Vibrational and NMR studies on *o*-, *m*- and *p*- chlorobenzoic acids

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The ^{1}H NMR, IR, and Raman spectra of *o*-, *m*- and *p*- chlorobenzoic acids were recorded and studied. The effect of position of substituents on the electronic properties (mainly π-electron system) of the molecules have been investigated. Three independent criteria : frequency and intensity of bands in vibrational spectra, chemical shifts of protons in ^{1}H NMR spectra, and calculated values of delocalization energy, were applied to estimate perturbation of the aromatic system of benzoic acid in compounds under study. Comparing spectral and semi-empirical data we have found correlations between the degree of perturbation of the aromatic system of benzoic acid and positions of substituents in the ring. Dependence between chemical shifts in NMR spectra and electronic charge density are also reported.

1 Introduction

The derivatives of benzoic acid are biologically important compounds being present in molecules of some enzymes. It is of a great interest to use them as models in investigations on properties of molecules occurring in living systems.

The effect of some metals on the electronic structure of benzoic, salicylic and nicotinic acids have been[1-4] established by vibrational and UV spectroscopy. At present, we are mainly interested in general influence of metals (their ionic potential, atomic mass, electronegativity and oxidation degree) and halogens in *o*-, *m*-, *p*- positions to the carboxy group, on the π-electron system. The aim of the present paper has been to get experimental data by means of various molecular spectroscopic methods to characterize aromaticity and electronic charge distribution of *o*-, *m*-, and *p*- chlorobenzoic acids. Our main questions were :

- do the results yielded by various methods lead to the same conclusions, and
- which position of substituent perturbs aromatic system to the highest degree.

2 Experimental

Spectra of all the compounds were measured as follows :

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–NMR spectra of acetone solution (0.2-0.3 mol/dm^3) were recorded with Varian –200 Unit at room temperature. TMS was used as internal reference.

– Raman spectra of solid samples in the range 4000–300 cm^{-1} were recorded with a Coderg Model PHO spectrometer with Spectra–Physics argon ion laser (488.0 nm excitation line).

–IR spectra in the range 4000–400 cm^{-1} were recorded with a Carl Zeiss IR-75 and FT-IR Perkin Elmer Model-2000 spectrophotometers using pressed potassium pellets.

3 Results

3.1 *Vibrational data*

Table 1 contains frequencies occurring in Raman and IR spectra. The assignment has been made on the basis of the literature data[5, 6]. The differences between the frequencies of the same vibration in the Raman and IR spectra do not exceed a few cm^{-1}. The total number of bands occurring, as well as number of aromatic bands in all compounds, are less than those in benzoic acid. The bands which characterise aromatic properties of benzene derivatives mainly occur within the range of 1600-1430 cm^{-1} [$\nu(C \overset{...}{-} C)_{ar}$ bands] and 1180-1040 cm^{-1} [β (C–H) bands]. Within this range, differences in frequency are considerable between *p*-, and *o*-, *m*- isomers, whereas small between *o*- and *m*- isomers. The frequencies of bands numbered as 8a, 19a, 14, 9a, 18b (bold in the Table 1) decrease in the order : $p > m \geq o$ (which means that the perturbation in the aromatic system increases). On the other hand, there are bands (8b, 19b, 18a), which are shifted to smaller frequency for *p*- isomer.

A comparison of frequency and intensity of aromatic bands for various isomers allows to divide them into two groups : para isomer forming the one group, while ortho and meta the other one.

3.2 *NMR data*

In the case of -*o* and *m*- chlorobenzoic acids all protons are shifted diamagnetically in comparison to benzoic acid (Table 2). In the case of *p*- isomer, two protons (1, 5) are slightly shifted diamagnetically, and two (2, 4) paramagnetically. This indicates a decrease in intensity of ring current in the order : benzoic acid, *p*-chlorobenzoic, *m*-chlorobenzoic, *o*-chlorobenzoic acids. The chemical shifts of protons being in the same position of the ring increase in order :

1st proton $m \rightarrow p$;
2nd proton $o \rightarrow p$;
3rd proton $o \rightarrow m$;
4th, 5th protons $o \rightarrow m \rightarrow p$;

Particularly important are the 4th and 5th protons which are present in all investigated compounds. Figure 1 represents the correlation between calculated formal charge on carbon atoms (independently on isomer and position in the ring) and chemical shifts of connected protons.

Table 1. Frequencies of chosen bands in Raman and IR spectra of *o*-, *m*-, *p*- chlorobenzoic acids

wavenumber (cm^{-1})							
o-chlorobenzoic acid		*m*-chlorobenzoic acid		*p*-chlorobenzoic acid		Assignment	Normal vibration of the aromatic ring [5]
IR	R	IR	R	IR	R		
-	3090s	-	3090s	-	3094m		20a
-	3084vs	-	3084s	-			20b
-	3056s	-	3076s	-			
1692s	-	1690s	-	-		$\nu(C{=}O)_{asym}$	
-	1645s	-	1645s	-		$\nu(C{=}O)_{sym}$	
1592s	1592s	1603s	1596vs	1572sh	-	$\nu(C \cdots C)_{ar}$	8b
1571s	**1571w**	**1576s**	-	**1598sh**	**1595vs**	$\boldsymbol{\nu(C \cdots C)_{ar}}$	**8a**
1479s	-	1480s	-	1422vw	1433m	$\nu(C \cdots C)_{ar}$	19b
1438s	**1440s**	-	**1439w**	**1489sh**	**1486m**	$\boldsymbol{\nu(C \cdots C)_{ar}}$	**19a**
1410s		1419s	1422w	-	-	β(O–H)	
1318vs	-	1304vs	1299s	-	-	ν(C–OH)	
1288m	**1297w**	**1262vs**	**1261m**	**1319sh**	**1320m**	$\boldsymbol{\nu(C \cdots C)_{ar}}$	**14**
1268s	1261m	-	-	1233sh	-		13
1174w	**1168m**	-	**1173w**	**1176vw**	**1176s**	**β(C–H)**	**9a**
-	-	1151s	1147m	-	-	β(C–H)	9b
1143w	1146w	1079w	1074m	1015w	1015m	β(C–H)	18a
1045s	**1048vs**	**1107w**	**1106vw**	**1110sh**	-	**β(C–H)**	**18b**
-	-	1092vw	1093vw	-	-	β(C–H)	
1052s	-	670vw	-	1092m	1094vs	β(C–H)	1
794m	799m	1008vw	1005vs	-	-	γ(C–H)	12
989vw	-	-	-	-	-		5
956m	-	853m	848m	852w	-		17b
915s	-	916m	-	-	-	γ(O–H)	
871vw	-	900m	-	972vw	-		17a
817	808	-	-	-	-		
695m	-	810m	811w	-	629vs		6b
745vs	-	-	746vw	-	-		11
712s	703s	721s	-	681vw	698m	φ(C–C)	4
695m	-	-	-	760w	762m	γ(C–H)	6a
-	-	691s	709s	-	-	β(C=O)	
647s	646m	657m	650m	-	-	γ(C=O)	
560s	-	550s	-	-	-		16a
456w	462s	-	-	538w	-		16b
422w	423m	-	422m	-	-		7a

β = in plane, ν = stretching, γ = out of plane, s = strong, m = medium, w = weak, sh = shoulder, v = very.

Table 2. Chemical shifts of protons [ppm]

proton position[a]	*o*-chlorobenzoic acid	*m*-chlorobenzoic acid	*p*-chlorobenzoic acid	benzoic acid
1	-	7.97	8.03	8.10
2	7.53	-	7.54	7.52
3	7.54	7.62	-	7.63
4	7.44	7.52	7.54	7.52
5	7.93	7.96	8.03	8.10

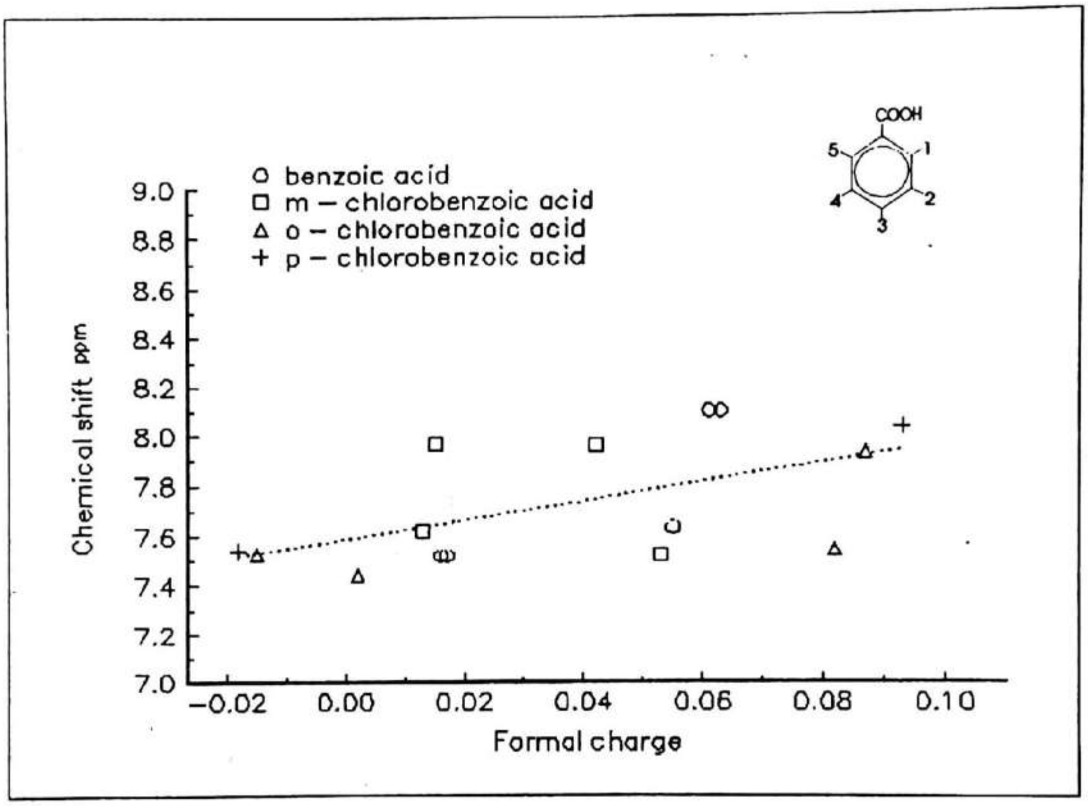

Fig 1. Dependence between chemical shifts of protons and calculated formal charge of carbon atoms.

3.3 *Calculations of delocalization energy E_D, energy of molecular orbitals and dipole moments*

The single point calculations were carried out with energy optimized molecules by INDO approximation. The results are given in the Table 3.

Table 3. Calculated values of E_D (defined as difference between heat of formation and energy of bonds), dipole moment, $\Sigma|\Delta q|$(where Δq is the difference between formal charge of carbon atoms being in the same position in isomer and benzoic acid), and ΔE (difference between energy of lowest unoccupied molecular orbital and highest occupied molecular orbital LUMO–HOMO)

	benzoic acid	*o*-chlorobenzoic acid	*m*-chlorobenzoic acid	*p*-chlorobenzoic acid
E_D [kJ/mol]	1628.0	1604.5	1604.8	1604.8
μ[dB]	2.1	5.8	4.5	4.7
$\Sigma|\Delta q|$	-	0.423	0.455	0.461
ΔE [eV]	14.9	14.6	14.7	14.5

The calculated values of E_D and μ indicate that the order of stability of molecule is as follows : benzoic acid > *p* ~ *m* > *o*.

4. Conclusions

On the basis of experimental data we conclude that chlorine in *o*-, *m*-, and *p*-positions disturb the electronic system of benzoic acid. The two effects responsible for this purturbation are :

– changes in the $(C \cdots C)_{ar}$ bonds polarity, and

– changes in total dipole moment of molecule.

The most significant perturbation in uniform charge distribution occurs for meta and ortho isomers. This conclusion has been confirmed by (i) vibrational data - decrease in frequencies and intensities of aromatic bands, (ii) NMR data - decrease in ring current intensity [Refs. 7, 8), and (iii) calculated data - decrease in E_D value [Ref. 9].

Further, Σ |Δq| increases as follows : *o* < *m* < *p*.

As is well known, both substituents (–COOH, –Cl) are electrophilic and that is why *o*- and *m*- positions affect uniform distribution of electronic charge in the ring to the highest degree. The perturbation degree defined as an increase in polarity of bonds increases as follows : *p* > *m* > *o*, while increase in dipole moment is as follows : *p* ~ *m* < *o*.

The correlation between change of calculated formal charges on carbon atoms and chemical shifts of analogous protons (corresponding to the same protons in benzoic acid) is shown in Table 4.

Table 4. Change of chemical shifts of protons (Δδ) and calculated formal charge on carbon atoms (Δρ) relative to the benzoic acid

carbon atom position	*o*-chlorobenzoic acid		*m*-chlorobenzoic acid		*p*-chlorobenzoic acid	
	Δρ	Δδ	Δρ	Δδ	Δρ	Δδ
1	−0.207	–	0.046	−0.13	−0.032	−0.07
2	0.032	0.01	−0.340	–	0.035	0.02
3	−0.027	−0.09	0.042	−0.01	−0.323	–
4	0.014	−0.08	−0.037	0.00	0.034	0.02
5	−0.024	−0.17	0.021	−0.14	−0.029	−0.07

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