The effect of alkali metal ions on the electronic structure of *p*-anisic acid¹

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Abstract. FT-IR (in solid state and solution), FT-Raman, UV and ¹H, ¹³C NMR spectra of *p*-methoxybenzoic (*p*-anisic) acid and lithium, sodium, potassium, rubidium and caesium *p*-methoxybenzoates (*p*-anisates) were registered, assigned and analyzed. The structures of anisic acid and Li, Na and K *p*-anisates were optimised at the B3LYP/6-311++G** level. The IR spectra and NPA, ChelpG and MK atomic charges were calculated. The effect of metal ions on the electronic charge distribution in ligand was discussed.

Keywords: *p*-Anisic acid, *p*-methoxybenzoic acid, alkali metal methoxybenzoates, FT-IR, FT-Raman, NMR, B3LYP/6-311++G**

1. Introduction

In order to understand the nature of interactions of biologically important ligands it is necessary to carry out the physico-chemical studies of these compounds with their biological targets (e.g., receptors in the cell or important cell components). Results of this study make it possible to predict some properties of a molecule, such as its reactivity, durability of complex compounds and affinity to enzymes. In this paper the effect of alkali metal cations (Li, Na, K, Rb, Cs) on the molecular structure of *p*-methoxybenzoic acid (*p*-anisic acid) was studied. Methoxybenzoic acids are known to be important inhibitors in growth of bacteria and they influence the catalytic activity of many enzymes [1]. From this point of view it is very important to study the effect of substituents and metal ions on the above mentioned biologically important ligand [5]. In this paper the spectroscopic (FT-IR, FT-Raman, UV and ¹H, ¹³C NMR) study of *p*-anisic acid and its alkali metal salts was done. Moreover, calculations at the B3LYP/6-311++G** level for *p*-methoxybenzoic acid and Li, Na and K *p*-methoxybenzoates were performed.

2. Experimental section

Preparation of Li, Na, K, Rb and Cs *p*-anisates was described previously [4]. The obtained salts were anhydrous, the metal:ligand ratio was 1:1. The IR spectra were recorded with the Equinox 55 Bruker FT-IR spectrometer within the range 4000–400 cm^{−1}. Samples in the solid state were measured in KBr matrix. Pellets were obtained with a hydraulic press under 739 MPa pressure. Moreover FT-IR spectra were registered by the use of ATR technique for solid samples and solutions with concentration

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$5 \cdot 10^{-2}$ mol/l. Raman spectra of solid samples in capillary tubes were recorded in the range of 4000–400 cm^{-1} with a FT-Raman accessory of the Perkin Elmer System 2000. The resolution of spectrometer was 1 cm^{-1} . The NMR spectra of DMSO solution were recorded with the Bruker Avance II 400 MHz unit at room temperature. TMS was used as an internal reference. The UV spectra were recorded with the DR 4000U HACH spectrophotometer between 190–300 nm. The compounds were studied in aqueous solutions with concentration $5 \cdot 10^{-5}$ mol/l.

The optimized geometries, NPA (Natural Population Analysis), ChelpG (Charges from Electrostatic Potentials using a Grid-based method), MK (Merz–Singh–Kollman) atomic charges and IR wavenumbers were calculated at the B3LYP/6-311++G** level of theory using the Gaussian 98W program [2]. The theoretical vibrational spectra were interpreted by means of potential energy distributions (PEDs) using VEDA 3 program [3].

3. Results and discussion

3.1. FT-IR and FT-Raman spectra

In Tables 1 and 2 wavenumbers of selected bands from the FT-IR (registered in KBr matrix and by the use of ATR accessory – for water solution and solid sample), FT-Raman and calculated spectra of *p*-anisic acid and Li, Na, K, Rb and Cs *p*-anisates are collected. The spectral assignments were done on the basis of the literature data [4,6] and presented in this paper IR spectra calculated for studied molecules. Notation used in this paper was described previously [4,6]. Replacement of the carboxylic group hydrogen with a metal ion, brought about characteristic changes in the IR and Raman spectra of the metal *p*-anisates in comparison with the spectra of ligand. Namely, a disappearance of bands of symmetric and asymmetric stretching $\nu(\text{C}=\text{O})$ at 1686 cm^{-1} (IR) and deforming $\gamma(\text{C}=\text{O})$ at 548 cm^{-1} (IR) vibrations of the carbonyl group; a disappearance of stretching $\nu(\text{O}-\text{H})$ vibrations of hydroxyl group in the range 3050–2500 cm^{-1} (IR); an appearance of bands of asymmetric and symmetric vibrations of the carboxylate anion $\nu_{\text{as}}(\text{COO}^-)$, $\nu_{\text{s}}(\text{COO}^-)$ as well as $\beta_{\text{as}}(\text{COO}^-)$, $\beta_{\text{s}}(\text{COO}^-)$, $\gamma_{\text{s}}(\text{COO}^-)$ are observed. In the spectra of salts some bands disappear or change their position and intensities compared with appropriate bands present in the spectrum of acid. In the range 3089–3005 cm^{-1} (IR, Raman) bands connected with stretching vibrations –CH of aromatic ring occur. In the spectra of salts these bands possess lower intensities, and band No. 20a is shifted toward higher wavenumbers and band No. 20b and $\nu(\text{CH})_{\text{ar}} \sim 3050 \text{ cm}^{-1}$ are shifted to lower wavenumbers compared with the appropriate bands from the spectra of acid. Bands derived from stretching vibrations –CH of methoxy group are located between 2986–2834 cm^{-1} (IR, Raman). Only band $\nu_{\text{as}}(\text{CH}_3) \sim 2986 \text{ cm}^{-1}$ undergoes distinct displacement in the IR and Raman spectra of salts compared with spectra of acid. The rest of $\nu(\text{CH}_3)$ bands remain almost unchanged in their wavenumbers. In the range 1651–1305 cm^{-1} (IR, Raman) bands of –CC– stretching vibrations of aromatic ring occur. Band No. 8b is located at considerably higher wavenumber and bands Nos 14 and 19a at lower wavenumbers in the spectra of anisates than anisic acid. Moreover, bands Nos 8b (IR Kbr, IR ATR_{solid}), 14 (IR Kbr, IR ATR_{solid}, Raman) and 19a (IR Kbr, IR ATR_{solid}, Raman) decrease in the wavenumbers along the alkali cation series: Li → Na → K → Rb → Cs *p*-anisates (in case of band No. 14 – Li *p*-anisate does not fit this trend). Bands derived from deforming in-plane and out-of-plane vibrations of –CH methoxy group occur between 1499–1169 cm^{-1} (IR, Raman). Wavenumbers of bands $\delta_{\text{as}}(\text{CH}_3) \approx 1480 \text{ cm}^{-1}$ and $\rho(\text{CH}_3) \approx 1170 \text{ cm}^{-1}$ from the IR spectra of anisates decrease along the alkali metal series. In the range 1180–1000 cm^{-1} (IR, Raman) bands assigned to deforming

Table 1

Wavenumbers, intensities and assignments of selected bands present in the experimental FT-IR (recorded in KBr; IR_{KBr}), FT-Raman and calculated IR (IR_{Calc.}) spectra *p*-anisic acid

IR _{KBr}		Raman		IR _{Calc.}		Assignment %PED (>10%)	Aromatic ring vibrations [6]
~3050–2500		~3080–2800		3775	105.6	100ν(OH)	
3079	w	3080	vw	3215	4.58	99ν(CH) _{ar}	20a
3054	m			3200	2.9	99ν(CH) _{ar}	
3030	m	3030	vw	3190	1.02	98ν(CH) _{ar}	20b
2986	m	2985	vw	3140	18.5	91ν _{as} (CH ₃)	
2941	m	2942	vw	3074	32.65	100ν _{as} (CH ₃)	
2844	m	2845	vw	3012	52.25	91ν _s (CH ₃)	
1686	s			1778	450.10	81νC=O	
1604	vs	1610	s	1647	217.27	54ν(CC) _{ar}	8a
1577	s	1581	w	1609	42.54	51ν(CC) _{ar} + 23α(CCC)	8b
1517	s			1542	66.76	56β(CH) + 10α(CCC)	19a
1466	m			1503	30.00	72δ _{as} (CH ₃) + 24φ(HCOC)	
1450	sh	1453	vw	1493	9.92	74δ _{as} (CH ₃) + 24φ(HCOC)	
1427	s	1421	vw	1364	111.85	10ν(OC) + 16ν(CC) _{ar} + 42β(OH)	
1324	s	1323	vw	1353	42.39	76ν(CC) _{ar}	14
1304	s	1304	vw	1095	202.15	48νC–(OH) + 10α(CCC)	
1262	vs	1271	m	1283	296.14	42νC–(O–CH ₃)	
1222	s			1216	76.39	10ν(CC) _{ar} + φ(HOC) + 27β(CH)	
1180	s	1186	w	1201	7.05	20ρ(CH ₃) + 62φ(HCOC)	
1168	s	1180	w	1183	302.54	16β(OH) + 37β(CH)	9a
1130	s	1135	vw	1166	0.62	27ρ(CH ₃) + 71φ(HCOC)	
1106	s			1135	3.62	10ν(CC) _{ar} + 50β(CH)	18b
1027	s	1023	vw	1052	72.12	70νO–(CH ₃)	
		1012	vw	1024	4.14	62α(CCC)	18a
928	s					γOH	
867	m			860	26.75	56γ(CH) + 23φ(OCC)	17b
844	s	846	vw	829	10.48	36ν(CC) _{ar} + 14ν(OC) + 12α(CCC)	1
823	m	825	m	823	1.00	87γ(CH)	10a
773	s	775	vw	778	70.15	10γ(CH) + 70φ(OCC)	11
735	m			724	4.7	25ν(OC) + 14ν(CC) _{ar} + 13α(CCC) + 22β(C=O)	
697	m	699	vw	697	23.78	54φ(CCC) + 21φ(OCC)	4
633	m	635	vw	647	2.43	68α(CCC)	6b
615	s	616	vw	605	64.15	10ν(OC) + 40β(C=O) + 13α(CCC)	
548	s			567	49.71	79γ(C=O)	
514	m			511	15.49	41β(C=O) + 12α(CCC)	
504	m			503	39.03	15γ(C=O) + 27φ(CCC) + 34φ(OCC)	16b
487	m			479	1.62	29β(OCC) + 32β(COC)	

Note: s – strong, vs – very strong, w – weak, vw – very weak, m – medium, sh – shoulder.

in-plane –CH vibrations of aromatic ring [β(CH)] are located. Band No. 9a is shifted toward lower wavenumbers in the IR and Raman spectra of salts compared with acid, and this band decrease in the wavenumbers along the alkali metal series: Li → Na → K → Rb → Cs. Bands of deforming out-of-plane –CH vibrations of aromatic ring [γ(CH)] are situated between 867–774 cm^{–1} (IR, Raman). Band

Table 2

Wavenumbers, intensities and assignments of selected bands present in the experimental FT-IR (recorded in KBr matrix: IR KBr, and by the use of ATR accessory – water solution: IR ATR_{H₂O}, and solid sample: IR ATR_{solid}), FT-Raman and calculated IR spectra of lithium, sodium, potassium, rubidium and caesium *p*-anisates

	Li		Na		K		Rb		Cs		Assignment	Aromatic ring vibrations [6]
IR KBr	3086	vw			3089	vw	3084	vw	3079	vw	$\nu(\text{CH})_{\text{ar}}$	20a
IR ATR _{solid}							3084	vw	3084	vw		
Raman	3088	vw	3083	m	3088	vw	3084	w	3079	vw		
Calc.	3209	8.48	3206	9.64	3204	10.67						
IR KBr	3006	w	3008	vw	3017	w	3017	w	3016	w	$\nu(\text{CH})_{\text{ar}}$	20b
IR ATR _{solid}	3005	w	3008	vw	3018	vw	3018	w	3016	w		
Raman	3006	w	3014	w	3018	m	3018	w	3017	vw		
Calc.	3186	3.31	3183	4.62	3180	5.45						
IR KBr	2964	w	2954	w	2958	w	2958	w	2957	w	$\nu_{\text{as}}(\text{CH}_3)$	
IR ATR _{solid}	2965	vw	2954	vw	2958	w	2957	w	2957	w		
Raman	2962	vw	2954	vw	2958	vw	2956	vw	2952	vw		
Calc.	3134	22.60	3130	25.24	3128	26.82						
IR KBr	2943	w	2935	w	2934	w	2934	w	2935	w	$\nu_{\text{as}}(\text{CH}_3)$	
IR ATR _{solid}	2943	vw			2931	vw	2931	vw	2935	vw		
Raman			2939	vw	2935	vw	2935	vw	2936	vw		
Calc.	3065	37.02	3061	39.74	3058	41.32						
IR KBr	2840	w	2834	w	2838	w	2839	w	2839	w	$\nu_{\text{s}}(\text{CH}_3)$	
IR ATR _{solid}	2836	vw	2834	w	2838	w	2838	w	2839	w		
Raman	2844	vw	2838	vw	2840	vw	2840	w	2841	vw		
Calc.	3006	58.02	3003	61.57	3002	63.61						
IR KBr	1607	vs	1612	s					1605	s	$\nu(\text{CC})_{\text{ar}}$	8a
IR ATR _{solid}			1611	sh	1607	sh	1607	sh	1604	sh		
IR ATR _{H₂O}	1645	w	1651	w			1638	w	1643	w		
Raman	1611	s	1616	s	1610	s	1609	m	1607	m		
Calc.	1645	170.76	1644	143.26	1643	133.94						
IR KBr	1599	vs	1597	vs	1597	vs	1597	vs	1595	vs	$\nu(\text{CC})_{\text{ar}}$	8b
IR ATR _{solid}	1601	vs	1596	s	1594	vs	1594	vs	1592	vs		
IR ATR _{H₂O}	1599	m	1597	m	1597	m	1599	s	1599	m		
Raman					1597	m	1596	w	1594	w		
Calc.	1619	79.05	1621	96.62	1623	106.57						
IR KBr	1555	vs	1545	vs	1546	vs	1548	vs	1548	vs	$\nu_{\text{as}}(\text{COO}^-)$	
IR ATR _{solid}	1551	vs	1541	vs	1544	vs	1547	vs	1547	vs		
IR ATR _{H₂O}	1535	s	1535	s	1535	s	1535	s	1535	s		
Raman	1559	vw	1568	vw	1556	vw	1554	vw	1551	vw		
Calc.	1529	364.23	1549	389.77	1559	335.55						
IR KBr	1514	m	1515	m	1509	m	1506	m	1505	m	$\nu(\text{CC})_{\text{ar}}$	19a
IR ATR _{solid}	1514	w	1515	sh	1507	m	1505	m	1504	m		
Raman	1516	vw	1518	vw	1510	vw	1508	vw	1507	vw		
Calc.	1541	23.44	1536	33.12	1535	35.64						

Table 2
(Continued)

	Li		Na		K		Rb		Cs		Assignment	Aromatic ring vibrations [6]
IR KBr	1499	w			1472	w	1471	w	1469	w	$\delta_{as}(\text{CH}_3)$	
IR ATR _{solid}	1503	w	1494	w	1492	w	1493	w	1493	w		
	1475	w	1473	w	1473	w	1469	vw	1468	w		
IR ATR _{H₂O}	1470	w	1466	w	1466	w	1458	w	1460	w		
Calc.	1504	19.58	1505	24.99	1506	25.80						
IR KBr	1428	vs	1421	vs	1409	s	1403	s	1401	s	$\nu_s(\text{COO}^-)$	
IR ATR _{solid}	1427	sh	1410	s	1386	s	1383	s	1377	s		
IR ATR _{H₂O}	1439	s	1435	s	1409	vs	1406	s	1401	m		
Calc.	1430	626.98	1407	588.27	1401	644.67						
IR KBr	1313	m	1314	w	1308	w	1307	m	1306	m	$\nu(\text{CC})_{ar}$	14
IR ATR _{solid}	1309	m	1313	m	1308	m	1307	m	1305	m		
IR ATR _{H₂O}	1310	w	1310	w	1312	m	1305	m	1306	m		
Raman	1314	vw	1319	vw	1310	vw	1308	vw	1306	vw		
Calc.	1346	36.70	1344	31.83	1343	30.75						
IR KBr	1176	m	1177	m	1173	m	1171	w	1170	m	$\rho(\text{CH}_3)$	
IR ATR _{solid}	1173	m	1175	m	1172	m	1171	m	1170	m		
IR ATR _{H₂O}	1179	w	1179	w	1179	m	1179	m	1179	m		
Raman	1177	vw	1180	vw	1181	m	1170	vw	1169	w		
Calc.	1201	18.83	1201	23.25	1201	25.45						
IR KBr	1146	m	1143	w	1132	w	1130	w	1129	m	$\beta(\text{CH})$	9a
IR ATR _{solid}	1144	m	1143	w	1132	w	1130	w	1129	m		
IR ATR _{H₂O}	1148	w	1138	w	1148	w	1144	w	1144	w		
Raman	1147	m	1146	m	1134	s	1132	m	1131	m		
Calc.	1192	68.68	1190	61.59	1189	56.89						
IR KBr	1106	m	1096	m	1099	m	1099	m	1099	m	$\beta(\text{CH})$	18b
IR ATR _{solid}	1106	m	1096	m	1099	m	1098	m	1098	m		
IR ATR _{H₂O}	1111	w			1113	w	1113	sh	1109	vw		
Raman			1098	vw	1102	vw	1100	vw				
Calc.	1124	15.32	1121	15.28	1119	15.43						
IR KBr	1034	m	1035	m	1031	m	1030	m	1030	s	$\nu\text{O}-(\text{CH}_3)$	
IR ATR _{solid}	1030	s	1034	m	1030	m	1031	m	1029	m		
IR ATR _{H₂O}	1028	w	1026	w	1022	m	1026	m	1026	m		
Raman	1037	vw			1030	vw	1031	vw	1028	vw		
Calc.	1058	61.86	1060	60.89	1061	56.45						
IR KBr	1008	w			1007	w	1004	w	1003	w	$\beta(\text{CH})$	18a
IR ATR _{solid}	1008	w			1007	w	1004	w	1002	w		
IR ATR _{H₂O}												
Raman												
Calc.	1025	1.47	1026	2.39	1026	2.58						
IR KBr	855	m	854	m	858	w	858	w	858	m	$\alpha(\text{CCC})$	1
IR ATR _{solid}	856	sh	852	sh	859	w	858	w	858	m		

Table 2
(Continued)

	Li		Na		K		Rb		Cs		Assignment	Aromatic ring vibrations [6]
Raman	858	m	856	vs	849	s	849	m	849	m		
Calc.	803	1.47	801	56.27	805	52.58						
IR KBr	849	sh	841	m	849	m	847	w	847	w	$\beta_s(\text{COO}^-)$	
IR ATR _{solid}	849	m	848	m	847	m	847	m	847	w		
Raman												
Calc.	876	29.63	865	26.16	856	45.62						
IR KBr					833	w	834	w	834	m	$\gamma(\text{CH})$	10a
IR ATR _{solid}	820	vw	826	vw	833	w	833	w	833	m		
Raman					835	m	836	m	836	s		
Calc.	827	0.03	826	0.52	827	2.28						
IR KBr	793	s			793	s	792	s	792	s	$\gamma_s(\text{COO}^-)$	
IR ATR _{solid}	792	vs			792	vs	792	vs	792	vs		
Raman	792	vw	786	m	793	w	793	vw	793	w		
Calc.	798	57.82	797	0.88	791	2.24						
IR KBr	779	m	778	s	780	m	778	sh			$\gamma(\text{CH})$	11
IR ATR _{solid}	774	sh	775	vs	778	m	777	m	776	w		
Raman	781	m	775	vw	779	m	778	m	777	m		
Calc.	710	14.70	711	14.46	711	14.95						
IR KBr	703	m	694	w	698	w	698	w	698	m	$\phi(\text{CCC})$	4
IR ATR _{solid}	701	m	692	m	698	m	698	m	698	m		
Raman	707	vw	696	vw	702	vw	700	vw	700	w		
IR KBr	635	m	635	w	637	w	637	w	636	w	$\alpha(\text{CCC})$	6b
IR ATR _{solid}	635	m	636	m	637	m	637	m	636	m		
Raman	637	m	636	m	638	m	638	m	637	m		
Calc.	646	17.44	650	9.33	649	7.22						
IR KBr	618	m	615	m	614	m	612	m	612	m	$\alpha(\text{CCC})$	
IR ATR _{solid}	614	s	612	s	611	s	611	s	610	s		
Raman			617	vw	615	vw	614	vw				
Calc.	598	45.96	631	48.54	626	58.36						
IR KBr	552	m	535	w	532	w	529	w	526	w	$\beta_{as}(\text{COO}^-)$	
IR ATR _{solid}												
Raman					533	vw	529	vw	526	w		
Calc.	541	1.77	535	6.66	533	7.22						

Note: s – strong, vs – very strong, w – weak, vw – very weak, m – medium, sh – shoulder.

No. 17b disappears from the spectra of salts, and bands Nos 10a and 11 possess lower intensities in the spectra of salts compared with acid. In the ranges 860–514 cm⁻¹ (IR, Raman) and 710–500 cm⁻¹ (IR, Raman) there are present bands assigned to respectively in-plane [$\alpha(\text{CCC})$] and out-of-plane [$\phi(\text{CCC})$] vibrations of aromatic ring. No regular displacements in case of these bands are observed. Wavenumbers of bands derived from carboxylic group vibrations (i.e., $\nu_{as}(\text{COO}^-)$, $\nu_s(\text{COO}^-)$, $\beta_{as}(\text{COO}^-)$) also change their location along the alkali cation series; the decrease in the wavenumber of these bands along series Li → Na → K → Rb → Cs *p*-anisates is connected with an increase in ionic character of bond

metal–oxygen. The analysis for linear correlation between selected metal ions parameters (ionic potential, ionic radius, reverse of atomic mass) and wavenumbers of bands from FT-IR and FT-Raman spectra was done. Among studied parameters the highest correlation coefficients were in most cases obtained for ionic radii of metal ions.

3.2. UV spectra

The maximum of $\pi \rightarrow \pi^*$ band for *p*-anisic acid is located at 252 nm. In the UV spectra of *p*-anisates the band is shifted toward lower wavelengths (to ~ 248 nm). The observed hypsochromic shift indicates a decrease in the delocalization energy and therefore a perturbation effect of alkali metals on the electronic system of ligand.

3.3. ^1H and ^{13}C NMR

One may observe a decrease in the chemical shifts in case of all protons in comparison to appropriate chemical shifts in the ^1H NMR spectra of ligand (Table 3, Fig. 1). It points at an increase in the screening of aromatic protons as a consequence of the circular current weakening. The chemical shifts of aromatic protons decrease in the series: $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \sim \text{Rb} \sim \text{Cs}$ *p*-anisates. In the ^{13}C NMR spectra of *p*-anisates the signals from carbons Nos 2–6 are slightly shifted downfield in comparison to the spectrum of ligand, whereas the signals from carbons Nos 1 and 7 are shifted upfield. Such small influence of alkali metal ions on the molecular structure of ligand in DMSO solution may be caused by interaction of DMSO with anisate molecules. Probably, the oxygen atom from DMSO takes part in alkali cations coordination and in this way weaken the effect of metal ions on the electronic charge density in anisate ligand.

3.4. Calculations

The formation of salts causes the most noticeable changes in the geometrical parameters of carboxylate and methoxy groups of anisates (Table 4), i.e., bond lengths: C7–O2, C7–O1, C1–C7, O–M, C4–O3,

Table 3

Chemical shifts of protons in the ^1H NMR and carbons in the ^{13}C NMR spectra of DMSO solution of *p*-anisic acid and alkali metal *p*-anisates (atom numbering for anisates in Fig. 1)

	<i>p</i> -anisic acid	Li	Na	K	Rb	Cs
Proton position						
H1 (carboxylic group)	12.34	–	–	–	–	–
H2, H6	7.90	7.90	7.83	7.76	7.75	7.77
H3, H5	7.00	6.83	6.80	6.75	6.75	6.76
H9, H8, H7	3.81	3.75	3.75	3.73	3.73	3.73
Carbon position						
C7	167.13	170.42	170.06	168.39	168.58	168.50
C4	162.92	160.28	159.90	159.37	159.51	159.42
C2, C6	131.43	130.93	130.65	130.38	130.49	130.40
C1	123.05	131.88	132.82	134.36	134.13	134.47
C3, C5	113.86	112.37	112.23	111.96	112.04	111.99
C8	55.45	55.04	54.99	54.88	54.94	54.91

Fig. 1. Atom numbering for anisates.

O3–C8 and angles: O1–C7–O2, C7–O–M. Along the metal series $\text{Li} \rightarrow \text{Na} \rightarrow \text{K}$ anisates the following bond lengths: C7–O2, C7–O1, O3–C8 decrease, whereas bond lengths: C1–C7, C4–O3 and angles: O1–C7–O2, C7–O–M increases. Calculated NPA, ChelpG and MK atomic charges are collected in Table 5. The most significant differences between atomic charges calculated different methods are related to carbon atom No. C1. In case of lithium anisate negative charge is located on C1 carbon atom according to NPA calculations, whereas for ChelpG and MK calculations positive charge is obtained. Similar situation is in case of sodium anisate. Beside the differences in the values of NPA, ChelpG and MK atomic charge obtained for particular atoms, general conclusions concerning the electronic charge distribution in molecules and the effect of metal ions on the structure of ligand may be drawn. On the basis of calculated bond lengths and atomic charges the resonance structures of ligand can be discussed. Values of atomic charges for aromatic ring of *p*-anisic acid molecule increase in the following order: $\text{C3} < \text{C5} < \text{C1} < \text{C2} < \text{C6} < \text{C4}$ (NPA), $\text{C5} < \text{C3} < \text{C1} < \text{C2} < \text{C6} < \text{C4}$ (ChelpG), $\text{C5} < \text{C3} < \text{C2} < \text{C1} < \text{C6} < \text{C4}$ (MK). Calculated bond lengths increase in the series: $\text{C5} - \text{C6} < \text{C2} - \text{C3} < \text{C1} - \text{C2} < \text{C3} - \text{C4} < \text{C4} - \text{C5} < \text{C1} - \text{C6}$. Taking into account that the highest negative charge is located on carbons Nos C5 and C3, and the shortest bonds in aromatic ring are C5–C6 and C2–C3 the contribution of structures A and C in resonance is more probable than structure B (Fig. 2). The form B possesses high positive charge on C4 atom and negative charge on C3 atom, so this structure should take part in resonance as well. Among the last three form (E, F and G) the most important seems to be structure E due to high positive charge located on C4 atom and the shortest bonds C5–C6 and C2–C3 in aromatic ring. According to calculated atomic charges (Table 5), substitution of alkali metal ions in the carboxylic group of *p*-anisic acid causes the most significant changes in the electronic charge distribution around atoms number C2, C3, C5, C6, O1 and O2.

4. Conclusions

(1) Changes in the positions of bands from FT-IR and FT-Raman spectra, (2) hipsochromic shifts of $\pi \rightarrow \pi^*$ bands from UV spectra, (3) a decrease in the chemical shifts in ^1H NMR spectra of salts in comparison to the spectra of ligand, show that alkali metal ions affect the whole structure of *p*-anisic acid molecule (aromatic ring, carboxylic and methoxy groups). The perturbation of the electronic structure of

Table 4
Bond lengths and angles calculated at B3LYP/6-311++G** level for *p*-anisates
(atom numbering for anisates in Fig. 1)

	<i>p</i> -anisates		
	Li	Na	K
Bonds (Å)			
C1–C2	1.395	1.394	1.394
C2–C3	1.393	1.394	1.395
C3–C4	1.399	1.398	1.398
C4–C5	1.402	1.401	1.401
C5–C6	1.384	1.385	1.386
C1–C6	1.403	1.402	1.401
C1–C7	1.490	1.501	1.507
C7–O2	1.276	1.271	1.269
C7–O1	1.275	1.271	1.269
O–M	1.852	2.204	2.514
(M – metal ion)	1.852	2.205	2.512
C4–O3	1.363	1.366	1.368
O3–C8	1.422	1.420	1.419
C8–H7	1.095	1.096	1.096
C8–H8	1.089	1.089	1.089
C8–H9	1.095	1.096	1.096
C2–H2	1.083	1.083	1.083
C3–H3	1.082	1.082	1.082
C5–H5	1.083	1.084	1.084
C6–H6	1.083	1.083	1.083
Angles (°)			
C1–C2–C3	121.1	121.2	121.3
C2–C3–C4	119.5	119.5	119.4
C3–C4–C5	119.9	119.8	119.8
C4–C5–C6	120.0	120.0	120.1
C5–C6–C1	120.7	120.8	120.9
C2–C1–C6	118.9	118.7	118.6
C1–C7–O2	119.8	118.5	118.1
C1–C7–O1	119.7	118.4	118.0
O1–C7–O2	120.6	123.0	123.9
C7–O–M	83.0	88.0	91.6
	83.0	88.0	91.7
C2–C1–C7	120.5	120.6	120.7
C6–C1–C7	120.6	120.7	120.7
C3–C4–O3	124.4	124.4	124.4
C4–O3–C8	118.8	118.6	118.5
O3–C8–H7	111.4	111.5	111.5
O3–C8–H8	105.8	105.9	105.9
O3–C8–H9	111.4	111.5	111.5
H7–C8–H8	109.3	109.3	109.3
H7–C8–H9	109.5	109.4	109.3
H8–C8–H9	109.3	109.3	109.3

Table 5
The NPA, ChelpG, MK atomic charges calculated at B3LYP/6-311++G** level for *p*-anisic acid and *p*-anisates

	<i>p</i> -anisic acid			<i>p</i> -anisates						
	NPA	ChelpG	MK	Li			Na			K
				NPA	ChelpG	MK	NPA	ChelpG	MK	
C1	−0.202	−0.079	−0.102	−0.186	0.012	0.086	−0.178	−0.037	0.018	−0.174
C2	−0.135	−0.063	−0.115	−0.300	−0.269	−0.282	−0.301	−0.268	−0.300	−0.302
C3	−0.296	−0.285	−0.304	−0.137	−0.121	−0.223	−0.145	−0.100	−0.190	−0.148
C4	0.351	0.498	0.546	0.339	0.474	0.524	0.333	0.476	0.537	0.328
C5	−0.242	−0.295	−0.378	−0.143	−0.083	−0.143	−0.150	−0.052	−0.104	−0.152
C6	−0.134	−0.036	−0.044	−0.247	−0.290	−0.367	−0.249	−0.315	−0.390	−0.251
C7	0.787	0.693	0.710	0.759	0.699	0.654	0.758	0.741	0.722	0.762
C8	−0.207	0.194	−0.040	−0.205	0.212	−0.032	−0.204	0.189	−0.027	−0.204
O1	−0.695	−0.625	−0.624	−0.842	−0.797	−0.791	−0.826	−0.800	−0.808	−0.829
O2	−0.608	−0.571	−0.573	−0.844	−0.796	−0.784	−0.829	−0.797	−0.799	−0.831
O3	−0.533	−0.432	−0.382	−0.540	−0.435	−0.385	−0.543	−0.436	−0.395	−0.545
H1 (M)	0.484	0.431	0.434	0.935	0.832	0.839	0.934	0.856	0.873	0.954
H2	0.225	0.119	0.157	0.210	0.125	0.139	0.207	0.119	0.139	0.206
H3	0.214	0.136	0.146	0.226	0.139	0.189	0.226	0.124	0.173	0.225
H5	0.222	0.140	0.174	0.228	0.136	0.179	0.227	0.121	0.163	0.226
H6	0.230	0.117	0.146	0.217	0.129	0.167	0.214	0.134	0.167	0.213
H7	0.195	0.052	0.111	0.191	0.040	0.103	0.189	0.044	0.100	0.188
H8	0.172	0.004	0.069	0.170	−0.004	0.064	0.168	0.001	0.061	0.168
H9	0.172	0.004	0.069	0.170	−0.004	0.064	0.168	0.001	0.061	0.168

Fig. 2. Resonance structures of *p*-anisic acid.

molecules increase along the series: $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$ *p*-anisates. The observed effect is slight but regular, and mainly depends on ionic radii of alkali cations. The calculated atomic charges show that substitution of alkali metal ions in the carboxylic group of *p*-anisic acid causes the most significant changes in the electronic charge distribution around atoms number C2, C3, C5, C6, O1 and O2.

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