

The spectroscopic (FT-IR, FT-Raman and ^1H , ^{13}C NMR) and theoretical studies of cinnamic acid and alkali metal cinnamates

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Abstract

The effect of alkali metals ($\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$) on the electronic structure of cinnamic acid (phenylacrylic acid) was studied. In this research many miscellaneous analytical methods, which complement one another, were used: infrared (FT-IR), Raman (FT-Raman), nuclear magnetic resonance (^1H , ^{13}C NMR) and quantum mechanical calculations. The spectroscopic studies lead to conclusions concerning the distribution of the electronic charge in molecule, the delocalization energy of π -electrons and the reactivity of metal complexes.

The change of metal along with the series: $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$ caused: (1) the change of electronic charge distribution in cinnamate anion what is seen via the occurrence of the systematic shifts of several bands in the experimental and theoretical IR and Raman spectra of cinnamates, (2) systematic chemical shifts for protons ^1H and ^{13}C nuclei.

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1. Introduction

Cinnamic acid (3-phenyl-2-propenoic acid), a derivative of phenylalanine, composes a relatively large family of organic acid isomers [1]. In nature, cinnamic acid derivatives are important metabolic building blocks in the production of lignins for higher plants. Cinnamic acid possesses antibacterial, antifungal and parasite fighting abilities [2]. A derivative of cinnamic acid is an important pharmaceutical for high blood pressure and stroke prevention and possess antitumour activity [3]. In wine, cinnamic acid and its derivatives join benzoic acid derivatives and flavonoids in creating pigments and tannin agents that give each vintage its characteristic bouquet and color. Cinnamic acid is extensively studied not only due to its important biological activity, but also because of its very specific structure. In the molecule of cinnamic acid the carboxylic group is separated from the aromatic ring by a double bond. It causes conjugation between the —C=C— bond and the π -electron system.

We find it very interesting to compare the electronic structures of cinnamic and benzoic acid, as well as the structures of alkali metal cinnamates and benzoates. This will allow us to evaluate to what extent the presence of a double bond in cinnamate affects the influence of metals on the electronic system of the ligand. We studied this effect by means of many complementary methods: infrared (FT-IR in KBr pellets and Ar matrix), Raman (FT-Raman), nuclear magnetic resonance (^1H , ^{13}C NMR) and quantum mechanical calculations in B3LYP/6-311++G**. In our previous paper the general conclusion concerning the effect of almost 50 metals on the electronic systems of different substituted benzoic acid molecules was presented [4–6].

There are few papers concerning the study of the cinnamic acid molecule. The polarized IR spectra of cinnamic acid was studied in order to study the existence of the hydrogen bonds in dimer [7]. The two polymorphic forms of *cis*-cinnamic acid were compared with that of *trans*-cinnamic acid by the use of IR, Raman and NMR spectroscopy [8]. Only partial assignment of the bands occurring in the IR and Raman spectra was done. Tian-Jye Hsieh et al. [9] studied the molecular structure of

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cinnamic acid using the B3LYP/6-31G*, but our calculations are performed with a larger basis set. It is worth mentioning that to our knowledge no spectroscopic data or calculations have been reported so far for alkali metal cinnamates.

2. Experimental

2.1. Sample preparation

The metal compounds were prepared by digesting appropriate weighed amount of cinnamic acid in aqueous solution of alkali metal hydroxides in a stoichiometric ratio 1:1. Then, water was evaporated at 120 °C in a dryer. The results of elementary analysis are as follows: for lithium cinnamate: C(%) = 70.39:70.15 (calcd. C(%) = 70.15), H(%) = 4.58:4.45 (calcd. H(%) = 4.57); for sodium cinnamate: C(%) = 62.80:63.00 (calcd. C(%) = 63.53), H(%) = 4.12:4.14 (calcd. H(%) = 4.14); for potassium cinnamate: C(%) = 58.23:57.98 (calcd. C(%) = 58.04), H(%) = 3.77:3.84 (calcd. H(%) = 3.79).

2.2. Measurement

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 KBr matrix pellets which were obtained with hydraulic press under 739 MPa pressure. Raman spectra of solid samples in capillary tubes were recorded in the range of 100–4000 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 DMSO solution were recorded with a Bruker unit at room temperature. TMS was used as an internal reference. In order to calculate optimized geometrical structures of studied compounds, a Density Functional Theory in B3LYP/6-311++G(d,p) level was used. Theoretical calculations were performed using the GAUSSIAN 03W package of programs [10] running on a SGI 2800 computer in ACK CYFRONET AGH. The calculated in this paper geometry-based aromaticity indexes were described elsewhere [11–13].

3. Results and discussion

3.1. IR and Raman spectra of cinnamic acid and cinnamates

The wavenumbers, intensities and assignments of the bands occurring in the IR and Raman spectra of cinnamic acid and alkali metal cinnamates are presented in Tables 1 and 2, respectively. The theoretical vibrational spectra were interpreted by means of potential energy distributions (PEDs) using VEDA 3 program [14]. The spectral assignments were done on the basis of the literature data [8,15] and calculated IR wavenumbers of studied compounds. Normal vibrations of the aromatic ring were given by Versanyi [15].

The FT-IR spectra of cinnamic acid recorded in KBr pellet and in argon matrix, as well as FT-Raman spectrum are presented in Fig. 1. In the region of the OH stretching vibrations there is intense band assigned to monomer (i.e., 3495 cm⁻¹ – IR, 3557 cm⁻¹ – IR Ar matrix) and the broad bands in the range 2982–2542 (IR), 3385–2535 (IR Ar matrix) assigned to the OH stretching vibrations of acid dimers. In this range there are as well the bands of the —CH stretching vibrations, what is seen in Fig. 2. In the infrared spectra of acid isolated in Ar matrix there are splitting bands assigned to the stretching vibrations of the C=O group (i.e., 1748, 1740 1721, 1696 cm⁻¹). This indicates the existence of different types of molecule packing – monomers and associates of cinnamic acid with the intermolecular hydrogen bonds C=O...H—O. Reva et al. [16,17] studied the FT-IR spectra of benzoic acid in Ar matrices with different matrix-to-sample ratios. They suggested that beside the monomers the cyclic dimers with two H-bonds and linear dimers with single H-bond existed.

Replacement of the carboxylic group hydrogen with a metal ion causes a breakdown of the intermolecular hydrogen bonding and therefore the characteristic changes in the IR and Raman spectra of the metal cinnamates in comparison with the spectra of acid appeared. Namely, a disappearance of bands which originate from stretching $\nu(\text{OH})$ and deformation $\beta(\text{OH})$ vibrations; a disappearance of bands of the symmetric and asymmetric stretching $\nu(\text{C—O})$ as well as out-of-plane bending $\gamma(\text{C—O})$ vibrations of the carbonyl group; an appearance of bands of the asymmetric and symmetric vibrations of the carboxylate anion $\nu_{\text{as}}(\text{COO}^-)$, $\nu_{\text{s}}(\text{COO}^-)$ as well as $\beta_{\text{as}}(\text{COO}^-)$, $\beta_{\text{s}}(\text{COO}^-)$, and a disappearance or changes in the positions and intensities of some aromatic bands were observed. The overlapping spectra of cinnamic acid and lithium cinnamate are shown in Fig. 3.

In the experimental FT-IR spectra of cinnamates the wavenumbers of asymmetric and symmetric stretching vibrations of carboxylic anion change their position along the series of alkali metals (Li → Na → K → Rb → Cs) (see Table 2). Namely, the band of $\nu_{\text{s}}(\text{COO}^-)$ is shifted towards lower wavenumbers in the FT-IR (experimental and theoretical) and FT-Raman spectra. Whereas the band of $\nu_{\text{as}}(\text{COO}^-)$ is shifted towards higher wavenumbers only in theoretical IR spectra, in experimental IR and Raman spectra the bands scatter along the series of alkali metal cinnamates. The difference between wavenumbers of asymmetric and symmetric stretches of the carboxylic anion vibrations $\Delta\nu(\text{COO}^-)$ also alters in a regular fashion along the metal series Li → Na → K → Rb → Cs and, respectively, amounts to: 144, 136, 147, 161 and 167 cm⁻¹ (IR exp. – except Na cinnamate); 120, 119, 137, 156 and 165 cm⁻¹ (Raman); 101, 145 and 163 (for Li → Na → K cinnamates from calcd. IR spectra). The explicit increase in the value of $\Delta\nu(\text{COO}^-)$ (except Na cinnamate in the exp. IR spectrum) means the increase in the ionic character of metal-oxygen bond. Moreover the band wavenumbers of $\beta_{\text{s}}(\text{COO}^-)$ and $\beta_{\text{as}}(\text{COO}^-)$ also decrease along the metal series both in the

Table 1

The wavenumbers and assignments of bands occurring in the experimental FT-IR, FT-Raman and theoretical FT-IR spectra of cinnamic acid

IR		IR Ar matrix		Raman		Calcd.	Int.	PED %	No. ^a
3495	w ^b	3557	m			3778	109	100 ν^c (OH) monomer	
3103	vw	3113	w			3199	8	92 ν (CH)	
3087	w	3092	w			3194	8	97 ν (CH)	20a
3066	m	3073	m	3068	w	3186	18	80 ν (CH)	
		3038	w	3038	vw	3178	11	94 ν (CH)	
3027	m	3013	w	3031	vw	3169	0,1	91 ν (CH)	
		2992	w			3165	3	83 ν (CH)	20b
		2955	w			3162	0	90 ν (CH)	
2982–2542	m	3385–2535	w					ν (OH) dimer	
		1748	s					ν (C=O) monomer	
		1740	s						
		1721	vs						
1685	vs	1696	s	–		1774	676	79 ν (C=O) dimer	
1629	vs	1638	vs	1638	vs	1677	66	56 ν (C=C) _{cinn}	
1600	sh	1597	m	1600	s	1639	10	56 ν (CC) _{ar} + 11 β (CH)	8a
1577	m	1582	w			1614	6	36 ν (CC) _{ar} + 14 β (CH) + 10 α (CCC)	8b
1495	m	1499	w	1496	vw	1526	4	50 β (CH) _{ar}	19a
1449	s	1454	m	1444	vw	1480	19	10 ν (CC) _{ar} + 43 β (CH) _{ar}	19b
1421	s	1427	m	–		1350	41	28 ν (CC) _{ar} + 12 β (CH) _{cinn} + 10 β (OH)	
1389	w	1387	w	–		1374	84	14 β (OH) + 12 β (CH) _{ar} + 26 β (CH) _{cinn}	3
1334	m	1335	m	1329	vw	1357	31	11 ν (CC) _{ar} + 10 β (OH) + 22 β (CH) _{ar} + 13 β (CH) _{cinn}	14
1313	s	1319	m	1308	vw	1328	0,0	13 ν (CC) _{ar} + 15 β (CH) _{ar} + 19 β (CH) _{cinn}	
1286	s	1290	w	1293	m	1176	402	21 ν C–(OH) + 10 ν (CC) _{ar} + 42 β (OH)	
1222	s	1225	m	1211	m	1289	28	46 β (CH) _{cinn} + 12 ν (CC) _{ar}	
1206	m	1206	m	–		1234	8	30 ν (CC) _{ar} + 14 β (CH) _{cinn}	13
				1132	s			overtone	
1176	m	1173	m	1179	m	1205	4	10 ν (CC) _{ar} + 52 β (CH) _{ar}	9a
1098	w	1098	vw	–		1185	3	67 β (CH) _{ar}	
1073	w	1074	w	–		1104	17	44 ν (CC) _{ar} + 13 β (CH) _{ar}	18b
1027	w	1030	vw	1027	w	1049	3	37 ν (CC) _{ar} + 11 β (CH) _{ar}	18a
						1024	34	79 γ (CH) _{cinn} + 22 γ (HCCO)	
999	w	995	w	1002	m	1016	1	34 ν (CC) _{ar} + 54 α (CCC)	12
						1000	2	57 γ (CH) _{ar} + 18 ϕ (CCC)	5
						981	0,0	80 γ (CH) _{ar}	17a
						936	0,2	54 γ (CH) _{ar}	17b
980	s	985	w	977	vw	910	27	49 ν (C–O) + 26 γ (C–C) _{cinn}	
944	m	951	w	952	vw				
925	m	928	vw	–		898	14	47 γ (CH) _{cinn} + 13 γ (OCCC) + 15 γ (OCOC)	
914	m	910	vw	–				γ (CCH) _{cinn}	
875	w	874	w	876	vw	850	1	71 γ (CH) _{ar}	10a
847	w	845	vw	849	vw	791	55	42 γ (CH) _{ar} + 27 γ (OCOC) + 14 γ (CCC)	
769	s	774	m	771	vw	724	7	39 γ (CH) _{ar} + 11 γ (HCCO) + 36 γ (OCOC)	11
711	s	716	w	714	vw	696	40	28 γ (CH) _{ar} + 43 ϕ (CCC)	4
698	m	708	w	688	vw	654	21	29 β (C=O) + 30 α (CCC)	
683	m	687	m	681	vw	633	0,2	82 α (CCC)	6b
620	w	623	vw	621	vw	585	46	28 β (C=O) + 22 α (CCC)	
590	m	594	w	592	vw	544	110	89 γ (C=O)	
542	m	544	w	–	–	518	10	46 γ (OCC) + 17 α (C=C–C) _{cinn}	
483	m	484	vw	–		493	0,3	51 ϕ (CCC)	16b

^a Ref. [15].^b s – strong; m – medium; w – weak; v – very; sh – shoulder.^c The symbol “ ν ” denotes stretching vibrations, “ β ” denotes in-plane bending modes, “ γ ” designates out-of-plane bending modes; “ ϕ (CCC)” denotes the aromatic ring out-of-plane bending modes, and “ α (CCC)” designates the aromatic ring in-plane bending modes.

experimental and calculated IR spectra and in the Raman spectra. $\Delta\beta(\text{COO}^-)$ does not undergo distinct changes.

Not only the bands which derive from the carboxylic anion vibrations are sensitive to change of metal. Several bands of aromatic system as well as bands which derive from the —C=C— double bond are shifted towards lower wavenumbers in the spectra of salts compared with the spectrum of acid. Among these bands are no. 19a, 19b,

18b and 18a which are shifted in the series $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$ cinnamates by max 5 cm^{-1} . Whereas bands connected with the —C=C— vibrations undergo higher displacement, i.e., bands at about 3036 cm^{-1} (IR); 1389 cm^{-1} (IR) and 1381 cm^{-1} (Raman); 1247 cm^{-1} (IR) and 1245 cm^{-1} (Raman); 968 cm^{-1} (IR) and 968 cm^{-1} (Raman); 536 cm^{-1} (IR) are shifted in the series $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$ cinnamates by 25 cm^{-1}

Table 2

Wavenumbers (cm^{-1}), intensities and assignments of bands occurring in the IR and Raman spectra of cinnamic acid and lithium, sodium, potassium, rubidium and caesium cinnamates

Li cinnamate			Na cinnamate			K cinnamate			Rb cinnamate		Cs cinnamate		Assignment	No. ^a
IR exp.	IR Calcd.	Raman	IR exp.	IR Calcd.	Raman	IR exp.	IR Calcd.	Raman	IR exp.	Raman	IR exp.	Raman		
3417 w ^b			3425 Vw			3448 vw					3423 vw			
3105 vw	3192		3105 vw	3191		3100 vw	3190		3100 vw		3100 vw		$\nu(\text{CH})_{\text{cinn}} + \nu(\text{CH})_{\text{ar}}$	
3084 w	3187	3069 w	3084 vw	3185	3074 w	3078 vw	3183		3080 w		3080 vw		$\nu(\text{CH})_{\text{ar}} + \nu(\text{CH})_{\text{cinn}}$	20b
3057 w	3181	3059 w	3058 vw	3177	3061 vw	3058 vw	3173	3061 w	3058 w	3064 w	3057 vw	3059 w	$\nu(\text{CH})_{\text{ar}} + \nu(\text{CH})_{\text{cinn}}$	
	3176	3050 vw	3043 vw	3174	3045 vw	3036 vw	3171	3040 vw	3031 w	3041 vw	3028 w	3045 sh	$\nu(\text{CH})_{\text{ar}} + \nu(\text{CH})_{\text{cinn}}$	
3031 w	3166	3034 vw	3027 vw	3164		3022 w	3163	3023 vw	3023 w	3033 vw		3030 vw	$\nu(\text{CH})_{\text{ar}} + \nu(\text{CH})_{\text{cinn}}$	
	3160	3013 vw	3005 vw	3158	3008 vw	3005 vw	3156	3007 vw	2996 w	2997 vw	2998 vw	3000 vw	$\nu(\text{CH})_{\text{ar}} + \nu(\text{CH})_{\text{cinn}}$	20b
2946 vw	3150		2936 w	3149		2936 vw	3146		2938 vw		2927 vw		$\nu(\text{CH})_{\text{cinn}} + \nu(\text{CH})_{\text{ar}}$	
1642 s	1687	1641 vs	1640 m	1688	1642 vs	1640 m	1689	1641 vs	1638 s	1638 vs	1639 s	1638 vs	$\nu(\text{C}=\text{C})_{\text{cinn}}$	
1652 ^c w														
	1639	1601 m	1599 vw	1639	1601 m	1597 sh	1639	1599 m		1599 m		1599 m	$\nu(\text{CC})_{\text{ar}} + \beta(\text{CH})$	8a
1578 vs	1614	1579 vw	1577 m	1613	1579 sh	1575 sh	1612	1575 vw		1579 vw		1578 vw	$\nu(\text{CC})_{\text{ar}} + \beta(\text{CH}) + \alpha(\text{CCC})$	8b
1567 vs	1532	1544 vw	1548 vs	1551	1539 vw	1558 vs	1562	1553 vw	1561 vs	1559 vw	1559 vs	1557 w	$\nu_{\text{as}}(\text{COO}^-)$	
1597 ^c s														
1496 w	1524		1495 m	1525	1495 vw	1493 m	1524	1494 vw	1492 m	1494 vw	1493 m	1496 vw	$\beta(\text{CH}) + \nu(\text{CC})_{\text{ar}}$	19a
1501 ^c w														
1451 vs	1479	1454 vw	1451 m	1478	1455 vw	1449 m	1477	1452 vw	1449 s	1451 vw	1447 m	1449 vw	$\beta(\text{CH}) + \nu(\text{CC})_{\text{ar}}$	19b
1453 ^c w														
1423 vs	1431	1424 w	1412 s	1406	1420 vw	1411 s	1399	1416 w	1400 s	1403 w	1392 s	1392 w	$\nu_{\text{s}}(\text{COO}^-)$	
1413 ^c m														
1407 sh	1361		1392 m	1369	1391 vw	1384 m	1357	1385 vw	1380 s	1381 vw	1382 s	1370 vw	$\beta(\text{CH})_{\text{ar}} + \beta(\text{CH})_{\text{cinn}}$	3
1366 ^c w														
1358 ^c w	1346	1326 vw	—	1344	1323 vw	—	1343	1318 vw		1318 vw		1321 vw	$\nu(\text{CC})_{\text{ar}} + \beta(\text{CH})$	14
1307 w	1320	1305 vw	1303 w	1318	1303 vw	1299 vw	1316	1299 vw		1298 vw		1300 vw	$\beta(\text{CH})_{\text{cinn}} + \nu(\text{CC})_{\text{ar}} + \beta(\text{CH})$	
1288 w	1266		1292 vw	1265		1286 w	1263		1285 w	1287 vw	1282 w	1282 vw	$\beta(\text{CH})_{\text{cinn}} + \nu(\text{CC})$	
1253 m		1250 m	1244 w		1246 m	1242 w		1245 m	1243 w	1246 m	1238 w	1240 m	$\beta(\text{CH})_{\text{cinn}}$	
1201 vw	1223	1202 vw	1199 vw	1221	1200 vw	1195 vw	1220	1197 vw	1194 vw	1197 vw	1193 w	1196 vw	$\beta(\text{CH})_{\text{cinn}} + \nu(\text{CC})_{\text{ar}}$	13
1223 ^c w														
1174 w	1202	1181 vw	1179 vw	1200	1180 vw		1199	1179 vw	1179 vw	1179 vw		1177 m	$\beta(\text{CH})_{\text{ar}} + \nu(\text{CC})_{\text{ar}}$	9a
1101 w	1183		1102 vw	1181		1101 vw	1181		1098 vw		1097 w		$\beta(\text{CH})_{\text{ar}}$	
1074 w	1102		1074 w	1100	1075 vw	1072 w	1099		1071 w		1071 w		$\beta(\text{CH})_{\text{ar}} + \nu(\text{CC})_{\text{ar}}$	18b
1030 w	1049	1031 w	1029 vw	1048	1031 w	1026 vw	1048	1028 w	1025 w	1028 w	1025 w	1028 w	$\beta(\text{CH})_{\text{ar}} + \nu(\text{CC})_{\text{ar}}$	18a
1034 ^c vw														
	1026			1025			1024					986 m	$\gamma(\text{CH})_{\text{cinn}} + \gamma(\text{HCCO})$	
1003 vw	1015	1003 m	1002 vw	1015	1002 m		1015	1000 m	1000 vw	1000 m		1001 m	$\alpha(\text{CCC}) + \nu(\text{CC})$	12
985 sh	998			996			996		977 m	978 vw	970 w		$\gamma(\text{CH})_{\text{ar}} + \phi(\text{CCC})$	5
978 m	988	979 w	970 m	981	969 vw	967 m	974	967 vw	963 m	965 vw	955 w	957 vw	$\gamma(\text{CCH})_{\text{cinn}}$	
918 vw	861		916 vw	858	917 vw	912 vw	856		914 vw	916 vw	920 vw		$\gamma(\text{CCH})_{\text{cinn}}$	
886 m	850	891 vw	878 w	849	878 vw	876 w	849	877 vw	877 m	879 vw	883 w	887 vw	$\gamma(\text{CH})_{\text{ar}}$	10a
854 vw	766	851 vw	852 vw	750	850 vw	848 vw	738	849 vw	846 w	848 vw	845 vw	846 vw	$\beta_{\text{s}}(\text{COO}^-) + \beta(\text{CH})_{\text{cinn}}$	
765 ^c vw														
779 m	732	783 vw	773 m	731	775 vw	770 m	729	774 vw	772 s	775 vw	774 m	777 vw	$\gamma(\text{CH})_{\text{ar}} + \gamma(\text{HCCO}) + \gamma(\text{OCOC})$	11
701 ^c w	699	725 vw	728 m	700	727 vw	725 w	700	724 vw	726 s	725 vw		720 vw	$\phi(\text{CCC}) + \gamma(\text{CH})_{\text{ar}}$	4
718 m			713 w			710 m			710 m		718 m		$\gamma_{\text{s}}(\text{COO}^-)$	
	636												$\alpha(\text{CCC}) + \text{Me—O}$	
688 m	632	688 vw	690 m	635		688 m	635		686 s		687 m		$\alpha(\text{CCC})$	6b
615 vw	574	621 vw	618 vw	603	620 vw	618 vw	599	620 vw	619 vw	619 vw	617 vw	620 vw	$\alpha(\text{CCC})$	
596 w			586 w		587 vw	584 vw		585 vw	583 m	585 vw	583 m		$\beta_{\text{as}}(\text{COO}^-)$	
547 w	540		530 w	532		529 w	531		528 m	529 vw	524 w		$\gamma(\text{OCC}) + \alpha(\text{C}=\text{C}—\text{C})_{\text{cinn}}$	
532 ^c vw														
488 m	500	490 vw	486 w	503	484 vw	484 w	503	482 vw	483 m		492 w		$\phi(\text{CCC})$	16b

The theoretical wavenumbers were calculated in B3LYP/6-311++G(d,p) level.

^a Ref. [15].

^b s, strong; m, medium; w, weak; v, very; sh, shoulder.

^c FT-IR spectra in Ar matrix.

(IR) and by 22 cm^{-1} (Raman) towards lower wavenumbers. This effect is caused by the increase in the polarity of bonds what brings about diminution of force constants of the bonds and displacement the bands towards lower wavenumbers simultaneously.

3.2. Calculated geometrical parameters and atomic charges for cinnamic acid and cinnamates

The bond lengths and angles calculated for cinnamic acid and Li, Na and K cinnamates can be obtained from

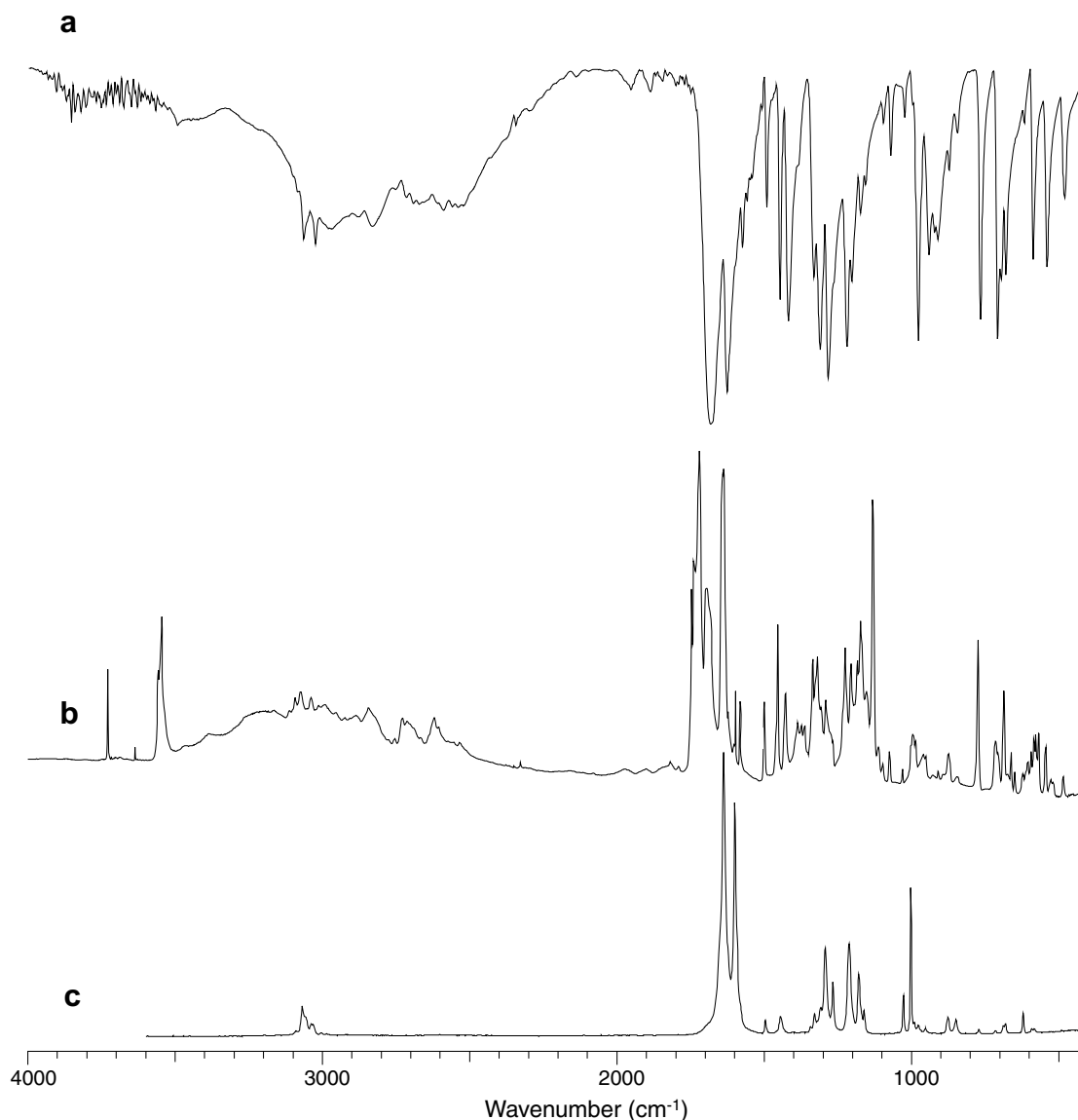


Fig. 1. The FT-IR spectrum registered in KBr pellet (a), the FT-IR spectrum in argon matrix (b), FT-Raman spectrum (c) of cinnamic acid.

the authors on request. The NPA, ChelpG and MK atomic charges are gathered in Table 3. The crystal structure of cinnamic acid was reported by Wierda et al. [18], Bryan et al. [19], Enkelmann et al. [20] and Tiane-Jye Hsieh et al. [9]. The changes in bond distances and angles between bonds as well as changes in the values of atomic charges suggest that alkali metal cations influence the molecular structure of cinnamic acid. First the metal influences the bond lengths and angles in the carboxylic group. In the isolated molecule of cinnamic acid the difference between two distances C—O in the carboxylic anion exists (C1—O1 1.21 Å; C1—O2 1.36 Å), but after metal coordination the bond equalization takes place (Li cinnamate: C—O 1.28 Å; Na cinnamate: C—O 1.27 Å; K cinnamate: C—O 1.27 Å). Then, the distance C9—C1 increases, C9—C8 decreases and C8—C7 increases in the series acid → Li → Na → K. The molecules are twisted around the —C=C— bonds, and the torsion angle C2—C1—C9—C8 increases in the

series: K → Na → Li → acid. The bond lengths and angles in the benzene ring remain almost unchanged. The changes in the values of distances and angles in molecule result from the changes in the electron density around particular atoms. The calculated atomic charges indicate a decrease in the electron density around C1 and C8 atoms and an increase in the electron density around C2, C4, C9, O1 and O2 atoms in the salts molecules comparing to the acid molecule. The total electron density in the aromatic ring and double bond increases, and in the carboxylic group decreases along with the series Li → Na → K cinnamates.

3.3. NMR spectra of cinnamic acid and cinnamates

The chemical shifts of protons and carbons from the experimental NMR spectra of cinnamic acid and its alkali salts are gathered in Table 4. In the ^1H NMR spectra of cinnamates the signals from all protons are shifted down-

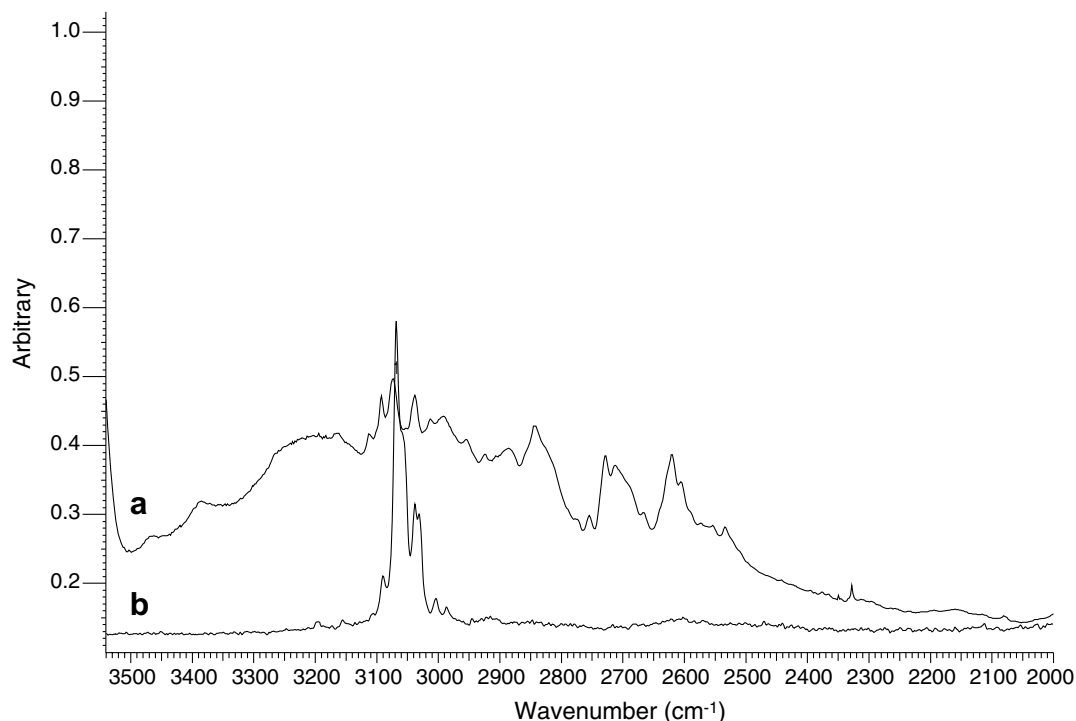


Fig. 2. The IR in Ar matrix (a) and Raman (b) spectra of cinnamic acid in the range 3550–2000 cm^{-1} .

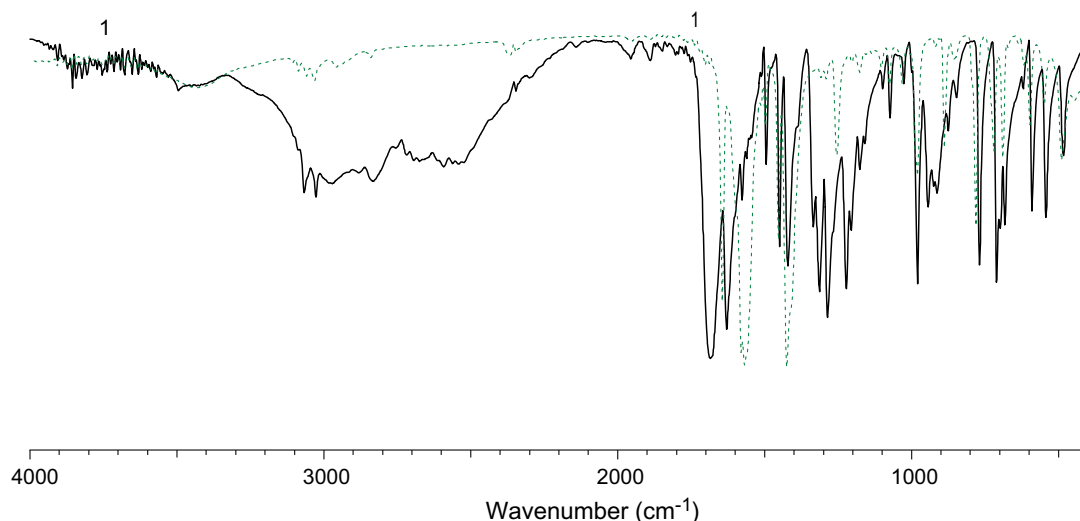


Fig. 3. The overlapped FT-IR spectra of cinnamic acid (solid line) and lithium cinnamates (broken line).

field in comparison to appropriate signals in the spectrum of acid. Moreover the general tendency in the decrease of chemical shift of particular protons in the series: $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$ (especially in case of protons no. E, G – the ring and C, B – the double bond) is noticeable. In the ^{13}C NMR spectra of cinnamates there is no regularity in the chemical shifts of carbons along the series of alkali metals cinnamates. The signals from carbons no. 2, 6, 3, 5 and 9 are shifted downfield in comparison to the appropriate signals in the spectrum of ligand, whereas the signals from carbons no. 1, 7 and 8 are shifted upfield. This indicate the decrease in the electron density around carbons no. 1, 7 and 8, and the increase in the electron density

around the other carbon atoms. The same relationship describe the calculated atomic charges mentioned before. Very interesting is the relationship between experimental chemical shifts from the ^{13}C NMR spectra and calculated atomic charges for cinnamic acid and cinnamates. The highest correlation coefficients were obtained for the linear correlation between the chemical shifts and the NPA (for cinnamic acid: 0.892; for Li salt: 0.978; for Na salt: 0.971; for K salt: 0.957) and APT (for cinamic acid: 0.960; for Na salt: 0.820) atomic charges. Whereas the lower ones were obtained for the Mulliken atomic charges (for cinnamic acid: 0.026; for Li salt: 0.001; for Na salt: 0.093; for K salt: 0.114).

Table 3

The atomic charges for benzoic and cinnamic acid as well as for lithium, sodium and potassium cinnamates calculated in the B3LYP/6-311++ G** level

Atom	Benzoic acid			Cinnamic acid				Li cinnamate			Na cinnamate			K cinnamate	
	NPA	CHelpG	MK	NPA	CHelpG	MK	APT	NPA	CHelpG	MK	NPA	CHelpG	MK	NPA	APT
C1 ^a	−0.170	0.001	0.122	−0.096	0.244	0.392	−0.108	−0.087	0.282	0.371	−0.081	0.283	0.400	−0.078	0.054
C2	−0.149	−0.095	−0.186	−0.165	−0.184	−0.268	−0.033	−0.171	−0.200	−0.253	−0.175	−0.211	−0.263	−0.177	−0.081
C3	−0.205	−0.081	−0.089	−0.196	−0.049	−0.066	−0.067	−0.199	−0.035	−0.074	−0.200	−0.036	−0.077	−0.200	−0.028
C4	−0.176	−0.059	−0.106	−0.184	−0.100	−0.152	−0.032	−0.195	−0.126	−0.162	−0.201	−0.126	−0.167	−0.204	−0.081
C5	−0.207	−0.107	−0.114	−0.200	−0.042	−0.083	−0.044	−0.202	−0.039	−0.090	−0.203	−0.051	−0.101	−0.203	−0.010
C6	−0.160	−0.071	−0.166	−0.165	−0.209	−0.255	−0.013	−0.171	−0.208	−0.233	−0.175	−0.209	−0.238	−0.178	−0.076
C7	0.794	0.660	0.587	0.758	0.809	0.825	1.528	0.730	0.819	0.800	0.730	0.858	0.841	0.733	1.444
C8	−	−	−	−0.294	−0.261	−0.269	−0.493	−0.277	−0.177	−0.201	−0.267	−0.211	−0.172	−0.260	−0.337
C9	−	−	−	−0.108	−0.150	−0.329	0.352	−0.127	−0.263	−0.384	−0.145	−0.241	−0.425	−0.156	0.119
O1	−0.601	−0.551	−0.528	−0.595	−0.604	−0.600	−0.766	−0.832	−0.821	−0.807	−0.817	−0.827	−0.813	−0.820	−1.134
O2	−0.694	−0.612	−0.612	−0.700	−0.643	−0.630	−0.933	−0.848	−0.828	−0.805	−0.832	−0.823	−0.823	−0.833	−1.066
H _A /Me	0.486	0.432	0.446	0.485	0.426	0.421	0.303	0.935	0.829	0.828	0.935	0.852	0.867	0.954	0.957
H _B	−	−	−	0.213	0.126	0.146	0.053	0.203	0.123	0.150	0.198	0.120	0.132	0.195	0.027
H _C	−	−	−	0.215	0.142	0.203	0.057	0.217	0.185	0.235	0.216	0.161	0.224	0.215	0.055
H _D	0.230	0.108	0.144	0.205	0.119	0.159	0.046	0.204	0.109	0.146	0.204	0.113	0.144	0.204	0.044
H _E	0.209	0.089	0.116	0.208	0.085	0.117	0.034	0.205	0.078	0.114	0.203	0.077	0.113	0.202	0.023
H _F	0.207	0.088	0.120	0.207	0.092	0.129	0.039	0.205	0.090	0.125	0.203	0.088	0.125	0.202	0.028
H _G	0.209	0.095	0.121	0.209	0.086	0.124	0.033	0.205	0.083	0.121	0.204	0.084	0.121	0.203	0.022
H _H	0.226	0.103	0.145	0.205	0.112	0.137	0.043	0.204	0.098	0.118	0.203	0.100	0.122	0.202	0.037
Sum:Ring	−1.067	−0.412	−0.539	−1.006	−0.340	−0.432	−0.297	−1.025	−0.326	−0.441	−1.035	−0.350	−0.446	−1.040	−0.222
—C=C—	−	−	−	−0.402	−0.411	−0.598	−0.141	−0.404	−0.440	−0.585	−0.412	−0.452	−0.597	−0.416	−0.218
COO—	−0.501	−0.503	−0.553	−0.537	−0.438	−0.405	−0.171	−0.950	−0.830	−0.812	−0.919	−0.792	−0.795	−0.920	−0.756

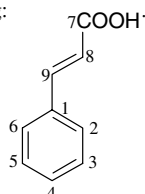
^a Atom numbering:

Table 4

The chemical shifts of protons in the ¹H NMR and carbons in the ¹³C NMR spectra of DMSO solution of cinnamic acid and alkali metal cinnamates

	Cinnamic acid	Li cinnamate	Na cinnamate	K cinnamate	Rb cinnamate	Cs cinnamate
<i>Proton number</i>						
A ^a	12.35					
B	6.53	6.49	6.37	6.36	6.35	6.33
C	7.68	7.49	7.47	7.45	7.45	7.45
D, H	7.56	7.36	7.36	7.34	7.34	7.34
E, G	7.40	7.20	7.09	7.07	7.04	7.00
F	7.47	7.28	7.27	7.27	7.26	7.25
<i>Carbon number</i>						
1	134.24	136.38	134.92	133.82	134.31	134.91
2,6	128.19	128.23	127.78	127.40	127.59	127.81
3,5	128.91	128.66	128.60	128.46	128.55	128.61
4	130.21	129.05	130.74	131.98	131.57	131.30
7	167.58	171.16	169.88	168.94	169.36	169.91
8	119.24	127.04	126.84	126.62	126.73	126.92
9	143.93	136.83	136.90	137.19	137.06	136.95

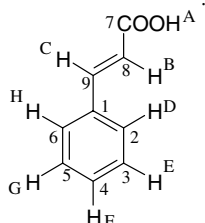
^a Atom numbering:

Table 5

The wavenumbers and intensities of selected bands from FT-IR and FT-Raman spectra of benzoic and cinnamic acid as well as their caesium salts

Compound		8a	8b	9a	19b	14	18b	18a	12	10a	11	4	6b
Benzoic acid [21]	IR	1604m	1586m	1498w	1455s	1324vs	1073m	1027m	1000w	856vw	–	668s	617vw
	R	1603s	1586vw	–	1460vw	1326w	–	1027m	1001vs	855vw	796s	–	616s
Cs benzoate [22]	IR	1596vs	–	–	–	1309vw	1069w	1024vw	–	–	–	–	–
	R	1596vs	–	–	–	–	–	1019w	–	–	–	–	–
Cinnamic acid	IR	1600sh	1577m	1495m	1449s	1334m	1073w	1027w	999w	875w	769s	711s	683m
	R	1600s	–	1496vw	1444vw	1329vw	–	1027w	1002m	876vw	771 vw	714vw	681vw
Cs cinnamate	IR	–	–	1493m	1447m	–	1071w	1025w	–	883w	774m	–	687m
	R	1599m	1578vw	1496vw	1449vw	1321vw	–	1028w	1001m	887w	777vw	–	–

3.4. Comparison of the influence of alkali metal ions on the electronic structure of cinnamic acid and benzoic acid

In cinnamic acid the carboxylic group is being separated from aromatic ring by a double bond (—C=C—). Therefore, the molecules of benzoic and cinnamic acids are good models for studying to what degree the double bond affects the interactions between alkali metals and π -electron system of cinnamic acid. In Table 5 the wavenumbers and intensities of selected bands from FT-IR and FT-Raman spectra of benzoic [21,22] and cinnamic acids as well as their caesium salts (as an example) were gathered. It is very clearly seen that caesium strongly influences the electronic structure of benzoic acid, because most bands in the spectrum of caesium benzoate disappeared and the other, i.e., 8a, 18a (IR, Raman) and 18b, 14 (Raman) were shifted towards lower wavenumbers. Whereas in the spectrum of caesium cinnamate only bands no. 8a, 8b, 14, 12 and 4 from the IR spectrum and 18b, 4 and 6b from the Raman spectrum disappeared, the other bands were shifted towards lower or higher wavenumbers. This means that the double bond between the carboxylic group and aromatic ring reduces the influence of metals on the π -electron system of cinnamic acid.

Comparing the total NPA atomic charges calculated for cinnamic acid, benzoic acid and their salts we noticed that alkali metal ions in a similar way influence the electronic charge distribution in these two ligands. Generally, in case of benzoic acid and benzoates the aromatic ring possesses higher electronic density compared to cinnamic acid and cinnamates. It suggest that the presence of a double bond between the carboxylic group and the ring causes a decrease in the electron density in the aromatic ring. And inversely, the electron density in the carboxylic anion in cinnamates is higher than in benzoates. We may also see that alkali metal ions slightly more affect the aromatic system of benzoic acid than cinnamic acid. The difference between the total NPA atomic charge of the ring calculated for cinnamic acid and cinnamates are: 0.019e (lithium), 0.029e (sodium) and 0.034e (potassium) whereas for benzoic acid and benzoates: 0.02e (lithium), 0.039e (sodium) and 0.049e (potassium).

Moreover, the geometric aromaticity indexes [11] obtained on the basis of structural data calculated in the

B3LYP/6-311++G** level informed us about the aromatic properties of studied acids. The indexes calculated for benzoic acid (HOMA = 0.982; A_j = 0.998; BAC = 0.950; I_6 = 96.89) are higher than those obtained for cinnamic acid (HOMA = 0.968; A_j = 0.995; BAC = 0.915; I_6 = 94.43). This suggest that the cinnamic acid molecule possesses lower aromatic properties than the benzoic acid molecule. The indexes calculated for cinnamates and benzoates differ slightly between each other.

4. Conclusions

In this paper, we studied the effect of alkali metal ions on the electronic system of cinnamic acid by means of IR (in KBr pellets and in Ar matrix), Raman, ^1H and ^{13}C NMR and ab initio calculations. The spectra of cinnamates definitely differ from the spectra of acid. The differences exist in the number, intensity and position of bands from experimental and theoretical IR, Raman spectra and chemical shifts from NMR spectra.

- (1) The substitution of metal ion in the carboxylic group clearly influences the vibrations of the carboxylic group and the —C=C— bond, and to a small extend the aromatic ring vibrations. The bands from the IR and Raman spectra assigned to the mentioned vibrations undergo displacement towards lower wavenumbers in the series: $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$ cinnamates. It is assumed that the evidence of an increase in the disturbance of the aromatic system is a decrease in the number, wavenumber and/or intensities of the bands in the IR and Raman spectra of metal complexes in comparison to the appropriate bands in the spectra of ligands [4]. It is caused by a decrease in the force constants of the bonds and polarization of the C—C, C—H bonds in the ring. Therefore the vibrational data suggest that perturbation of the electronic system of molecules increase along with the series: $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$ cinnamates. Alkali metal ions stronger affect the electronic structure of the —C=C— bond than of the aromatic ring of ligand. Comparing the vibrational spectra of alkali metal cinnamates and benzoates, we may said that the presence of a double bound in

cinnamic acid diminishes the influence of metals on the aromatic system of ligand. Moreover the conjugations between the —C=C— and the π -electrons cause the decrease in the electron density in the aromatic ring of cinnamic acid compared with benzoic acid. Accordingly to the geometric criterion of aromaticity, the benzoic acid molecule possesses higher aromatic properties than the cinnamic acid molecule.

- (2) In the ^1H and ^{13}C NMR spectra of cinnamates the signals are downshifted compared with the appropriate signals in the NMR spectra of acid. It suggests the increase in the electron density around carbon (except carbons no. 1, 7, 8) and protons in the alkali metal cinnamate molecules. The displacement of the chemical shifts of protons is often the criterion of the decrease or increase in the aromaticity of studied system [23]. The chemical shifts of protons decrease in the following series: $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$ cinnamates as consequence of the circular current weakening and therefore an increase in the screening of aromatic protons. This is an evidence that alkali metal perturb the aromatic system of the molecule.
- (3) The calculations were performed in the B3LYP/6-311++G** level. The comparison of the optimized structures of Li, Na and K cinnamates and cinnamic acid leads to the conclusion on the effect of alkali metal ions on the electronic charge distribution in molecule. Namely, the substitution of metal ion in the place of carboxylic hydrogen causes the increase in the C9—C1 and C8—C7 bond lengths and a shortening of C7—O and C9—C8 bonds along with the series $\text{Li} \rightarrow \text{Na} \rightarrow \text{K}$ cinnamates. Moreover, the electron density around particular atoms changes in the same fashion. As a consequence the total electron density of —C=C— and the aromatic ring increase in the series $\text{Li} \rightarrow \text{Na} \rightarrow \text{K}$ cinnamates.

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