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Spectroscopic (FT-IR, FT-Raman and ^1H and ^{13}C NMR) and theoretical in MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels study of benzenesulfonic acid and alkali metal benzenesulfonates

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ABSTRACT

The FT-IR, FT-Raman and NMR (^1H and ^{13}C) spectra of benzenesulfonic acid as well as lithium, sodium, potassium, rubidium and caesium benzenesulfonates were registered, assigned and compared. The molecular structures of ligand and alkali metal salts were discussed. On the basis of quantum mechanical calculations in MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels the geometric parameters, infrared spectra, NMR spectra, the magnetic and geometric aromaticity indices for acid and alkali metal benzenesulfonates and benzoates were obtained. The effect of alkali metal ions on the electronic charge distribution of benzenesulfonic acid was studied and compared with the alkali metal benzoates and benzoic acid.

1. Introduction

In our previous papers the effect of alkali metals, transition and heavy toxic metals on the aromatic system and carboxylic anion of benzoic and pyridine-carboxylic acid derivatives [1–7] was investigated. The studies showed that alkali and heavy toxic metals perturb the electronic charge distribution of above mentioned ligands, whereas 3d and 4f metals stabilize it.

In this paper the influence of alkali metals (i.e. Li, Na, K, Rb and Cs) on the electronic system of the aromatic ring of benzenesulfonic acid and the sulfonic anion was studied. Then the influence of metals on the aromatic system of ligands through the carboxylic and sulfonic groups was compared. The following spectroscopic methods were used: FT-IR, FT-Raman, NMR (^1H and ^{13}C) as well as theoretical calculations in MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels (NBO, ChelpG, AIM study, theoretical IR spectra and chemical shifts from ^1H and ^{13}C NMR spectra). Moreover the geometrical and magnetical aromaticity indices for optimized structures were calculated.

The coordination chemistry of the sulfonate group for many metal complexes was widely investigated in recent years [8]. For instance, in a variant of organometallic compounds, including Sb^{5+} [9–18], Bi^{5+} [19,20], Sn^{4+} [21,22], Tc^+ [23], Ru^{2+} [24], Rh^+ [25,26], Pd^{2+} [27], Ag^+ [28], and Re^{2+} [29] ions, besides the carbon-coordinated organic ligands, the metal ions are also coordinated by a monodentate (Fig. 1a) $C_6H_5SO_3^-$ ligand or its substituted benzenesulfonate analogues. The weak coordination nature of $—SO_3^-$ makes its coordination mode very flexible and sensitive to the chemical environment. For instance, the coordination modes of $—SO_3^-$ to Na^+ range from $\eta^3\mu^3$ bridging in sodium(I) 1,5-naphthalenedisulfonate dihydrate [30] to $\eta^7\mu^5$ in sodium(I) 4,4′-biphenyletherdisulfonate [8]. In the series of lanthanide 1,5-naphthalenedisulfonate complexes $[Ln(OH)(1,5nds)(H2O)]_n$ (Ln = La, Pr and Nd) [31], the disulfonate ligands are coordinated by five different Ln ions in an unusual asymmetrical $\eta^2\mu^2–\eta^3\mu^3$ mode (Fig. 1). Three solid-state structures of alkali metal 1,5-naphthalenedisulfonates were investigated [30]. Li^+ is coordinated by one water molecule and three different $—SO_3^-$ groups. Every $—SO_3^-$ oxygen atom is coordinated by one Li^+ and the $—SO_3^-$ group functions as a $\eta^3\mu^3$ bridge, connecting three Li^+. While Na^+ is 5-coordinated by three different $—SO_3^-$ groups and two water molecules. Every $—SO_3^-$ oxygen is coordinated by one Na^+ ion and the $—SO_3^-$ group functions as a $\eta^3\mu^3$ bridge connecting three Na^+ ions. The K^+ ion is 8-coordinated by three water molecules and five $—SO_3^-$ oxygen atoms from four different groups. Two of the $—SO_3^-$ oxygen atoms are coordinated by two K^+ ions, which make the $—SO_3^-$ group function as a $\eta^5\mu^4$ bridge. Additionally, the K^+ ion

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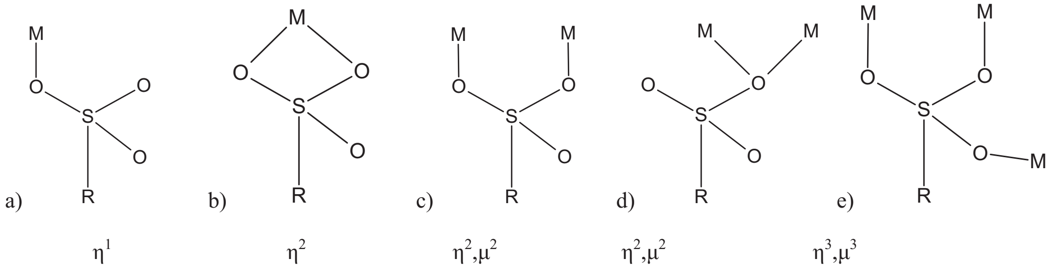


Fig. 1. Coordination types for single sulfonate group.

is coordinated by two oxygen atoms from the same $-SO_3^-$ group. The corresponding characteristic of the OH stretching and SO vibrational frequencies in their IR spectra also clearly indicate the different coordination behaviour of the sulfonate groups. In the complex of caesium 4-methylenebenzenesulfonate [32] the caesium ion is surrounded by six oxygen atoms from five sulfonate groups. Four sulfonate groups coordinate caesium ion in a monodentate fashion (Fig. 1a), whereas the other in bidentate fashion (Fig. 1b).

Sulfonate compounds have important functions in many fields such as medicine, chemical separation and catalysis. Salts of sulfonic acid are applied as surface-active agents in light industry [32].

2. Experimental

2.1. Sample preparation and measurement

The alkali metal benzenesulfonates were obtained by dissolving benzenesulfonic acid in an aqueous solution of the appropriate alkali metal bases in a stoichiometric ratio 1:1. The dried lithium, sodium, potassium, rubidium and caesium benzenesulfonates were obtained after the solutions were evaporated on the vapour bath and then dried in 140 °C. The IR spectra were recorded with an Equinox 55 spectrometer within the range of 400–4000 cm^{-1}. Samples in the solid state were measured in Zn/Se plate (for acid) and in KBr matrix pellets (for salts) obtained with hydraulic press under 739 MPa pressure. Moreover the FT-IR spectra of acid were also recorded in H_2O solution using ATR accessory. FT-Raman spectra of solid samples were recorded in capillary tubes in the range of 400–4000 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 D_2O saturated solution were recorded with a Bruker unit 200 MHz at room temperature. TMS was used as an internal reference.

2.2. Theoretical calculations

All theoretical calculations (geometries, NBO, ChelpG, IR and NMR spectra) in MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels were performed by the use of the GAUSSIAN 03W package of programs running on a PC computer [33]. The optimized geometries correspond to the ground state stationary points. No imaginary frequencies were found. Theoretical wavenumbers were scaled according to the formula: $\nu_{\text{scaled}} = 0.9\nu_{\text{calculated}}$ [34]. The chemical shifts were calculated using GIAO (gauge including atomic orbitals) method. Chemical shifts (δ_i) were calculated by subtracting the appropriate isotopic part of the shielding tensor (σ_i) from that of TMS (σ_{TMS}): $\delta_i = \sigma_{\text{TMS}} - \sigma_i$) [ppm]. The isotropic shielding constants for TMS calculated in the B3LYP/6-311++G** and MP2/6-311++G** levels were equal to 31.99762 ppm for the ^1H nuclei and 184.1700 ppm for the ^{13}C nuclei (B3LYP) and 31.8974 ppm for the ^1H nuclei and 198.6150 ppm for the ^{13}C nuclei (MP2) [34]. QTAIM was used to obtain atomic charges Q AIM. This analysis was performed with the help of the AIMAll [35].

2.3. The geometric and magnetic criteria of aromaticity

The idea of the geometric aromaticity indices is based on the fact that the essential factor in aromatic stabilization is the π delocalization manifested in: planar geometry, equalization of the bonds lengths and angles, and symmetry. These indices were successfully applied to determination of aromatic character of many compounds, e.g. global and local aromaticity in porphyrins [36], substituent effects [37], structural aromaticity of systems with BN bonds [38].

^1H NMR spectroscopy is very useful for studying aromatic character of molecules. Exocyclic protons exhibit characteristic low-field (diatropic) chemical shift due to the induction of a diamagnetic ring current in a cyclic π-system. The ^1H NMR data have been used in discussion of the aromatic character of an extensive range of compound classes, e.g. tellurophene [39], benzofuran series [40], 1,10-phenantroline [41], analogues of pentadienyl anion [42]. According to Schleyer the most representative aromatic indices are those based on diamagnetic susceptibility, because the diamagnetic susceptibility completely depends on π-electron structure [9,10]. Moreover according to Krygowski and co-workers studies on interrelations between energies of rings in benzenoid hydrocarbons, NICS values, and HOMA and its components, led to the conclusion that NICS correlates best with the energy and HOMA, and much less with other aromaticity indices [11].

The geometric and magnetic aromaticity indices, i.e. HOMA [12], I_6 [13], BAC [15] and NICS [16], χ, $\Delta\chi$ [17,18] were calculated according to the described below formulas on the basis of obtained theoretical parameters:

$$HOMA = 1 - \frac{\alpha}{n}\sum (R_{opt} - R_i)^2$$

The notations are as follows: n is the number of bonds taken into account; α is an empirical constant chosen to give HOMA = 0 for hypothetical Kekulé structure of benzene and HOMA = 1 for the system with all bonds equal to the optimal value R_{opt}; R_{opt} is a length of the CC bond for which the energy of the compression to the length of a double bond and expansion to the length of a single bond in 1,3-butadiene is minimal; R_i is an individual bond length. The value of HOMA index is equal 1 for the entirely aromatic system, HOMA = 0 when structure is non-aromatic and HOMA < 0 for anti-aromatic ring [12].

$$BAC = \sqrt{\sum_n (R_n - R_{n+1})^2}$$

where R and R_{n+1} are consecutive bond length in the ring and the summation runs over a defined cyclic route [12].

$$I_6 = 100 \cdot \left[1 - \frac{V}{V_k}\right]$$

where

$$V = \left(\frac{100}{N_{av}}\right) \cdot \left[\sum_{r=1}^{n} \frac{(N_r - N_{av})^2}{n}\right]^{1/2} \quad \text{and} \quad N = \frac{a}{R^2} - b$$

The notations are as follows: R is the observed bond length, N_r is the individual bond order, N_{av} is the mean bond order, n is the number of bonds, V_k, a and b are constants [13].

Magnetic susceptibility χ is defined:

$$\chi = \frac{\chi_{aa} + \chi_{bb} + \chi_{cc}}{3}$$

where χ_{aa}, χ_{bb}, χ_{cc} are diagonal elements of magnetic susceptibility tensor. The aromatic compounds possess magnetic susceptibility.

Diamagnetic susceptibility anisotropy is defined [16]:

$$\Delta\chi = \chi_{cc} - \frac{\chi_{aa} + \chi_{bb}}{2}$$

where c is perpendicular direction to plane of the ring.

The NICS (Nucleus Independent Chemical Shift) is defined as a negative value of the absolute magnetic shielding computed in the centers of rings [10]. The more negative are the NICS and $\Delta\chi$ value, the more aromatic is the system.

pEDA, applied by Oziminski and Dobrowolski [43]:

$$pEDA = \sum_{j=1}^{6} \pi^{j}_{R-C_6H_3} - \sum_{j=1}^{6} \pi^{j}_{C_6H_6}$$

where π_i^j denotes sum of occupancies of all atomic orbitals of the jth benzene ring C-atom contributing to the valence π-molecular orbitals in the molecule indexed by i.

3. Results and discussion

3.1. Vibrational assignment

In Table 1 the wavenumbers, intensities and assignment of the selected bands occurring in the FT-IR and FT-Raman spectra of benzenesulfonic acid and its alkali metal salts are gathered. The spectral assignment was based on the literature data [44–47] and the theoretical calculations presented in this paper. The calculated structures are shown in Fig. 1. One may divide the bands occurred in the spectra of benzenesulfonic acid and benzenesulfonates into two groups:

1) those bands connected with sulfonic anion vibrations:
   a) wide and intense bands of the stretching vibrations of S=O group (1200–1195 cm^{-1} – IR; 1222–1198 cm^{-1} – Raman); asymmetric $\nu_{as}(SO_3^-)$ (1186 cm^{-1} IR, 1183–1176 cm^{-1} – Raman) and symmetric $\nu_s(SO_3^-)$ (1062–1041 cm^{-1} – IR; 1061–1041 cm^{-1} – Raman) stretching vibrations;
   b) bands of medium intensity assigned to symmetric in-plane deformation of the sulfonate anion $\delta_s(SO_3^-)$ (587–568 cm^{-1} – IR; 571–562 cm^{-1} – Raman) as well as asymmetric in-plane deformation of the sulfonate anion $\delta_{as}(SO_3^-)$ (494–484 cm^{-1} – IR; 492–485 cm^{-1} – Raman).
2) those bands connected with aromatic ring vibration that were observed in the whole spectral range, i.e. $\nu(CH)_{ar}$ in the range: 3175–2926 cm^{-1} – IR, 3176–3060 cm^{-1} – Raman; ν(CC): 1621–1217 cm^{-1} – IR, 1589–1218 cm^{-1} – Raman; β(CH): 1243–1016 cm^{-1} – IR, 1244–1019 cm^{-1} – Raman; γ(CH): 998–732 cm^{-1} – IR, 998–732 cm^{-1} – Raman; α(CCC): 690–611 cm^{-1} – IR, 616–617 cm^{-1} – Raman; ϕ(CCC): 635–623 cm^{-1} – IR, 632–626 cm^{-1} – Raman.

3.2. What changes in the spectrum of ligand are caused by the replacement of sulfonic group's hydrogen with a metal ion?

3.2.1. Experimental IR and Raman spectra

The replacement of the sulfonic group's hydrogen with a metal ion brings about characteristic changes in the IR and Raman spectra of the complexes in comparison with the spectra of ligand. There could be observed a disappearance of the symmetric and asymmetric valence vibration bands: stretching $\nu(SO_3H)$, as well as deformation vibration bands of the sulfonyl group; disappearance of group vibration bands ν(O—H), β(O—H) and γ(O—H); as well as appearance of asymmetric and symmetric vibration bands of the sulfonate anion $\nu_{as}(SO_3^-)$, $\nu_s(SO_3^-)$ as well as $\delta_{as}(SO_3^-)$ and $\delta_s(SO_3^-)$ and disappearance or changes in positions and intensities of some aromatic bands.

The influence of metals in the series: Li → Na → K → Rb → Cs on the vibrational structure of sulfonate anion was small but a general tendency may be observed. Namely, in the above series the decrease in the wavenumbers of $\nu_s(SO_3^-)$ both in the IR and Raman spectra is observed (from 1062 cm^{-1} to 1042 cm^{-1} in IR spectra and in the range 1061–1041 cm^{-1} in Raman spectra). Moreover in Raman spectra of benzenesulfonates the wavenumbers of band $\nu_{as}(SO_3^-)$ decreases as well along the series: Li = Na → K → Rb → Cs salts (1183–1176 cm^{-1}).

The bands assigned to stretching νCH_{ar} vibrations occur in the range 3175–2927 cm^{-1} (IR) and 3176–3002 cm^{-1} (Raman). The band no. 20b is located at higher wavenumber in the spectra of acid compared with the spectra of salts. The bands of stretching νCC_{ar} vibrations are located from 1621 cm^{-1} to 1217 cm^{-1} (IR) and 1589–1218 cm^{-1} (Raman). The appropriate bands are of similar wavenumbers both in the spectra of acid and salts. In the region of 1143–1020 cm^{-1} (IR) and 1146–1010 cm^{-1} (Raman) the bands of in-plane deformations βCH_{ar} are present. A visible decrease in the wavenumber of band no. 9a occurs (the band is located at 1143, 1139, 1134, 1133 and 1132 cm^{-1} in the IR spectra, and 1143, 1142, 1139, 1136 and 1134 cm^{-1} in the Raman spectra of Li, Na, K, Rb and Cs benzenesulfonates, respectively). The peaks assigned to out-of-plane deforming γCH_{ar} vibrations occur at 915–732 cm^{-1} (IR) and 998–733 cm^{-1} (Raman). Generally, these bands are located at higher wavenumbers in the spectra of benzenesulfonates compared to benzenesulfonic acid. In the region of 692–611 cm^{-1} (IR) and 632–616 cm^{-1} (Raman) the bands of in-plane and out-of-plane deformations CCC of the aromatic ring (ϕCCC, αCCC) are placed.

3.2.2. Theoretical IR spectra

Theoretical wavenumbers of infrared vibrations for benzenesulfonic acid and its salts were calculated in B3LYP/6-311++G(d,p) level and gathered in Table 1. Satisfactory results were obtained for the compared band wavenumbers from experimental and theoretical IR spectra of studied compounds. Mostly all bands from the theoretical spectra of alkali metal benzenesulfonates are located at lower wavenumbers than appropriate bands from the spectra of ligand. Moreover the wavenumber of almost all bands slightly decrease along the series: Li → Na → K benzenesulfonates. This may suggest that the specific effect of alkali metal ions on the electronic structure of ligand depend on certain metal ion parameters

The structures of benzenesulfonic acid and lithium, sodium and potassium benzenesulfonates were calculated in MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels. The obtained bond lengths and angles were gathered in Table 2 and the appropriate structures are presented in Fig. 2. The replacement of the sulfonic group's hydrogen with an alkali metal ions brings about distinct changes in the bond lengths and angles of sulfonic anion, but insignificant changes in the bond lengths and angles between carbons in the aromatic ring. This may explain small or lack of shifts of bands derived from aromatic ring vibrations and regular changes

Table 1

The selected wavenumbers, intensities and assignments of bands from the IR (experimental and calculated in level B3LYP/6-311++G(d,p)) and Raman spectra of benzenesulfonic acid and its alkali metal salts.

Benzenesulfonic acid					Benzenesulfonates																Assignments	
Exp.			Calc.		Lithium				Sodium				Potassium				Rubidium		Caesium			
IR[a]	IR[b]	Raman	IR	Intens.	Exp.		Calc.		Exp.		Calc.		Exp.		Calc.		Exp.		Exp.			
					IR	Raman	IR	Intens.	IR	Raman	IR	Intens.	IR	Raman	IR	Intens.	IR	Raman	IR	Raman		
3390m[c]	–		3757	126.4	–	–	–		–	–	–		–	–	–		–	–	–		ν(OH)	
–	–	3173vw	3208	5.4	–	3176vw	3202	6.9	–	3171vw	3202	6.1	–	3175vw	3200	6.8	3172w	3171vw	3175m	3175vw	νCH_{ar}	
–	–	–	3206	1.4	–	3162vw	3200	2.0	–	–	3200	3.6	–	–	3199	3.9	–	3158vw	–	3155vw	νCH_{ar}	
3069vw	–	3074vw	3194	6.3	3056s	3068m	3189	10.7	3059s	3067m	3186	14.9	3061m	3061m	3184	17.3	3062m	3065w	3061m	3060m	νCH_{ar}	20b[d]
–	–	–	3185	8.5	–	–	3178	11.1	–	3002vw	3175	13.8	2965w	–	3172	15.3	2961w	3015vw	2960w	3015vw	νCH_{ar}	
–	–	–	3173	0.7	2927m	–	3167	0.2	2926m	–	3164	0.1	2926w	–	3162	0.1	2926w	–	2927w	–	νCH_{ar}	
–	–	–	1625	1.5	–	–	1626	0.1	1621s	–	1627	0.6	–	–	1627	0.9	–	–	–	–	νCC_{ar}	8a
–	–	1589vw	1628	0.2	1604s	1590m	1625	0.0	–	1590m	1624	0.0	1608w	1590m	1623	0.0	–	1588m	–	1588w	νCC_{ar}	8b
1483m	1484w	–	1509	3.9	1485s	–	1510	5.7	1485m	–	1509	6.1	1483m	–	1509	6.1	1482m	–	1484m	–	νCC_{ar}	19a
1448m	1448m	–	1479	18.6	1446vs	–	1475	13.6	1445vs	–	1474	12.4	1445s	–	1473	11.6	1446s	1445vw	1445s	1443vw	νCC_{ar}	19b
–	–	–	1348	1.0	1240vs	1244w	1346	2.0	–	–	1345	1.4	–	–	1344	1.1	1243s	1233vw	–	–	βCH_{ar}	3
–	–	–	1333	3.5	–		1327	0.1	1222vs	–	1327	0.1	1217vs		1326	0.2	1219vs	1218w	–	–	νCC_{ar}	14
–	1181vw	1185vw	1316	224.2	1198vs	1205vw	1251	262.7	1200vs	1209vw	1225	284.8	1195vs	1222vw	1217	305.7	1196vs	1201w	1195vs	1198w	νSO	
–	–				1186vs	1182w	–	–	1186vs	1183w	–		–	1178w	–		–	1177w	–	1176w	$\nu_{as}SO_3$	
–.	–	–	1201	1.1	1143vs	1146s	1200	1.5	1139vs	1142s	1198	3.7	1134s	1139m	1197	6.1	1133s	1136s	1132vs	1134s	βCH_{ar}	9a
1127vs	1128vs	1130m	1167	276.2	–	–			–	–	–	–	–	–	–		–	–	–	–	$\nu_s SO_3H$	
1072s	1074w	–	1102	11.7	–	–	1102	1.9	1070m	–	1101	7.3	1070m	–	1102	20.5	1071m	–	1071m	–	βCH_{ar}	18b
–	–	–			1062vs	1061w	946	216.4	1050vs	1053w	952	235.5	1045s	1049w	958	240.1	1041s	1044m	1042vs	1041m	$\nu_s SO_3$	
1036s	1037s	1038vw	1100	28.0	–	–	–	–	–	–	–	–	–	–	–		–	–	–	–	βOH	
1016vw	1019s	–	1081	15.8	1022s	1023w	1113	57.1	1020s	1024vs	1115	57.6	1021s	1023w	1115	62.3	1020s	1021w	1020s	1020w	βCH_{ar} νSC_{ar}	18a
995s	998m	998vs	1015	3.2	998m	998vs	1017	1.5	998s	998w	1017	2.4	998m	998vs	1017	3.6	998m	997vs	998s	997vs	γCH_{ar}	12
–	–	–	–	–	927w	932vw	1005	0.0	924m	–	1001	0.03	924vw	–	999	0.02	922w	932vw	–	–	γCH_{ar}	17a
–	–	–	856	0.2	861m	–	854	0.3	–	–	856	0.3	–	–	856	0.2	–	854w	864vw	855vw	γCH_{ar}	10a
756s	755w	–	747	285.2	755s	–	–	–	752vs	–	–	–	753s	–	–		754s	–	753s	–	$\nu S–(OH)$	
732s	732w	733w	712	39.6	738vs	739m	768	30.4	738vs	741m	764	31.3	734s	738m	763	29.4	734s	736m	733vs	735m	γCH_{ar}	11
690s	–	–	700	52.2	691vs	–	724	26.6	690vs	–	721	25.8	692s	–	721	28.8	692s	–	692s	–	α(CCC)	6a
–	–	–			630vs	628vw	708	43.2	630vs	632vw	706	40.9	635s	629vw	708	42.5	623s	628w	623vs	626vw	ϕ(CCC)	
611s	–	616w	627	0.01	–	617w	629	0.02	–	617w	630	0.02	–	617w	630	0.01	–	617w	–	617w	α(CCC)	6b
–	–	–	–	–	587s	–	612	62.5	573vs	571vw	606	0.1	568s	562vs	604	143.2	568s	567w	568s	564w	$\delta_s SO_3$	–
562w	–	–	557	122.4	–	–			–	–	–	–	–		–		–	–	–	–	γOH	–
–	–	–	–	–	494w	492vw	537	24.1	485w	485vw	520	11.3	484vw	485vw	520	11.3	–	490w	485w	489vw	$\delta_{as}SO_3$	

[a] Spectrum recorded in Zn/Se plate.

[b] Spectrum recorded in H_2O solution.

[c] s – strong; m – medium; w – weak; v – very; sh – shoulder.

[d] Normal vibrations of the aromatic ring were used according to the nomenclature applied by Vársanyi [47].

Table 2
The theoretical geometric parameters calculated in B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels for benzenesulfonic acid and benzenesulfonates.

	Benzenesulfonic acid		Benzenesulfonates					
	MP2	B3LYP	Lithium		Sodium		Potassium	
			MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
Bond lengths [Å]								
C1–C2	1.399	1.393	1.399	1.393	1.399	1.393	1.399	1.393
C2–C3	1.399	1.393	1.399	1.393	1.399	1.393	1.399	1.394
C3–C4	1.400	1.394	1.401	1.395	1.401	1.395	1.401	1.395
C4–C5	1.401	1.395	1.401	1.395	1.401	1.395	1.401	1.395
C5–C6	1.398	1.392	1.399	1.393	1.399	1.393	1.399	1.394
C6–C1	1.399	1.393	1.399	1.393	1.399	1.393	1.399	1.393
C1–S	1.773	1.792	1.779	1.799	1.784	1.804	1.785	1.806
S–O1	1.441	1.447	1.451	1.456	1.458	1.463	1.459	1.465
S–O2	1.450	1.457	1.513	1.521	1.506	1.514	1.500	1.509
S–O3	1.637	1.651	1.513	1.521	1.506	1.514	1.500	1.509
O3–H/metal	0.968	0.969	1.883	1.867	2.268	2.222	2.550	2.542
Angles [°]								
C1–C2–C3	118.603	118.687	118.854	118.958	119.076	119.149	119.225	119.264
C2–C3–C4	120.277	120.134	120.298	120.197	120.287	120.199	120.272	120.195
C3–C4–C5	120.178	120.369	120.068	120.167	119.969	120.071	119.914	120.020
C4–C5–C6	120.336	120.180	120.280	120.197	120.287	120.199	120.288	120.196
C5–C6–C1	118.558	118.657	118.872	118.958	119.077	119.149	119.210	119.263
C1–S–O1	108.761	108.858	108.131	108.429	107.508	107.875	107.279	107.560
C1–S–O2	108.749	109.054	105.762	106.280	105.261	105.747	105.051	105.570
O1–S–O2	101.836	102.405	115.741	115.480	114.915	114.713	114.858	114.502
O2–S–O3	107.301	106.797	104.847	104.165	108.108	107.315	108.790	108.383
S–O3–H/metal	107.920	108.423	88.010	87.874	93.103	92.785	96.825	96.695
Dipole moment [Debye]	4.934	5.054	5.891	5.760	8.112	7.832	9.761	9.374
Energy [hartree]	−854.437	−856.202	−861.401	−863.218	−1015.788	−1017.982	−1453.263	−1455.629

in the wavenumbers of bands of sulfonate group vibrations from the spectra of benzenesulfonates compared to the spectra of acid.

3.2.3. Experimental and theoretical ^{1}H and ^{13}C NMR spectra

The values of chemical shifts of protons from the experimental ^{1}H NMR spectra of benzenesulfonic acid and its salts are gathered in Table 3. The differences between particular chemical shifts of appropriate protons do not exceed 0.03 ppm and there is no regular relationship along the series of Li→. . .→Cs compounds. In the theoretical ^{1}H NMR spectra of benzenesulfonates a regular decrease in the chemical shifts of protons H3, H4, H5 along the series Li → Na → K was observed. A decrease in the chemical shifts points at an increase in the screening of aromatic protons as a consequence of circular current weakening [7]. Therefore one may say that disturbance of the aromatic system increases in the series: Li → Na → K benzenesulfonates.

In case of experimental and theoretical ^{13}C NMR spectra of studied compounds a decrease in the value of chemical shifts of all carbons, (except C1) compared to spectra of ligand was observed (Table 4). This means a decrease in the electronic charge distribution around atom C1 and an increase in the electronic charge distribution around the other carbons in the benzene ring. There is no regularity in the changes of location of the chemical shifts from the ^{13}C NMR spectra in the series of alkali metal benzenesulfonates. Considerably good correspondence was found between calculated and experimentally obtained chemical shifts from NMR spectra.

3.3. In what way alkali metal ions influence the electronic charge distribution in benzenesulfonic acid?

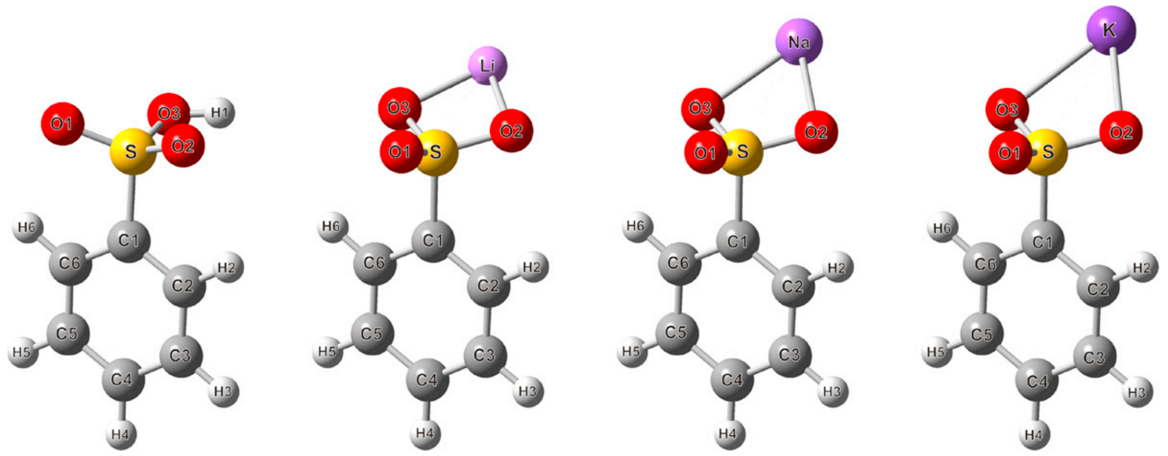
During salt formation, first the metal ion influences the M—O bond and this effect is transferred to the S—O bonds, then the force constant of the O—S-ring bonds is changed which reflects in the displacement of electronic charge around C—C bonds in the aromatic ring. Therefore the structure of sulfonate anion is very important in the view of change in the electronic charge distribution in the ring.

In the experimental IR and Raman spectra of benzenesulfonates two bands derived from stretching vibrations of sulfonate anion exist: $\nu(SO_3^-)$ and $\nu(SO)$. The wavenumbers of $\nu(SO)$ do not change in a significant way along the series of alkali metal benzenesulfonates. The magnitudes of separation $\Delta\nu(SO_3^-)$ between the experimental wavenumbers of asymmetric $\nu_{as}(SO_3^-)$ and

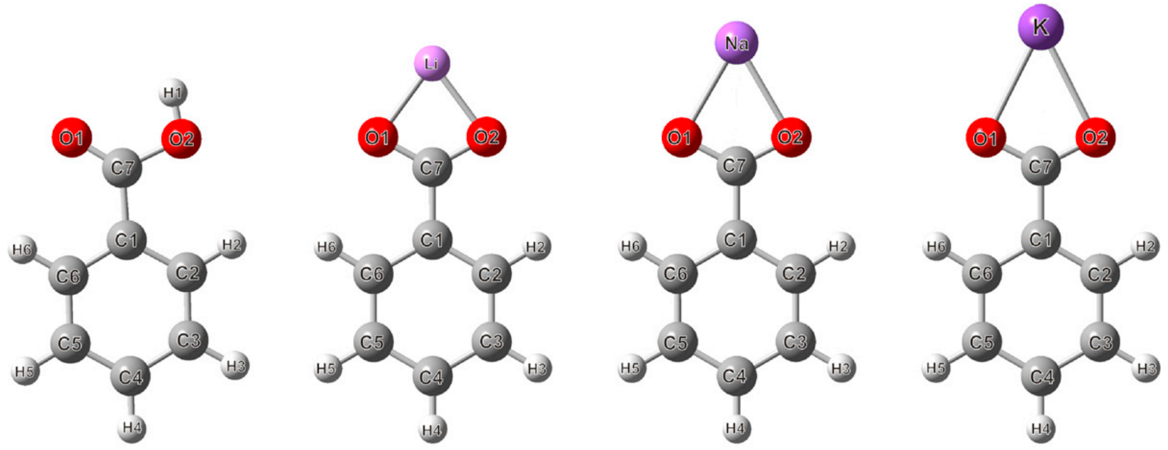
Table 3
Chemical shifts from experimental and theoretical (in level B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)) ^{1}H NMR spectra of benzenesulfonic acid and alkali metal benzenesulfonates.

Proton atom	Benzenesulfonic acid			Benzenesulfonates												
	Exp.	Calc.		Lithium			Sodium			Potassium			Rubidium		Caesium	
		MP2	B3LYP	Exp.	Calc.		Exp.	Calc.		Exp.	Calc.		Exp.	Calc.	Exp.	Calc.
					MP2	B3LYP		MP2	B3LYP		MP2	B3LYP				
H2 (d)	7.62	8.09	8.08	7.59	8.22	8.09	7.61	7.54	8.10	7.62	8.25	8.13	7.63	–	7.64	–
H3 (t)	7.33	7.86	7.62	7.30	7.74	7.50	7.32	7.66	7.45	7.31	6.32	7.41	7.32	–	7.32	–
H4 (t)	7.37	7.81	7.77	7.35	7.63	7.56	7.34	8.25	7.43	7.36	7.48	7.39	7.37	–	7.37	–
H5 (t)	7.35	7.92	7.66	7.33	7.42	7.50	7.33	7.66	7.45	7.34	7.32	7.41	7.35	–	7.35	–
H6 (d)	7.65	8.29	8.22	7.63	7.22	8.09	7.64	8.25	8.10	7.65	8.25	8.11	7.66	–	7.67	–

(d) – doublet, (t) – triplet.



a) Benzenesulfonic acid b) Lithium benzenesulfonate c) Sodium benzenesulfonates d) Potassium benzenesulfonates



e) Benzoic acid f) Lithium benzoate g) Sodium benzoate h) Potassium benzoate

Fig. 2. The theoretical structures of benzenesulfonic and benzenesulfonates (a–d) and benzoic acids and benzoates (e–h).

symmetric $\nu_s(SO_3^-)$ amount to: 121, 130, 129, 133 and 135 cm^{-1} (Raman) for Li, Na, K, Rb and Cs benzenesulfonates, respectively. An increase in the value of $\Delta\nu(SO_3^-)$ in the series indicates a decrease in the symmetrization of the bidentate structure of the sulfonate ion in the series of $Li \rightarrow Na = K \rightarrow Rb \rightarrow Cs$ compounds. The same effect in case of alkali metal benzoates and pyridinecarboxylates was observed [4]. Then the changes in the electronic charge distribution, which lead to the asymmetrization of the sulfonate ion structure, are transmitted to the aromatic ring of molecules.

On the basis of the calculated geometrical parameters for benzenesulfonic acid and its salts (Table 2, Fig. 2) one can see that metal ions narrowly affect the aromatic ring of ligand but the geometry of sulfonate group undergoes modification after substitution of alkali metal ions in the sulfonic group of acid. As the bond between metal ion and oxygen atom lengthens the bond length S–O1 increases in the series: acid → Li → Na → K compounds. Whereas the bond lengths S–O2 and S–O3 become equal and decrease in the series: Li → Na → K benzenesulfonates. The value of angle C1–S–O1 remains almost unchanged taking into account the structures of acid and salts whereas angles C1–S–O2 and O1–S–O2 decrease in the series: Li → Na → K salts. The values of angles O1–S–O2 and S–O3–metal are smaller in the benzenesulfonate molecules compared to acid and increase in the above series.

Table 4

Chemical shifts from experimental and theoretical (in level B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)) ^{13}C NMR spectra of benzenesulfonic acid and alkali metal benzenesulfonates.

Carbon atom	Benzenesulfonic acid			Benzenesulfonates												
	Exp.	Calc.		Lithium			Sodium			Potassium			Rubidium		Caesium	
		MP2	B3LYP	Exp.	Calc.		Exp.	Calc.		Exp.	Calc.		Exp.	Calc.	Exp.	Calc.
					MP2	B3LYP		MP2	B3LYP		MP2	B3LYP				
C1	147.16	146.22	151.91	148.25	150.79	156.83	147.89	152.34	158.30	148.20	159.51	159.58	147.81	–	148.06	–
C2	128.56	125.54	131.96	127.65	125.51	131.32	127.77	126.14	131.86	127.66	142.20	131.85	127.86	–	127.74	–
C3	125.96	133.11	134.67	125.48	131.70	133.99	125.53	131.06	133.76	125.51	138.94	133.24	125.58	–	125.50	–
C4	129.83	132.42	139.29	128.45	130.35	136.35	128.66	129.31	135.10	128.52	144.01	134.48	128.78	–	128.62	–
C5	125.96	133.64	134.12	125.48	131.70	133.99	125.53	131.06	133.76	125.51	138.94	133.31	125.58	–	125.50	–
C6	128.56	127.58	134.12	127.65	125.50	131.32	127.77	126.14	131.86	127.66	142.20	131.89	127.86	–	127.74	–

Table 5
Results of charge density analysis for benzenesulfonic acid and lithium, sodium and potassium benzenesulfonates calculated in B3LYP/6-311++G(d,p) level.

Atom	Benzenesulfonic acid			Lithium benzenesulfonate			Sodium benzenesulfonate			Potassium benzenesulfonate	
	Q AIM [a.u.]	NBO	ChelpG	Q AIM [a.u.]	NBO	ChelpG	Q AIM [a.u.]	NBO	ChelpG	Q AIM [a.u.]	NBO
C1	0.007	−0.190	−0.048	0.009	−0.191	−0.064	0.006	−0.193	−0.055	0.004	−0.195
C2	0.001	−0.193	−0.087	−0.006	−0.196	−0.080	−0.010	−0.199	−0.091	−0.012	−0.201
C3	−0.005	−0.175	−0.042	−0.011	−0.189	−0.055	−0.014	−0.195	−0.068	−0.016	−0.198
C4	0.002	−0.192	−0.095	−0.005	−0.196	−0.080	−0.010	−0.199	−0.091	−0.012	−0.201
C5	0.016	−0.180	−0.042	0.009	−0.191	−0.064	0.006	−0.193	−0.055	0.005	−0.194
C6	−0.136	−0.280	−0.111	−0.133	−0.264	−0.124	−0.129	−0.262	−0.109	−0.129	−0.262
H2	0.071	0.236	0.102	0.064	0.232	0.132	0.062	0.231	0.122	0.060	0.230
H3	0.036	0.214	0.097	0.028	0.209	0.081	0.023	0.207	0.082	0.020	0.205
H4	0.035	0.212	0.090	0.026	0.208	0.085	0.021	0.205	0.086	0.018	0.204
H5	0.038	0.215	0.099	0.028	0.209	0.081	0.023	0.207	0.082	0.020	0.205
H6	0.076	0.238	0.123	0.064	0.232	0.132	0.062	0.231	0.122	0.060	0.230
S	2.861	2.251	1.136	2.963	2.264	1.191	2.986	2.269	1.198	3.006	2.282
O1	−1.261	−0.905	−0.545	−1.262	−0.895	−0.535	−1.274	−0.917	−0.569	−1.281	−0.927
O2	−1.246	−0.875	−0.501	−1.345	−1.057	−0.763	−1.336	−1.063	−0.765	−1.331	−1.066
O3	−1.089	−0.869	−0.589	−1.345	−1.057	−0.763	−1.336	−1.063	−0.765	−1.331	−1.066
H1/metal	0.594	0.494	0.413	0.919	0.883	0.826	0.920	0.936	0.875	0.918	0.955

The values of NBO, ChelpG, and AIM atomic charges obtained for benzenesulfonic acid and benzenesulfonates are collected in Table 5. For the calculated structures only one type of coordination was assumed. The formation of alkali metal salts causes an increase in the electronic charge density around atoms O1, O2 and O3 (compared to acid molecule). In the series Li → Na → K salts the negative charge gathered on O1 atom increases. In the case of O2 and O3 atoms the atomic charges do not change significantly and their values depend on the applied methods. The electronic charge density around S atom decreases in the series: benzenesulfonic acid → Li → Na → K benzenesulfonates. The negative atomic charge gathered on carbon atoms of the ring no. C2, C3, C4 and C5 is higher in case of benzenesulfonates than benzenesulfonic acid molecule, whereas in case of atoms C1 and C6 the opposite situation is observed. The alteration of the values of atomic charges is regular in the series Li → Na → K salts.

Table 6.

3.4. *The comparison of the influence of* $-SO_3H$ *and* $-COOH$ *substituents on the vibrational structure of ligand*

In our previous papers the FT-IR and FT-Raman spectra of benzoic acid and benzoates were reported and studied [2,3]. Comparing the spectra of benzenesulfonic and benzoic acids in the region of bands deriving from aromatic system vibrations one may notice subtle but characteristic changes. Namely, in the spectrum of benzenesulfonic acid most of these bands are shifted towards lower wavenumbers or they disappear compared with the spectrum of benzoic acid (Table 7). The shift of the aromatic system bands towards lower wavenumbers results from weakening of the bonds in benzene ring of benzenesulfonic acid caused by a decrease in the force constants of the bonds and polarization of the bonds in the ring [3].

The wavenumbers of selected bands from FT-IR, FT-Raman spectra of caesium benzoate and benzenesulfonate are gathered in Table 7. One may see that in the spectrum of benzoate the bands are shifted towards lower wavenumbers or disappeared compared with the spectrum of acid. On the other hand, in the spectrum of benzenesulfonate the bands generally are located at the same wavenumbers as in the spectrum of benzenesulfonic acid. This suggests that alkali metal ions stronger affect the electronic system of benzoic acid than benzenesulfonic acid.

In Tables 7 and 8 the geometrical parameters and atomic charges calculated for benzoic acid and benzoates in B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels are shown. The main parameters affected by substitution of alkali metal ions in the carboxylic group of acid are bonds: C1–C7, C7–O1, C7–O2 and O–metal as well as angles: C1–C7–O1, C1–C7–O2, O1–C7–O2. Similarly as it was shown in case of structures of benzenesulfonates the bond lengths C—O become equal in the molecules of benzoates and decrease in the series Li → Na → K salts. On the basis of calculated atomic charges (Table 8) one may see that benzoic acid and benzoate molecules possess higher electronic charge density in the ring than benzenesulfonic acid and benzenesulfonates, respectively. On the other hand, the atomic charges gathered on oxygen atoms of sulfonate group are more negative than in carboxylate group. The formation of alkali metal compounds causes similar changes in the values of atomic charges of carbon atoms of the ring in benzoates and benzenesulfonates compared to appropriate acids, i.e. the electronic charge density increases around atoms C2, C3, C4 and C5. But in case of C1 and C6 the opposite result is seen. In benzoate molecules the electronic charge density around atoms C1 and C6 increases but in benzenesulfonates it decreases.

3.5. *The application of the indices for quantitative measurement of aromaticity of the studied compounds*

The calculated geometric and magnetic indices are gathered in Table 9. Lower values of HOMA, I_6, BAC and higher values of NICS, $\Delta\chi$ were obtained for benzoic than for benzenesulfonic acid. According to the criterion of aromaticity, benzoic acid and benzoates posses lower aromatic properties than benzenesulfonic acid and benzenesulfonates. Moreover the differences in the values of appropriate indices are higher for ligands than for their metal complexes. That means that substitutents in benzene ring affect the electronic charge distribution to a higher extend than substitution of metals in the coordinated group, i.e. carboxylic and sulfonic groups. The values of HOMA, BAC, I_6 and NICS indices undergo small alternations or remain unchanged along the series: acid → Li → Na → K salts. In case of benzoates the differences are more visible, especially in case of BAC and I_6 indices. It may suggests that alkali metal ions stronger affect the molecular structure of benzoic acid than benzenesulfonic acid. The indices pEDA and π-total suggest a decrease of the aromatic properties of benzenesulfonates compared to the acid molecule.

Most of the applied indices do not reflect the aromatic properties of benzoates and benzenesulfonates. In some studies the magnetic indices are considered to be better in describing the aromaticity of molecules. According to Schleyer the magnetic indices are the most representative criteria among all applied aromaticity indices, because they depend on the magnetic susceptibility which is completely dependent on π-electron structure of molecule

Table 6
The experimental wavenumbers of selected band accruing in the FT-IR and FT-Raman spectra of benzoic and benzenesulfonic acids and their caesium salts.

		8a	8b	19a	19b	14	18b	18a	12	10a	11	6b
Benzoic acid	IR	1604	1586	1498	1455	1324	1073	1027	1000	856	–	617
	R	1603	1586	–	1460	1326	–	1027	1001	855	796	616
Cs benzoate	IR	1596	–	–	–	1309	1069	1024	–	–	–	–
	R	1596	–	–	–	–	–	1019	–	–	–	–
Benzenesulfonic acid	IR	–	–	1483	1448	–	1072	1016	995	–	732	611
	R	1589	–	–	–	–	–	–	998	–	733	616
Cs benzenesulfonate	IR	–	–	1484	1445	–	1071	1020	998	864	733	–
	R	–	1588	–	1443	–	–	1020	997	855	735	617

Table 7
The theoretical geometric parameters calculated for benzoic acid and benzoates in B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels.

	Benzoic acid		Benzoate					
	MP2	B3LYP	Lithium		Sodium		Potassium	
			MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
Bond lengths [Å]								
C1–C2	1.404	1.400	1.403	1.399	1.403	1.398	1.403	1.398
C2–C3	1.398	1.392	1.398	1.392	1.399	1.393	1.399	1.393
C3–C4	1.400	1.395	1.401	1.395	1.401	1.395	1.401	1.395
C4–C5	1.401	1.396	1.401	1.395	1.401	1.395	1.401	1.395
C5–C6	1.397	1.390	1.398	1.392	1.399	1.393	1.399	1.393
C6–C1	1.403	1.400	1.403	1.399	1.403	1.398	1.403	1.398
C1–C7	1.490	1.486	1.500	1.497	1.511	1.507	1.514	1.513
C7–O1	1.213	1.209	1.275	1.274	1.272	1.269	1.269	1.267
C7–O2	1.358	1.358	1.275	1.274	1.272	1.269	1.269	1.267
O2–H/metal	0.968	0.968	1.880	1.856	2.250	2.208	2.530	2.517
Angles [°]								
C1–C2–C3	119.559	119.858	119.847	120.094	120.097	120.284	120.198	120.375
C2–C3–C4	120.268	120.106	120.152	120.018	120.175	120.048	120.177	120.051
C3–C4–C5	119.909	120.129	119.849	120.043	119.691	119.898	119.620	119.840
C4–C5–C6	120.133	119.986	120.153	120.017	120.180	120.048	120.177	120.051
C5–C6–C1	119.754	120.039	119.847	120.095	120.093	120.284	120.201	120.376
C1–C7–O1	124.850	125.100	119.146	119.608	117.913	118.329	117.555	117.980
C1–C7–O2	112.521	113.026	119.145	119.611	117.908	118.328	117.529	117.977
O1–C7–O2	122.629	121.873	121.709	120.780	124.178	123.343	124.917	124.044
C7–O2–H/metal	105.557	106.661	82.809	82.960	87.912	87.926	91.162	91.573
Dipole moment [Debye]	1.817	2.128	3.721	3.273	6.709	6.095	8.317	7.775
Energy [hartree]	−419.953	−420.949	−426.727	−427.947	−581.112	−582.709	−1018.863	−1020.354

Table 8
Atomic charges calculated for benzoic acid and benzoates in B3LYP/6-311++G(d,p) level.

Atom	Benzoic acid			Lithium benzoate			Sodium benzoate			Potassium benzoate	
	Q AIM [a.u.]	NBO	ChelpG	Q AIM [a.u.]	NBO	ChelpG	Q AIM [a.u.]	NBO	ChelpG	Q AIM [a.u.]	NBO
C1	−0.010	−0.169	0.000	−0.017	−0.154	0.109	−0.018	−0.147	0.091	−0.021	−0.145
C2	−0.004	−0.159	−0.070	−0.010	−0.160	−0.166	−0.013	−0.167	−0.154	−0.016	−0.171
C3	−0.009	−0.206	−0.105	−0.017	−0.211	−0.078	−0.021	−0.213	−0.070	−0.024	−0.214
C4	−0.012	−0.175	−0.058	−0.019	−0.187	−0.072	−0.022	−0.195	−0.102	−0.025	−0.199
C5	−0.008	−0.205	−0.081	−0.017	−0.211	−0.078	−0.021	−0.213	−0.070	−0.024	−0.214
C6	−0.001	−0.150	−0.097	−0.010	−0.160	−0.166	−0.013	−0.167	−0.154	−0.016	−0.171
H2	0.058	0.225	0.103	0.059	0.227	0.136	0.056	0.226	0.119	0.054	0.225
H3	0.026	0.209	0.095	0.017	0.204	0.081	0.011	0.201	0.076	0.008	0.199
H4	0.027	0.207	0.088	0.017	0.203	0.080	0.012	0.200	0.084	0.009	0.199
H5	0.028	0.209	0.090	0.017	0.204	0.081	0.011	0.201	0.076	0.008	0.199
H6	0.065	0.229	0.108	0.059	0.227	0.136	0.056	0.226	0.119	0.054	0.225
C7	1.492	0.790	0.659	1.518	0.764	0.675	1.543	0.764	0.687	1.560	0.772
O1	−1.144	−0.600	−0.551	−1.258	−0.818	−0.785	−1.241	−0.818	−0.779	−1.234	−0.823
O2	−1.091	−0.691	−0.612	−1.257	−0.818	−0.785	−1.241	−0.818	−0.779	−1.234	−0.823
H1/metal	0.585	0.486	0.432	0.918	0.889	0.833	0.902	0.919	0.856	0.900	0.940

[9,10]. Moreover high linear correlation between the magnetic indices and energy of studied systems was found. The geometrical indices do not correlate in a linear fashion with the magnetic ones. This suggests that aromaticity indices, which are based on different physico-chemical properties of molecules, do not reflect the same aspects of aromaticity. The multidimensional character of aromaticity has been proved for many groups of compounds [12]. Small differences between geometric indices calculated for particular compounds may be explained as follows: chemical factors which reveal the character of substituents in benzene ring weakly influence the aromaticity of system in contradiction to topological factors [48].

Table 9
The aromaticity indices calculated for benzoic and benzenesulfonic acids and their alkali metal salts (on the basis of data calculated in B3LYP/6-311++G(d,p) level).

	Benzoic acid	Benzoates			Benzenesulfonic acid	Benzenesulfonates		
		Lithium	Sodium	Potassium		Lithium	Sodium	Potassium
HOMA	0.983	0.984	0.984	0.984	0.993	0.991	0.991	0.991
GEO	0.003	0.002	0.001	0.001	0.003	0.000	0.00	0.000
EN	0.014	0.014	0.015	0.015	0.007	0.008	0.009	0.009
I_6	96.88	97.74	98.03	98.21	99.11	99.21	99.42	99.42
BAC	0.951	0.964	0.969	0.972	0.987	0.990	0.990	0.990
NICS	−8.01	−7.94	−8.02	−8.01	−9.27	−9.25	−9.24	−9.24
π-total	5.035	5.938	5.955	5.957	5.982	6.004	6.029	6.802
pEDA	–	0.9032	0.917	0.922	–	0.022	0.047	0.819

3.6. Conclusions

The molecular structure of benzenesulfonic acid and alkali metal benzenesufonates was discussed in this paper on the basis of experimental and theoretical FT-IR, FT-Raman, ^{1}H and ^{13}C NMR spectra and calculated geometrical parameters and atomic charges (AIM, NBO, ChelpG). Alkali metal ions mostly affect the electronic charge density of sulfonate group whereas the structure aromatic ring is slightly affected. Some bands from FT-IR, FT-Raman, NMR as well as values of atomic charges gathered on some atoms undergo regular placement in the series: Li → Na → K → Rb → Cs benzenesulfonates. This suggests that certain metal ion parameters (such as ionic potential, ionic radius, atomic mass) play an important role in the influence of metal ions on the molecular structure of ligand. Alkali metal ions mostly affect the electronic charge density in sulfonate group than in the rest of molecule. The substitution of alkali metal ions in the sulfonic group of acid causes an increase in the electronic charge density around atoms O1, O2 and O3 and a decrease around S atom in salt molecules compared to acid. Then the negative atomic charge gathered on carbon atoms of the ring no. C2, C3, C4 and C5 increases whereas in case of atoms C1 and C6 decreases. Alkali metal ions in a different way affect the structure of benzenesulfonic acid and benzoic acid. Benzoic acid and benzoate molecules possess higher electronic charge density in the ring than benzenesulfonic acid and benzenesulfonates, respectively. Whereas the atomic charges gathered on oxygen atoms of sulfonate group are more negative than in carboxylate group. The electronic charge density around atoms C2, C3, C4 and C5 is higher in benzenesulfonate and benzoate molecules compared to appropriate acids. Whereas the negative atomic charge collected on atoms C1 and C6 increases in benzoates compared to benzoic acid and decreases in benzenesulfonates compared to benzenesulfonic acid. Among studied aromaticity indices pEDA and π-total in the best way describe the influence of alkali metal ions on the aromatic system of ligands.

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