	7.831

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Table 4. Experimental chemical shifts in ^{1}H and ^{13}C NMR spectra of alkali metal 4-nitrobenzoates in comparison to 4-nitrobenzoic acid

	Experimental chemical shifts δ [ppm]					
Atom position*	H	Li	Na	K	Rb	Cs
H2a	8.15	8.10	8.10	8.08	8.07	8.06
H3a	8.25	8.13	8.13	8.10	8.10	8.08
H5a	8.25	8.13	8.13	8.10	8.10	8.08
H6a	8.15	8.10	8.10	8.08	8.07	8.06
C1	136.43	145.95	146.70	147.11	147.61	147.77
C2	130.73	130.31	129.98	129.92	129.95	130.10
C3	123.71	122.67	122.55	122.49	122.52	122.51
C4	150.04	149.00	147.68	147.58	147.29	146.31
C5	123.71	122.67	122.55	122.49	122.52	122.51
C6	130.73	130.31	129.98	129.92	129.95	130.10
C7	165.86	167.88	167.68	167.03	167.06	167.09

*The atoms are numbered as in Fig. 1.

Table 5. Values and direction of differences of chemical shifts in ^{1}H and ^{13}C NMR spectra of 4-nitrobenzoates in comparison to 4-nitrobenzoic acid, $\Delta\delta$ [ppm]

	4-nitrobenzoates				
Atom position*	Li	Na	K	Rb	Cs
H2a	−0.05	−0.05	−0.07	−0.08	−0.09
H3a	−0.12	−0.12	−0.15	−0.15	−0.17
H5a	−0.12	−0.12	−0.15	−0.15	−0.17
H6a	−0.05	−0.05	−0.07	−0.08	−0.09
C1	9.52	10.27	10.68	11.18	11.34
C2	−0.42	−0.75	−0.81	−0.78	−0.63
C3	−1.04	−1.16	−1.23	−1.19	−1.20
C4	−1.04	−2.36	−2.46	−2.75	−3.73
C5	−1.04	−1.16	−1.23	−1.19	−1.20
C6	−0.42	−0.75	−0.81	−0.78	−0.63
C7	2.02	1.82	1.17	1.20	1.23

*The atoms are numbered as in Fig. 1.

protons (^{1}H NMR) and carbons (^{13}C NMR) in the series of alkali metals express the influence of studied metal on the electronic charge density around those atoms. The changes of chemical shift values on account of alkali salts formation from 4-nitrobenzoic acid are presented in Fig. 2 (of protons) and Fig. 3 (of carbon atoms).

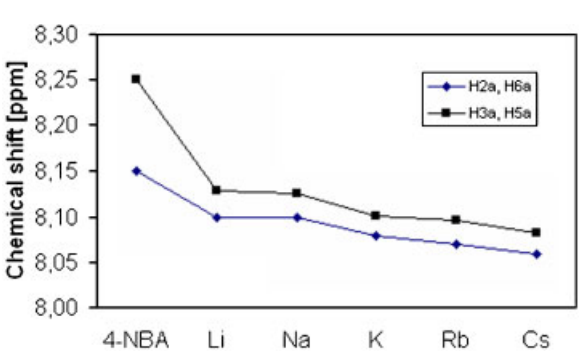

Figure 2. The values of chemical shifts for 4-nitrobenzoic acid and its alkali metal salts in ^{1}H NMR spectra

In the case of studied compounds, all values of protons are diamagnetically shifted in comparison to 4-nitrobenzoic acid. It indicates about decreasing of intensity of the ring current and an increase in the screening of these protons in 4-nitrobenzoates and finally about decreasing of aromaticity.

The chemical shifts of protons numbered 2a and 6a, and 3a and 5a are the same in pairs. The value of chemical shift of the second pair is higher than δ of the first one. It means that electronic charge density is higher around positions 2a and 6a comparing to positions 3a and 5a, therefore an increase in the screening of these protons proceed.[22] The differences in chemical shifts of protons along alkali metal 4-nitrobenzoates series are rather small although they are clear. Obtained results show that electronic charge density increases around protons (2a, 3a, 5a, 6a) in the order Li-Na-K-Rb-Cs 4-nitrobenzoates (Fig. 2).

The dependencies of chemical shifts (H3a, H5a) upon atomic mass, inverse of atomic mass, electronegativity,

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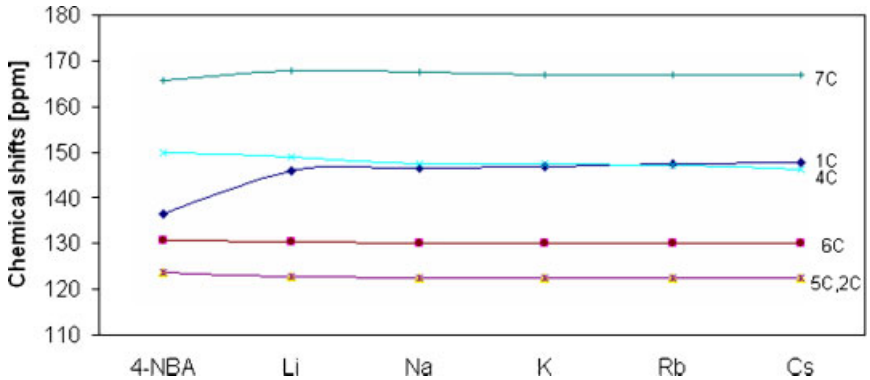

Figure 3. The values of chemical shifts for 4-nitrobenzoic acid and its alkali metal salts in ^{13}C NMR spectra

affinity, atomic and ionic radius, ionization and ionic potential of alkali metal were investigated to estimate which parameter mainly influences on the electronic charge distribution. The statistical analysis shows the best correlation for ionization potential ($R = 0.992$). High values of correlation coefficients are obtained for atomic and ionic radius of alkali metal (−0.975, −0.977, respectively).

The similar effect is observed in the case of carbon atom chemical shifts. The chemical shifts of C2, C3, C4, C5, and C6 atoms are shifted diamagnetically, but the values for C1 and C7 are shifted to higher values comparing to free acid (Table 5). The largest changes of chemical shifts are observed at C1 atom, it means a decrease in electronic charge density around this nucleus and a decrease in the screening effect. The chemical shifts of C2 and C6 carbon atoms are higher than of C3 and C5. The differences between chemical shifts of carbon atoms along metal series are small (Fig. 3). Only the values obtained for C1 atom clearly increase in comparison to 4-nitrobenzoic acid and increase in the series from lithium to cesium 4-nitrobenzoates. The correlation between chemical shifts of C1 atom and atomic mass, inverse of atomic mass, electronegativity, affinity, atomic and ionic radius, ionization and ionic potential of alkali metal was investigated. It was found that all parameters well correlate with values of chemical shifts, but the best correlation is obtained for atomic radius ($R = 0.990$). This correlation is presented at Fig. 4. The values of chemical shifts for other carbon atoms insignificantly decrease. An increase of electronic charge density in the order Li-Na-K-Rb-Cs 4-nitrobenzoates is observed (Fig. 3). The correlation between chemical shifts of C4 atom and above-mentioned parameters of alkali atoms was also investigated and slightly worse correlation coefficients were obtained. The supreme value ($R = 0.962$) was obtained for electronegativity. The chemical shifts for C7 atom also increase in comparison to 4-nitrobenzoic acid, but they decrease in the series from lithium to potassium 4-nitrobenzoates, but for other salts, these values are almost equal.

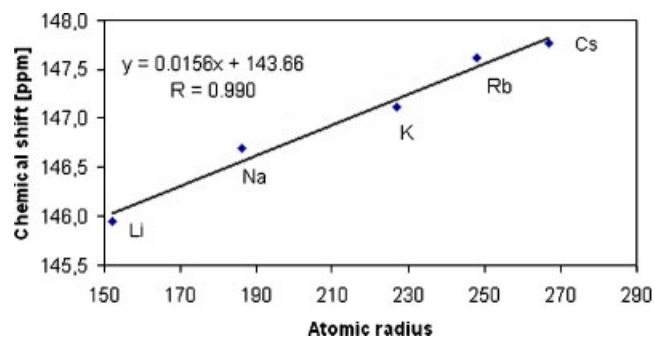

Figure 4. The correlation between chemical shifts of C1 atom and values of atomic radius of alkali metal

The linear correlation between the differences in the charges on the carbon atoms and corresponding nuclear shielding as result of 4-nitrobenzoates formation is noted. A linear correlation between differences in atomic charges on aromatic ring carbon atoms and its theoretically obtained chemical shifts (Table 6) exemplary for lithium 4-nitrobenzoates is presented in Fig. 5. Correlation coefficients for sodium and potassium salts are amount to 0.973 and 0.818, respectively. Comparing differences in charge on carbon atoms and differences in theoretically obtained nuclear shieldings, the highest values are observed on C1 carbon atom, which is situated near to carboxylic group.

A linear correlation between differences of atomic charge on C7 atom as result of replacing H11 atom by alkali metal and differences of chemical shifts of C7 atom in experimentally obtained ^{13}C NMR spectra is observed too. The correlation coefficient is 0.967. Similarly, dependencies for other carbon atoms are done. It is interesting to note that the highest value of correlation coefficient is obtained for C2 atom (0.999).

Theoretical ^{1}H and ^{13}C NMR spectra of lithium, sodium, and potassium salts were also obtained. Geometrical structures of studied compounds were optimized by B3LYP/6-311++G** method. The GIAO method was used for prediction of DFT nuclear

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Table 6. Theoretical chemical shifts of 4-nitrobenzoic acid and its alkali metal salts in ^{1}H and ^{13}C NMR spectra, δ [ppm]

	4-nitrobenzoic acid		Lithium 4-nitrobenzoate		Sodium 4-nitrobenzoate		Potassium 4-nitrobenzoate	
Atom position*	B3LYP/ 6-311++G**	B3LYP/ 6-311+G*	B3LYP/ 6-311 ++G**	B3LYP/ 6-311+G*	B3LYP/ 6-311++G**	B3LYP/ 6-311+G*	B3LYP/ 6-311++G**	B3LYP/ 6-311+G*
C1	141.06	138.77	146.61	145.02	148.29	146.70	150.65	149.05
C2	139.57	137.29	137.24	135.65	137.00	135.40	136.81	135.21
C3	130.94	128.66	129.64	128.05	129.03	127.44	129.07	127.48
C4	159.47	157.20	157.93	156.34	155.79	154.20	156.62	155.02
C5	130.85	128.57	129.64	128.05	129.03	127.43	129.07	127.47
C6	137.75	135.47	137.24	135.65	136.98	135.39	136.81	135.21
C7	170.90	168.62	187.91	186.32	180.55	178.96	181.21	179.61
H2a	8.60	8.52	8.61	8.52	8.62	8.53	8.57	8.49
H3a	8.58	8.50	8.51	8.42	8.46	8.37	8.41	8.32
H5a	8.54	8.50	8.51	8.42	8.46	8.37	8.41	8.32
H6a	8.43	8.34	8.61	8.52	8.62	8.53	8.57	8.49

*The atoms are numbered as in Fig. 1.

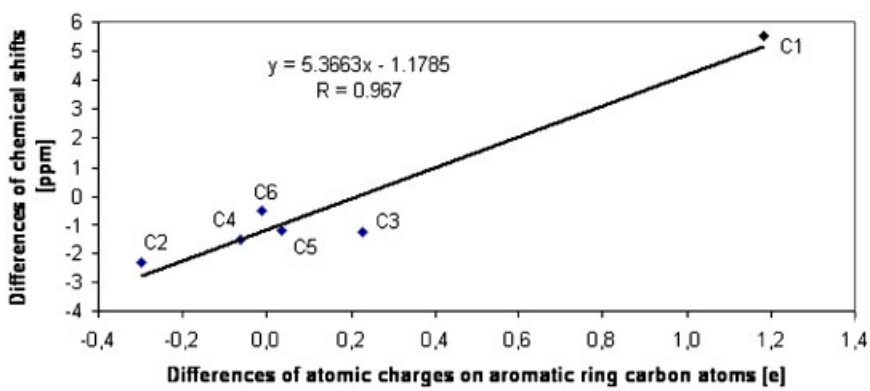

Figure 5. The correlation between differences of atomic charges on aromatic ring carbon atoms and differences of their chemical shifts for lithium 4-nitrobenzoates

shieldings. Cheeseman recommended these methods for studied compounds, as mentioned in the documentation for the Gaussian program.[16] Theoretically obtained chemical shifts of lithium, sodium, and potassium 4-nitrobenzoates in comparison to 4-nitrobenzoic acid are gathered in Table 6. The linear correlation between ^{13}C NMR shieldings and experimental data is noted. The data show a good correlation between predicted and observed carbon chemical shifts (Fig. 6).

FT-IR and FT-Raman spectra

The vibrational spectra of the synthesized 4-nitrobenzoates were recorded and assigned. The observed IR and Raman bands together with their relative intensities and band assignments of studied metal salts with 4-nitrobenzoic acid are presented in Table 7. The bands are numbered along with the notation used by Varsányi.[23] The calculated wavenumbers and intensities

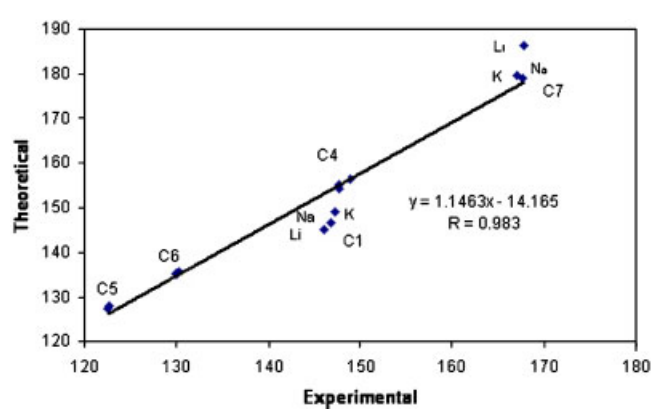

Figure 6. The correlation between theoretical (B3LYP/ 6-311+G*) and experimental chemical shifts ^{13}C NMR

of IR and Raman spectra of lithium, sodium, and potassium 4-nitrobenzoates obtained by B3LYP method at 6-311++G** level are shown in Table 8. The theoretical vibrational spectra were interpreted by means

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Table 7. Wavenumbers [cm^{-1}], intensities and assignments of selected bands in the IR and Raman spectra of 4-nitrobenzoates in comparison to 4-nitrobenzoic acid

4-nitrobenzoates of													
Lithium		Sodium		Potassium		Rubidium		Cesium		4-nitrobenzoic acid			
IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	Assignment	
3108 w	3114 w	3212 w	3113 w	3115 w	3109 vw	3115 w	3105 vw	3106 w	–	3117 m		ν(CH)	2
3081 w	3085 m	3082 vw	3085 m	3074 w	3087 vw	–	3087 w	3083 w	3087 w	3063 m	3064 vw	ν(CH)	20b
3051 w	–	3052 w	3049 vw	3043 w	3046 vw	3046 w	–	3045 w	3051 vw	3081 m	3096 m	ν(CH)	20a
										1693 vs	1631 w	ν(C=O)	
1621 s	1622 w	1622 s	1625 vw	1634 s	1616 vw	1626 m	1613 vw	1618 s	1613 vw	1608 s	1599 s	ν(CC)	8b
1597 vs	1599 vs		1598 vs	1622 s	1595 vs	1620 s	1595 vs	1599 s	1596 vs			ν(CC)	8a
1577 vs	–	1590 vs	–	1587 vs	–	1576 vs	–	1590 vs	–	1543 vs	1543 w	$\nu_{as}(NO_2)$	
1522 s	1521 w	1525 s	1521 w	1530 s	1510 w	1520 s	1518 w	1518 s	1516 w			ν_{as}(COO)	
1491 w	1493 vw	1491 w	1491 vw	1490 vw	1486 vw	1491 vw	1486 vw	–	1485 vw	1495 m	1493 w	ν(CC)	19a
1414 vs	1433 m	1408 vs	1426 m	1395 vs	1397 m	1388 s	1394 s	1374 s	1383 s			ν_s(COO)	
1403 sh	1408 w	1369 sh	1405 w	1381 m	1385 w	–	–	–	–	1430 vs	1442 vw	ν(CC)	19b
1350 vs	1350 s	1353 vs	1358 s	1353 vs	1348 vs	1350 vs	1344 vs	1346 vs	1339 vs	1352 vs	1353 vs	$\nu_s(NO_2)$	
1319 m	–	1318 m	–	1319 m	–	1321 m	–	1321 m	–	1312 m		ν(CC)	14
1286 w	–	–	–	1282 sh	–	–	–	1293 vw	–			β(CH)	3
1172 w	1175 w	1172 w	1182 w	1166 vw	1172 w	1167 vw	1169 vw	1185 w	1169 w	1198 sh		ν(CC)	9a
1144 w	1146 w	1139 w	1142 w	1130 w	1134 w	1134 w	1135 w	1130 vw	1132 w	1127 m	1131 w	ν(CC)	7a
1106 m	–	1105 m	–	1106 m	–	1105 m	–	1105 m	–	1110 s	1109 s	β(CH)	18b
1090 vw	1111 s	1085 sh	1107 m	1084 w	1109 s	1088 vw	1107 s	1074 w	1107 s	1178 m	1179 m	ν(C–N)	
1015 m	1017 vw	1016 m	1019 w	1013 m	1016 w	1011 w	1015 w	1009 w	1014 w	1014 s	1015 vw	β(CH)	18a
987 w	–	981 w	–	980 vw	–	980 vw	–	989 vw	–	977 m	975 vw	γ(CH)	17a
964 w	967 vw	964 vw	972 w	–	–	972 w	972 vw	965 vw	970 vw	860 s	863 s	γ(CH)	17b
881 m	–	878 m	–	881 m	–	881 m	–	879 m	–	879 vs		$\beta_s(NO_2)$	
867 w	869 s	–	869 s	863 w	866 s	860 w	867 s	859 w	867 s	822 m		γ(CH)	10a
837 s	837 vw	833 s	835 w	823 s	832 vw	827 m	827 vw	827 m	829 vw			β_s(COO)	
804 s	800 w	799 s	800 w	800 s	802 w	802 s	802 w	802 m	802 w			γ_s(COO)	
										801 s	792 m	β(C=O)	
764 vw	–	–	–	–	–	765 w	–	763 w	–			β(CH)	
727 vs	730 vw	724 vs	–	724 vs	–	725 vs	–	723 vs	–	717 vs	720 vw	$\gamma_s(NO_2)$	
671 vw	714 w	670 w	711 w	672 w	710 w	670 vw	711 w	673 vw	712 w	649 vw		γ(CH)	4
628	628 m	626 vw	627 m	626 w	628 m	625 vw	629 m	–	629 m	627 sh	629 m	α(CCC)	6b
526 m	–	506 m	559 w	511 m	548 w	510 m	551 w	509 m	549 w	513 s	522 vw	$\beta_{as}(NO_2)$	
514 m	517 vw		510 w		–		503 vw		507 vw			β_{as}(COO)	
464 m	459 vw	–	459 vw	442 w	–	447 w	–	–	454 vw	447 m		φ(CC)	16b
401 w	415 vw	411 w	410 w	406 w	409 vw	420 w	–	411 w	415 vw	413 w	414 vw	φ(CC)	16a

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Table 8. Theoretical obtained IR and Raman spectra for 4-nitrobenzoates (B3LYP)

4-nitrobenzoates of													
Lithium				Sodium				Potassium					
Calc. [cm^{-1}]	Int. IR	Int.R	PED [%]	Calc. [cm^{-1}]	Int. IR	Int.R	PED [%]	Calc. [cm^{-1}]	Int. IR	Int.R	PED [%]	Assignment	
3224	0.83	124.33	49	3223	0.44	177.19	86	3221	0.32	176.32	85	ν(CH)	2
3223	0.51	62.99	50	3222	0.25	11.75	81	3220	0.07	13.63	80	ν(CH)	20b
3206	0.54	50.61	76	3205	0.78	52.81	82	3203	1.02	51.19	80	ν(CH)	
3205	1.27	30.66	78	3205	2.10	27.52	86	3203	1.83	30.61	85	ν(CH)	20a
1648	2.16	7.39	22	1647	0.01	8.21	25	1647	1.69	6.88	23	ν(CC)	8b
1637	1.58	257.44	53	1635	0.41	230.32	53	1633	1.37	247.32	53	ν(CC)	8a
1585	590.40	1.70	63	1590	734.67	0.59	55	1597	660.48	0.39	66	$\nu_{as}(NO_2)$	
1556	112.11	23.72	60	1565	0.01	25.10	47	1566	33.78	18.93	61	ν_{as}(COO)	
1516	4.20	3.21	58	1513	0.03	0.99	61	1511	0.07	0.78	61	ν(CC)	19a
1434	396.40	147.49	55	1410	295.35	94.01	61	1403	295.92	150.94	33	ν_s(COO)	
1427	12.40	2.74	30	1427	4.22	0.11	28	1427	3.24	0.18	62	ν(CC)	19b
1368	481.78	216.45	74	1366	555.38	247.38	89	1364	637.43	248.27	75	$\nu_s(NO_2)$	
1358	49.11	0.29	60	1356	43.87	0.09	62	1357	41.42	0.14	62	ν(CC)	14
1314	0.64	0.12	85	1312	0.34	0.14	88	1310	0.23	0.11	88	β(CH)	3
1189	1.12	1.77	65	1187	1.03	1.81	64	1186	0.90	1.79	63	ν(CC)	9a
1153	0.05	13.99	19	1149	0.06	14.77	20	1147	0.50	17.47	20	ν(C-COO)	
1118	9.75	0.42	67	1115	9.61	0.03	69	1114	9.84	0.03	69	β(CH)	18b
1115	42.87	83.35	35	1115	50.03	91.75	37	1115	53.53	96.47	37	ν(C-N)	
1034	8.53	1.51	65	1033	11.70	3.91	65	1032	11.58	3.85	64	β(CH)	18a
999	0.21	0.30	26	1000	0.09	0.33	26	999	0.10	0.34	26	γ(CH)	17a
899	19.87	0.07	22	903	18.95	0.07	20	907	18.89	0.35	22	γ(CH)	17b
885	0.01	49.82	33	880	4.86	52.46	30	877	6.28	40.74	36	$\beta_s(NO_2)$	
861	0.02	0.002	29	861	0	0.01	30	860	0	0.01	29	γ(CH)	10a
857	90.15	0.84	33	848	78.66	6.32	38	839	100.13	4.36	41	β_s(COO)	
797	34.83	1.07	51	804	38.3	1.18	48	804	34.74	2.10	45	γ_s(COO)	
735	9.79	0.84	20	730	1.74	1.15	20	725	5.31	0.52	23	β(CH)	
719	44.63	0.79	75	719	40.26	0.71	76	720	38.87	0.52	77	$\gamma_s(NO_2)$	
663	2.34	0.03	73	665	2.24	0.02	68	665	2.17	0	71	γ(CH)	4
641	0.02	8.70	49	642	0	8.83	47	641	0.003	9.07	48	α(CCC)	6b
619	254.77	2.96	77	526	39.55	0.82	26	518	38.76	0.06	28	ν_s(O-Li)	
551	0.10	1.45	27	549	0.24	1.42	35	549	0.19	1.45	34	$\beta_{as}(NO_2)$	
510	0.18	0.51	34	503	4.24	0.54	40	502	4.40	0.58	32	β_{as}(COO)	
491	8.36	0.45	32	526	40.82	0.82	26	518	38.76	0.06	28		
457	0.71	0.02	39	458	0.68	0.02	27	457	0.99	0.05	39	φ(CC)	16b
423	0.06	0.001	71	424	0	0.001	36	425	0	0.001	71	φ(CC)	16a
409	35.68	0.08	68	316	2.87	0.71	29	300	0.48	0.81	28	β_{as}(O-Me)	
267	7.23	1.33	63	266	2.08	1.30	35	263	0.80	1.84	35	$\rho(NO_2)$	
282	2.53	3.02	23	232	15.62	3.69	43	186	26.81	1.48	50	O-Me	
145	77.68	0.24	70	114	34.82	0.12	48	99	21.65	0.003	29		

(*Continues*)

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Table 8. (Continued)

4-nitrobenzoates of												
Lithium				Sodium				Potassium				
Calc. [cm^{-1}]	Int. IR	Int.R	PED [%]	Calc. [cm^{-1}]	Int. IR	Int.R	PED [%]	Calc. [cm^{-1}]	Int. IR	Int.R	PED [%]	Assignment
141	2.55	0.003	49	107	6.68	0.04	37	87	7.21	0.12	31	ρ(COO)
75	0.11	0.20	90	72	0	0.17	86	71	0	0.13	84	υ(COO)
38	0.01	0.03	90	40	0	0.03	86	40	0	0.02	84	$\upsilon(NO_2)$

υ: stretching; β: in plane; γ: out of plane deformations; δ: scissoring; ω: wagging; τ: twisting; ρ: rocking; α: skeleton vibration in plane φ: skeleton vibration out of plane; s: strong; vs: very strong; m: medium; sh: shoulder; w: weak.

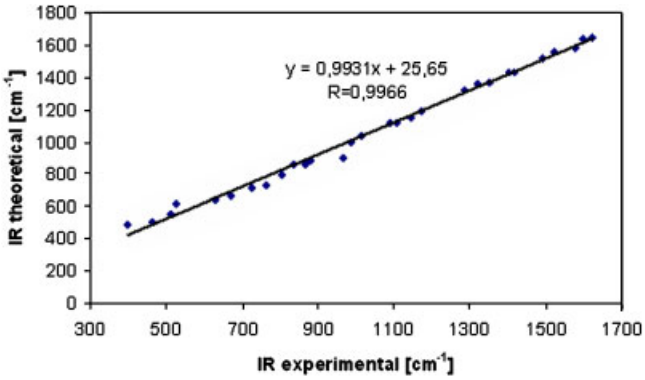

Figure 7. Experimental and theoretical spectra of lithium 4-nitrobenzoates

of PEDs using VEDA 3 program.[14] The correlation between observed and calculated IR spectra for lithium 4-nitrobenzoate (exemplary) are shown at Fig. 7. The correlation coefficients for sodium and potassium salts in IR spectra are 0.9987 and 0.9988, respectively. In Raman spectra, they are 0.9990 (Li 4-NB), 0.9987 (Na 4-NB), and 0.9992 (K 4-NB).

The changes of wavenumbers of the bands of aromatic system of studied salts are discussed comparing to the free acid. The wavenumbers of aromatic bands numbered as 4 in IR spectra, 7a and 8b in IR and Raman, 10a (IR), 14 (IR), 17a (IR), 17b (IR, R), 18a (except of rubidium and cesium salts in Raman spectra), 20b (IR, R) increase in comparison to free acid. However, the wavenumbers of other bands decrease in comparison to free acid. There are such as: 9a (IR), 18a (except of lithium and sodium salts in IR), 18b (IR), 19a (IR), 19a (except of lithium in Raman spectra), 19b in IR and Raman spectra in lithium, sodium, and potassium salts (in rubidium and cesium 4-nitrobenzoates, we do not observe this band), 20a (IR, R). The decrease of bands intensity in the case of bands numbered as 2 (IR), 8b (R), 10a (IR), 16b (IR), 17a (IR), 17 b (IR, R), 18a (IR), 18b (IR), 19a (IR, R), 20a (IR, R), 20b (IR) are observed. Intensity of 18a (except of lithium salt in Raman spectra), 20b (except of potassium salt in Raman) bands increase in comparison to free acid (except of potassium salt) but other bands do not change.

The wavenumbers of bands responsible for the nitro group in the IR and Raman spectra of salts also change in comparison to 4-nitrobenzoic acid. The wavenumbers of bands assigned to the symmetric stretching vibration of the nitro group in IR spectra (except of sodium and potassium salts) and Raman (except of sodium salt), $\beta_{as}(NO_2)$ in IR (except of lithium salt) and ν(C-N) in Raman spectra decrease comparing to the free acid. The wavenumbers of bands representing $\beta_s(NO_2)$ vibrations in IR spectra insignificantly increase except of sodium and cesium salts. However, wavenumbers of the asymmetric stretching vibration of the nitro group $\nu_{as}(NO_2)$, ν(C-N) except of cesium salt and of $\gamma(NO_2)$

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in IR and $\beta_{as}(NO_2)$ in Raman spectra considerably increase comparing to the free acid. The intensities of $\beta_s(NO_2)$ and $\beta_{as}(NO_2)$ decrease in IR spectra, but intensities of ν(CN) decrease in IR and increase (except of sodium salt) in Raman spectra. The intensities of $\gamma(NO_2)$ do not change in IR comparing to 4-nitrobenzoic acid but of the symmetric and asymmetric $\nu(NO_2)$ do not change except of lithium and sodium nitrobenzoates in Raman spectra, in the case of them, the intensities decrease. These changes in wavenumbers of nitro group bands occurring under the influence of metal action on 4-nitrobenzoic acid may be caused by hydrogen bond breaking. Ligand set containing nitrogen atoms and carboxylic groups is inclined to form molecular complexes with head-to-head carboxylic acid hydrogen bonds. The bases such as NaOH or KOH may cause breaking hydrogen bonding in these molecular complexes.

The influence of the metal on vibration structure of 4-nitrobenzoates expressed in the shift of selected bands along the metal series was investigated. The wavenumbers of the aromatic ring bands change toward the series of metal ion. Some of them show decreasing tendency along the metal series: 2 (Li > Na > K > Rb), 19a (Li > Na > K = Rb > Cs), 8b (except of sodium salt Li < Na > K > Rb = Cs), 9a (except of lithium salt Li < Na > K > Rb = Cs) in Raman spectra and 10a (Li > Na > Rb > Cs), 2 (except of lithium salt Li < Na > K = Rb > Cs), 7a (except of potassium salt Li > Na > K < Rb > Cs), 18a (except of lithium Li < Na > K > Rb > Cs) in IR spectra. But those of 8b band (IR) increase from lithium to potassium 4-nitrobenzoates but decrease from potassium to cesium salts Li < Na < K > Rb > Cs and similar tendency was observed of 8a (IR) band Li < Na = K > Rb > Cs. The other aromatic bands almost do not change or are scattered. The wavenumbers of the symmetric stretching bands of carboxylic anion ν_s (COO^-) in IR and Raman spectra decrease in the series Li → Cs. The wavenumbers of the asymmetric vibrations $\nu_{as}(COO^-)$ increase from lithium to potassium and decrease from potassium to cesium salts. The wavenumbers of the asymmetrical stretching bands of carboxylic anion group $\nu_{as}(COO^-)$ in IR and Raman spectra scatter but the magnitudes of separation between wavenumbers due to asymmetrical and symmetrical stretching vibration of COO^- group ν_{as}–ν_s increase in the series Li < Na < K < Rb < Cs nitrobenzoates in Raman (in IR spectra, this value for potassium salt is larger than for rubidium). These values in IR spectra are respectively as follows: 108, 117, 135, 132, and 144 cm^{-1} (in Raman: 88, 95, 113, 124, 133). It indicates on the higher degree of ionic bond.[24,25]

The correlation between wavenumbers of some bands and some metal parameters was also studied. The $\nu_s(COO^-)$ and $\beta_s(COO^-)$ bands in IR and Raman spectra correlate with such metal parameters as: electronegativity, ionic potential (defined as ratio of cation charge and ionic radius), atomic mass, inverse of atomic mass and affinity. In the case of symmetric in plane deformations $\beta_s(COO^-)$ in Raman spectra the best correlation coefficient was obtained for atomic radius (0.938) and it was presented at Fig. 8. The larger values of correlation coefficients were obtained for the symmetric stretching vibration bands in IR spectra for atomic mass (−0.973) and in Raman spectra for potential of ionization (0.999) (Fig. 9). All results for $\nu_s(COO^-)$ band in Raman spectra indicate good correlation in the linear fashion with all tested factors at the statistically important level.

The correlation between magnitude of differences of wavenumbers of asymmetric and symmetric stretching vibrations $\Delta\nu_{as-s}(COO^-)$ in IR and Raman spectra was done and the best correlation was obtained for potential of ionization (Fig. 10).

The correlation between lengths of C7–O9 and O9–Me11 bonds and wavenumbers of the $\beta_s(COO^-)$ and $\beta_{as}(COO^-)$ bands in IR and Raman spectra were observed. Exemplary correlation is presented at Fig. 11.

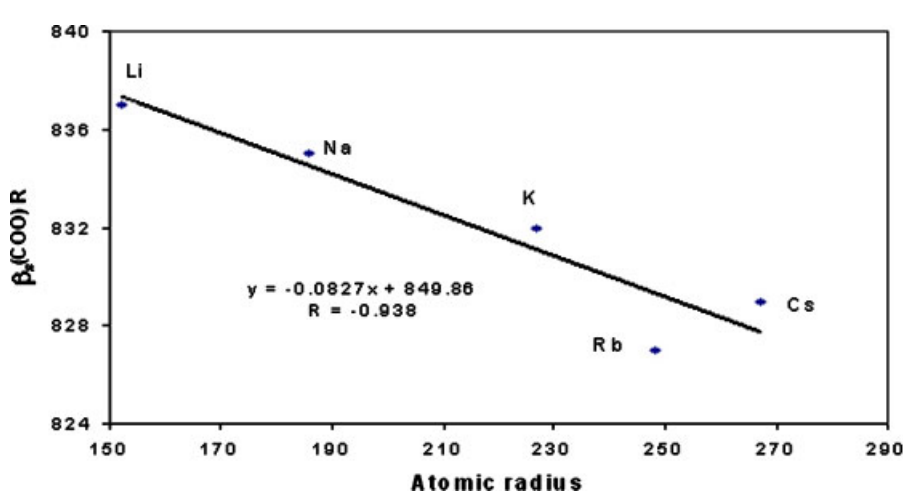

Figure 8. Correlation between the wavenumber of symmetric in plane deformations $\beta_s(COO^-)$ in Raman spectra and atomic radius of alkali metal

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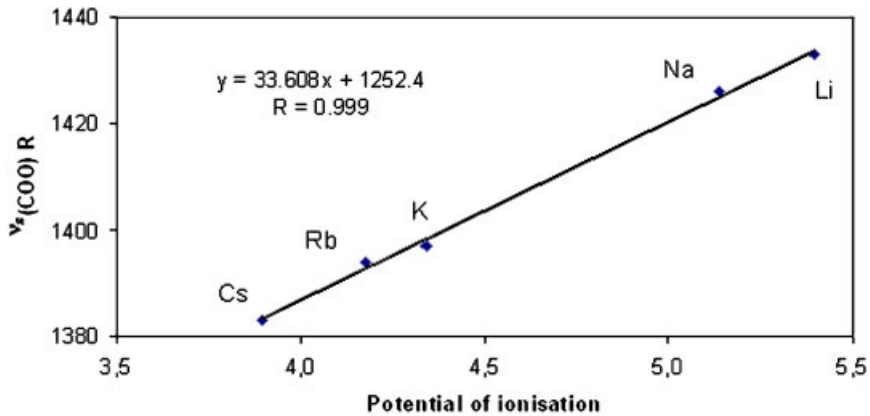

Figure 9. Correlation between the wavenumber of symmetric stretching vibration $\nu_s(COO^-)$ in Raman spectra and ionization potential of alkali metal

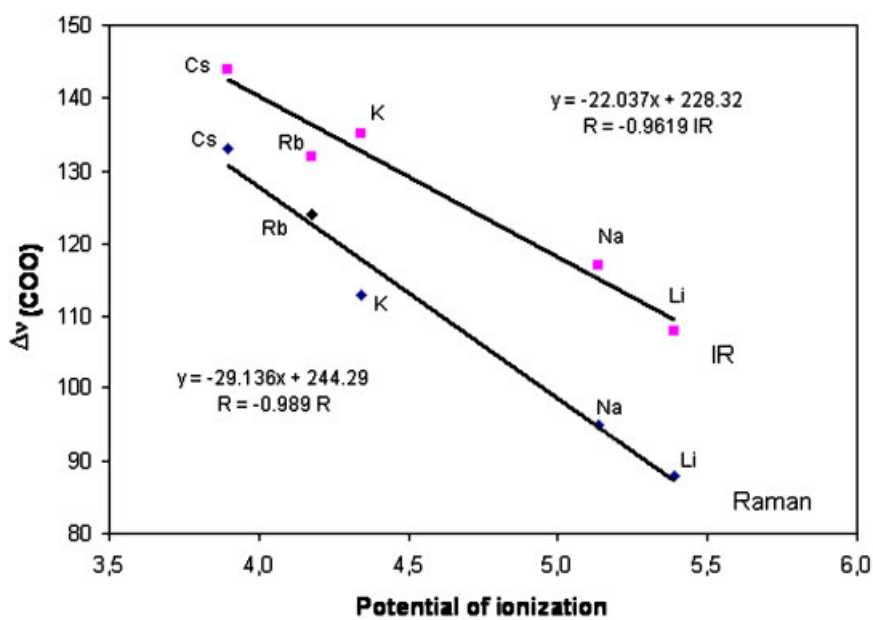

Figure 10. The correlation between magnitude of differences of wavenumbers of asymmetric and symmetric vibrations bands and ionization potential of alkali metals, which created 4-nitrobenzoates

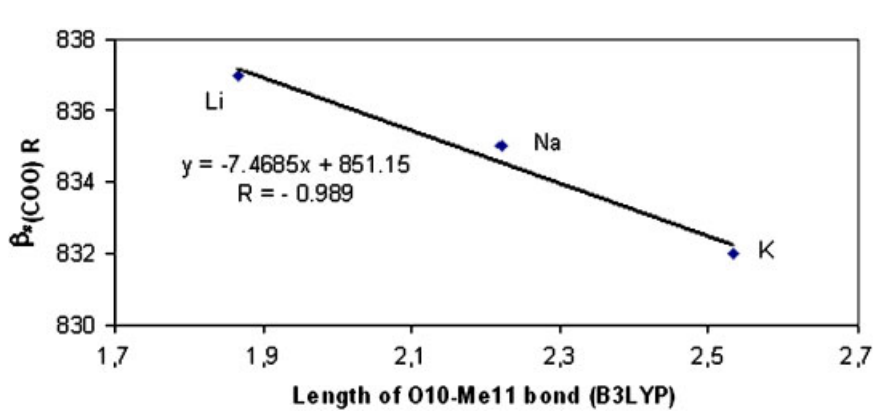

Figure 11. Correlation between lengths of O10-Me11 bond and wavenumbers of $\beta_s(COO^-)$ band in Raman spectra

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CONCLUSIONS

Spectral characteristics (experimental and theoretical IR, Raman, NMR spectra) and calculated geometrical structures (bond lengths, angles, energies, dipole moments, aromatic indices, polarity) of the alkali metal 4-nitrobenzoates were investigated.

The changes in the IR and in the Raman spectra as well as in the NMR spectra show that aromaticity of salts generally decreases in comparison to free acid:

I The intensity of a large majority of aromatic bands decreases in the IR and Raman spectra of salts in comparison to free acid, which suggest an increase of the destabilization of the electronic charge distribution of the salt molecules.

II However, the wavenumbers of aromatic ring bands of salts (IR and/or Raman spectra) increase (4, 7a, 8b, 10a, 14, 17a, 17b, 20b) as well as decrease (9a, 18b, 19a, 19b, 20a) in comparison to 4-nitrobenzoic acid, so basing on this criterion, it is difficult to say what changes undergo the aromaticity of molecules,

III In the case of NMR spectra, the chemical shifts of protons for 4-nitrobenzoates are changed diamagnetically in comparison to free acid. It indicates about the decrease of aromatic properties of salts. The chemical shifts of carbon atoms also decrease except of C1 and C7 atoms.

The calculated geometrical structures show that substitution of alkali metal cation instead of hydrogen cation in carboxylic group caused insignificant increase of aromaticity. On the other hand, the aromaticity indices based on magnetism NICS indicate that aromaticity of salt molecules decreases compared to acid. According to Schleyer,[18] magnetic aromaticity indices are more representatively indices because they depend on electronic structure of molecule.

In the order $Li \rightarrow Na \rightarrow K \rightarrow Rb \rightarrow Cs$ salts of 4-nitrobenzoic acid generally (with some exceptions), the destabilization of electronic and aromatic systems increase, although the differences between studied salts are very small. The correlation between degree of the disturbance of the electronic system and such metal parameters as: electronegativity, ionic potential, atomic mass, inverse of atomic mass and affinity take place. On the basis on the data obtained in this work, it is not possible to explicitly evaluate, which of them decide about disturbance of electronic system of studied compounds.

Partly discrepancies between obtained conclusions from experimental and theoretical data could be explained by intra- and intermolecular interaction in real supramolecular structure of studied compounds. Lack of crystallographic data in the literature and difficulties in growing monocrystals prevent comparison of our results with data of x-ray diffraction.

Our present conclusions seemingly are partly opposite of those come from our investigation of 4-aminobenzoates.[4] It is necessary to bear in mind that nitro and amino groups have totally extreme properties: electron withdrawing ($-NO_2$) and electron donating ($-NH_2$) groups. That is why the mechanism of influence of alkali metal on 4-amino- and 4-nitrobenzoic acids is different.

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