BONDING BETWEEN THE CESIUM CATION AND SUBSTITUTED BENZOIC ACIDS OR BENZOATE ANIONS IN THE GAS PHASE: A DENSITY FUNCTIONAL THEORY AND MASS SPECTROMETRIC STUDY

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This article is dedicated to the memory of Professor Otto Exner, an outstanding physical organic chemist, a collaborator, a master and a friend, who resided several times at the University of Nice-Sophia Antipolis, where he initiated a number of studies on substituent effects related to the gas-phase basicity.

Substituent effects on the formation of cesium cation complexes with a series of 17 benzoic acids (AH), benzoates (A−), and the ion pairs (Cs+A−) are studied by density functional theory (DFT) and mass spectrometry. This study is positioned in the context of the fate of cesium in the environment, with emphasis of the influence of natural organic matter and humic substances. The bond length Cs+-(carboxylic O) in the various adduct geometries are discussed as regards the interaction strength, but quantitative relationships are limited by secondary effects arising mostly from long-distance interactions in systems bearing polar groups in meta-position. Relative cesium cation affinities of [Cs+A−] were experimentally determined by the kinetic method, i.e. by dissociating the required cesium cluster formed by electrospray ionization in a quadrupole ion-trap. Experiments and calculations are in agreement, except for the adducts derived from 3- and 4-hydroxybenzoic acids. A change in the localization of the negative charge is proposed as a possible explanation for the divergence.
Keywords: Cesium cation; Affinity; Basicity; Gas phase; DFT calculations; Mass spectrometry; Substituent effects; Benzoic acids.

Among the alkali metals, cesium is poorly characterized in terms of the intrinsic interaction (in the gas phase, with no influence of solvent and counter-ions) between the Cs^+ cation and neutral organic molecules, and the situation is even worse for its interaction with anions[1]. However, cesium is of great importance from the environmental point of view, the main reason being the anthropogenic dispersion of the radioactive isotopes [134]Cs (half-life 2 years) and [137]Cs (half-life 30 years) in the environment, caused by the atmospheric nuclear tests in the 1960's and the Chernobyl accident in 1986. The presence of these radionuclides is observed nowadays in five continents: Europe[2], Africa[3], North[4] and South America[5], Australia[6] and Asia[7]. In general, ^{137}Cs is found in the upper layer (about 5–10 cm) of soil, where plants have their roots, whatever the soil nature (highly or weakly organic) is. In highly mineral soils, clays are the most important binding agents of cesium, but in the more organic soils, the clay/organic matter interactions contribute to the cesium mobility[2a,8]. More generally, adsorption of cesium depends in a complex manner on interactions between inorganic and organic fractions[9]. The natural organic matter (NOM) is in a large part constituted of humic substances that are further subdivided into fulvic acids (FA), humic acids (HA) and humin, according to their solubility properties[10]. Moreover, NOM plays an important role in the cesium bioavailability and the resulting accumulation in plants[11]. The factors affecting the bioavailability of cesium, and of the strontium and technetium radionuclides, and the associated models have been reviewed recently[12]. HA and FA are complex organic systems of high molecular weights, which include Brønsted acid functionalities like phenolic hydroxy and carboxyl groups[13]. Moreover, plant roots themselves excrete various mono- and polycarboxylic acids[14], often characterized as low-molecular-weight (LMW) acids, that play a role in cesium uptake[15].

For a better understanding of the interactions between cesium and organic acids, we undertook joint studies by mass spectrometry (MS) and quantum chemical calculations[16], using density functional theory (DFT). The experimental MS approach was designed to provide information on the affinities of organic moieties to Cs^+ in the gas phase. The MS experiments, based on collision-induced dissociation of clusters formed between carboxylic acids (actually carboxylates, $RCOO^-$), the anion of the cesium salt (nitrate, iodide, etc.) and Cs^+, provided relative gas-phase affinities of the salt $RCOO^-Cs^+$ (as isolated molecules, hereafter named ion pair) for Cs^+. The MS results were scaled according to the DFT results. For the sake of simplicity, AH stands for substituted benzoic acids (unionized) in the following, and A^- for the corresponding anions. The present study is devoted to

meta- and para-substituted benzoic acids, with the aim of characterizing the substituent electronic effects[17] controlling the Cs^+ complexing ability of the carboxyl group in its neutral and anionic forms. We did not include ortho substituents to avoid further complications, such as steric effects and other direct substituent/function interactions. A set of substituents was chosen for sampling a broad range of electron-donor and electron-acceptor ability. Groups with simple structure were selected for minimizing the size and complexity of the calculations. We have calculated the most stable structures and energy parameters of five species: the neutral benzoic acids AH and their Cs^+ adducts $[Cs^+ \cdots AH]$, the anions A^- and their Cs^+ adduct $[Cs^+ \cdots A^-]$ (salt "molecule" or ion pair), and the Cs^+ adducts of $[Cs^+ \cdots A^-]$, $[Cs^+ \cdots A^- \cdots Cs^+]$. In these formulae, the dotted line indicating the non-covalent interaction between the cation and the neutral or negatively charged ligands will be omitted in the following text. From the energetics of these species, it is easy to extract:

– The gas-phase proton acidity of benzoic acids, measured (following the usual terminology) by the enthalpy, $\Delta_{acid}H$, and the Gibbs free energy, $\Delta_{acid}G$, of the reaction:

$$AH \rightarrow A^- + H^+. \qquad (1)$$

– The gas-phase cesium cation affinities (CsCA) and basicities (CsCB) of any species L (L stands for ligand, i.e. neutral molecule AH, neutral ion pair $[Cs^+A^-]$, or anion A^-), defined, respectively, as the enthalpy and Gibbs energy of the dissociation reaction:

$$LCs^+ \rightarrow L + Cs^+. \qquad (2)$$

In parallel, MS experiments were carried out on a few typical benzoic acids for providing quantitative experimental data on Cs^+ interaction with the $[Cs^+A^-]$ ion pairs and, in addition, a test of the consistency of the DFT with experimental results. The unsubstituted benzoic acid was already included in a previous study on a series of mono- and dicarboxylic acids[16b].

METHODOLOGIES

Computational Method

All calculations were performed using the Gaussian 03 program package[18]. B3LYP hybrid density functional[19], which includes Becke's exchange func-

tional and the correlation part due to Lee, Yang and Parr, was used with Dunning/Huzinaga valence double-zeta basis set augmented with polarization functions (D95V**)[20] on hydrogen and first-period atoms (C, N, O, F), using pure Cartesian basis functions, i.e. five d-type basis functions per atom, and Stuttgart/Dresden effective core potentials, (SDD, also known as Stuttgart RSC 1997 ECP)[21], augmented with Glendening's polarization functions[22] on the cesium atoms. In addition, diffuse basis functions[23] were added to the second-period atoms to allow for a better description of the anionic systems. Full conformational searches, geometry optimizations and vibrational analyses were performed for the neutral acids, anions, and three different Cs^+ adducts: Cs^+/AH, Cs^+/A^- and $Cs^+/[Cs^+A^-]$. All stationary points were found to be true minima (NImag = 0). In systems involving Cs^+, different initial positions of the metal were tested. The gas-phase enthalpies and Gibbs energies of reactions (*1*) and (*2*) were calculated from *H* and *G*, given by the Gaussian program for the five species AH, A^-, $[Cs^+A^-]$, $[Cs^+AH]$ and $[Cs^+A^-Cs^+]$.

These thermodynamic values take into account zero-point energies, finite temperature correction (0 to 298 K) and the pressure–volume work term. Unscaled frequencies from vibrational analysis were used. This method was validated in a previous paper[16b] by comparison of experimental and calculated cesium cation affinities and basicities for several simple species. CsCA and CsCB calculations on unsubstituted benzoic acid and cesium benzoate were published previously[16b] and are included in this work.

Chemicals

Methanol, cesium iodide and organic acids were of commercial origin and were used without further purification: methanol (Roth "Rotisolv" >99.95% LCMS Grade), cesium iodide (Aldrich >99.999%), benzoic acid and its 4-amino, 3-hydroxy, 4-nitro, 3-nitro derivatives (Aldrich >98%), and 4-hydroxybenzoic acid (Fluka >99%).

Mass Spectrometry

The experiments were conducted in a way similar to our previous studies[16]. Electrospray mass spectra were recorded on a Finnigan MAT (Thermo Electron, Courtaboeuf, France) LCQ ion-trap mass spectrometer. The electrospray ion source was operated under the following conditions: flow rate 3 μl/min; Electrospray ionization voltage 4.5 kV; capillary voltage (potential difference between the capillary exit and the tube lens) adjusted ac-

cording to a "tune file" created for each mixture of benzoic acid and cesium iodide, and applied to the two identical spectrometers used for measurements; capillary temperature 200 °C; drying and nebulizer gas – nitrogen. Cesium iodide was dissolved in ultrapure water to obtain a solution at about 3 mg/ml (1.5×10^{-2} mol/l). Organic acids were dissolved in methanol to obtain solutions of the same concentrations. Electrosprayed solutions were prepared from equal volumes of an aqueous cesium iodide solution and a methanolic solution of the acid. To avoid the formation of methyl esters of benzoic acids in methanol[24], freshly prepared solutions were used. Methanol was chosen in accord with the literature results, showing a better signal-to-noise ratio compared with acetonitrile[24]. The *m/z* range was set between 50 and 2000. Collision-induced dissociation experiments were carried out by trapping the precursor ion isolated within an *m/z* range of ±1.5 (ref.[25]). The helium buffer gas pressure was set automatically by the regulated inlet at about 2×10^{-3} Pa (ion gauge reading). Typical operating conditions for carrying out collision-induced dissociation (CID or MS/MS) experiments were: ion injection time 200 ms, activation $q_z = 0.250$, activation time 30 ms, activation amplitude set at 17% of the maximum voltage (determined by the *m/z* under consideration). The ion intensity ratios in the CID experiments are the means of the values obtained in three separate experiments (about 5 spectra each), each spectrum resulting from the accumulation of about 40 scans (3 microscans per scan). The composition of ions was inferred from CID spectra, isotopic peaks distribution and cesium mass defect.

RESULTS AND DISCUSSION

Structural Aspects

The calculations of the structures for benzoic acid, benzoate anion and their substitution derivatives are relatively straightforward. Concerning their Cs+ adducts, several initial conformations were tested to check the convergence to a given energy minimum. The substituents were also considered as possible ligation sites. It was found in several cases that coordination to these sites, rather than to the carboxyl functions (COOH, COO−, and COO−Cs+), leads to adducts that are the most stable or of stability close to the carboxyl-bound adduct. As the study was aimed at characterization of the carboxyl and carboxylate groups as ligands, the complexation to this site was investigated, either if it corresponded to the most stable structure or not. Therefore, the results will be tabulated for the function-bound

adducts that may assume different conformations as well as for other stable adducts corresponding to complexation to the substituent.

The distance(s) between the cesium atom and the functional oxygen atom(s) may be considered a first approach to the strength of interaction in the adduct. The corresponding bond lengths are listed in Tables I–III for the adducts with substituted benzoic acids, benzoate anions and cesium benzoates, respectively.

In the functional group complexation of neutral acids, the Cs atom nearly lines up with the C=O bond, without significant contribution of the O(H) to bonding. A notable exception was found for the 3-COOH sub-

TABLE I
Bond lengths and interatomic distances (in Å), calculated by DFT, in Cs^+ adducts with undissociated substituted benzoic acids

Substituent	Cs–O(COOH) bond length, Å[a]	Cs–substituent distance(s), Å[a]		
H	2.863			
3-F	2.884	2.944		
4-F	2.871	[b]		
3-CF$_3$	2.901	3.210	3.210	[c]
4-CF$_3$	2.892	3.271	3.516	3.352
3-NH$_2$	2.850	3.291		
4-NH$_2$	2.819	[d]		
3-CN[e]	2.911	3.023		
4-CN[e]	2.899	3.025		
3-NO$_2$[e]	2.945	3.145	3.179	
4-NO$_2$[e]	2.909	3.171	3.171	
3-OH	2.866	3.174		
4-OH	2.848	3.078		
3-COOH	3.320[f]	3.322[f]		
4-COOH	2.883			
3-CH$_3$	2.855			
4-CH$_3$	2.851			

[a] For the closest atom(s). [b] Cs^+ coordinated to the fluorine atom is not a stable structure. [c] The third Cs^+–F interaction is not significant (>4.4 Å). [d] Cs^+ coordinated to $N(H_2)$ is not a stable structure. [e] Cs^+ coordinated to substituent corresponds to the most stable structure. [f] Cs^+ forms a quasi-symmetrical chelate with the two carboxyl groups.

stituent (isophthalic acid), for which the monocoordinated Cs^+ was much higher in energy. Rather, a symmetrical structure with Cs^+ chelated by the two carboxyl functions was obtained. This quite unusual chelation by two distant groups in meta-position on benzene ring is attributable to the long Cs–O bonds. The Cs–O bond lengths in the carboxyl complexes of the neutral acids (Table I) are in the range 2.82–2.95 Å, corresponding to 4-NH_2 and 3-NO_2, respectively. The variations of Cs–O bond lengths in the carboxyl complexes apparently follow the electron-donating properties of the substituent, a shorter bond corresponding to a stronger interaction. This possible connection will be examined in the following subsection dealing with the energetics of interaction.

The case of the system A^-/Cs^+ (Table II) is relatively simple, as the cation is linked to two carboxylate oxygen atoms in a quasi-symmetric way with bond lengths from 2.81 Å for 4-aminobenzoate to 2.86 Å for the longest Cs–O(C) bond in the 3-nitrobenzoate adduct. There are few experimental structures of cesium carboxylates, only in the solid state, for significant comparisons with the DFT results. The hydrogencarbonate ion HCO_3^- has been proposed as a model for carboxylate[26]. In the study of the cesium hydrogencarbonate crystal, the closest approach to oxygen is 3.06 Å for a collinear Cs···O–C, and 3.12–3.15 Å for a double interaction of the cation with the two oxygen atoms bearing no hydrogen. Similarly, the Cs–O(C) distances in the solid state are in the 3.06–3.16 Å range for cesium

TABLE II
The two cesium–oxygen bonding distances (in Å) calculated by DFT in adducts with benzoate anions

Substituent	Cs–O		Substituent	Cs–O	
H	2.821	2.821	3-NO_2	2.834	2.857
3-F	2.827	2.833	4-NO_2	2.845	2.845
4-F	2.826	2.826	3-OH	2.828	2.821
3-CF_3	2.834	2.834	4-OH	2.819	2.816
4-CF_3	2.837	2.836	3-COOH	2.834	2.839
3-NH_2	2.820	2.818	4-COOH	2.835	2.833
4-NH_2	2.812	2.812	3-CH_3	2.821	2.820
3-CN	2.837	2.848	4-CH_3	2.819	2.819
4-CN	2.843	2.838			

TABLE III
Cesium–oxygen bonding distances (in Å) calculated by DFT in the adducts cesium cation/cesium benzoates

Substituent	In-out structure[a]			Propeller structure[a]		One Cs+ on substituent[a]				
	Cs–O (in-plane Cs+)		Cs–O (out-of-plane Cs+)	Cs–O	Cs–O	Cs–O (carboxylate)		Cs+–closest atom(s) of substituent		
H	2.841	3.103	2.880	2.693	2.694					
3-F	2.842	3.127	2.878	2.707	2.700	2.928	2.852	2.864		
4-F	2.847	3.119	2.876	2.700	2.700	2.881	2.880	2.852		
3-CF₃	2.840	3.146	2.925	2.722	2.710	2.912	2.863	3.297	3.282	3.170
4-CF₃	2.850	3.135	2.885	2.714	2.713	2.886	2.886	3.255	3.363	3.190
3-NH₂	2.848	3.069	2.897	b	b	b				
4-NH₂	2.842	3.062	2.880	2.679	2.679	b	2.965			
3-CN	2.840	3.173	2.887	2.727	2.712	2.912	2.868	2.969		
4-CN	2.844	3.173	2.878	2.719	2.721	2.890	2.893	3.093		
3-NO₂	2.832	3.173	3.031, 3.412[c]	2.766	2.719	2.920	2.883	3.096	3.081	
4-NO₂	2.847	3.177	2.877	2.723	2.723	2.903	2.904	2.924	3.095	
3-OH	2.837	3.103	2.877	2.715	2.696	b		2.824		
4-OH	2.844	3.086	2.875	2.690	2.687	b			3.320	
3-COOH	2.825	3.128	3.046, 3.336[c]	2.801	2.709	2.926	2.869			
4-COOH	2.845	3.129	2.882	2.708	2.710	2.874	2.903			
3-CH₃	2.843	3.091	2.880	2.690	2.691					
4-CH₃	2.843	3.091	2.876	2.689	2.689					

[a] See text for description of the structure and Fig. 1 for illustration. [b] No such stable structure found. [c] The distance to the closest oxygen atom of the substituent.

salicylate[26]. The DFT-calculated distances are smaller because, in the solid, Cs^+ is coordinated to 8–10 oxygen atoms, which leads to crowding and repelling of the ligands, compared with a pure 1:1 interaction in the gas phase. The calculated Cs–O bond lengths in the anion/cation complexes are only slightly shorter than for the carboxyl complexes of the neutral acids ranging from 2.82 to 2.95 Å, for 4-amino- and 3-nitrobenzoic acid, respectively (see Table I), as compared with 2.81–2.86 Å. With an anionic ligand, a much shorter Cs–O distance than for a neutral one is expected. Considering that the negative charge centre borne by the two oxygen atoms in the carboxylate is in fact closer to Cs^+, this corresponds actually to the expected stronger interaction. When the electron-donating effect of the substituent increases, basicity enhancement, inducing a parallel decrease in the Cs–O bond length, is expected, as stated for the interaction with neutral molecules. This is roughly what is observed in Table II for the $[Cs^+A^-]$ systems, but the variations are small and the two Cs–O bonds exhibit large dissimilarities in several cases. A possible relationship between the Cs–O bond length and thermochemical basicity will be examined in the next section.

The case of the adducts between the $[Cs^+A^-]$ ion pairs and Cs^+, giving $[Cs^+A^-Cs^+]$, is more intricate. We examined this species in detail (Table III), because mass spectrometry measurements can be performed on them, leading to quantitative informations on relative Cs^+ affinities or basicities of $[Cs^+A^-]$. The presence of the two cations increases the number of conformations that are energetically permissible. Three main types of Cs^+ localization were found, two of them corresponding to Cs^+ linked to the carboxylate group: (i) quasi-symmetrical positions of the two Cs^+, each being linked to one oxygen atom of the carboxylate; this form is labeled "propeller"; (ii) one Cs^+ is coordinated to the two oxygens of the carboxylate, the second Cs^+ being situated above the plane of the CO_2^- group and oriented toward the benzene ring; this form is labeled "in plane-out of plane" or "in-out"; (iii) one Cs^+ is bonded to the carboxylate, but the second is linked to the substituent. The corresponding structures are depicted in Fig. 1 for a typical case, and the relevant bond lengths are given in Table III.

In the case of the "in-out" structure, the short bond with Cs^+, in the plane of CO_2^-, shows very small variations (2.83–2.85 Å) without apparent ordering as regards the electronic effect of the substituent. On the contrary, the longer Cs–O bond changes from 3.06 (4-NH_2) to 3.18 Å (4-NO_2), in relation to the logic of substituent effects. The Cs–O distance with the other Cs^+, lying outside the carboxylate plane, displays minor changes as regards substituent effects, with the notable exception for 3-carboxy and 3-nitro de-

rivatives for which the presence of a polar C=O or N=O bond in favorable position makes possible chelation of the cation. This interaction is reflected in the longer Cs–O bond in the carboxylate and a significant interaction (3.3–3.4 Å) with one of the substituent oxygen atoms.

The propeller structures, in which each oxygen atom of the carboxylate is bonded to one Cs$^+$, present the shortest Cs–O bond lengths, in the range 2.68–2.80 Å. The electronic effect of the substituents seems to be blurred by other effects, in particular for meta substituents.

The last peculiar structure of the [Cs$^+$A$^-$Cs$^+$] adducts that was examined corresponds to the second cation attached to the substituent. This kind of bonding was found to be stable only for the dipolar substituents F, CF$_3$, CN, NO$_2$, and COOH. As the properties of the substituents are altered by Cs$^+$ complexation, and only electron-withdrawing substituents are concerned, no regularity in bond lengths can be expected.

Energetic Aspects

Although our primary objective was the description of Cs$^+$/carboxylic acid interactions, the gas-phase Brønsted acidity in the benzoic acid series was also calculated as a first approach to their acid-base properties. The DFT-
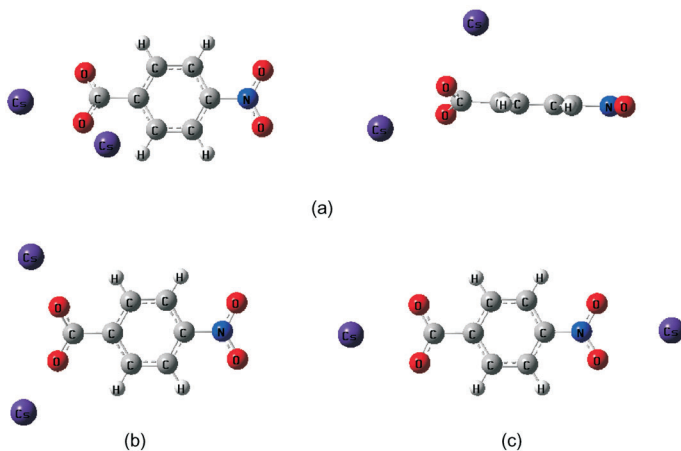

(a)

(b)   (c)

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The three forms of a typical [Cs$^+$A$^-$Cs$^+$] adduct (A$^-$ = 4-nitrobenzoate). a The in plane-out of plane (or in-out) form, with a Cs$^+$ almost in the CO$_2^-$ plane, and the other above the CO$_2^-$ plane; two views are presented to show the Cs$^+$ locations; b the propeller form with the two Cs$^+$ in a quasi-symmetric position; c one Cs$^+$ on the carboxylate, the other on the substituent

calculated $\Delta_{acid}H$ and $\Delta_{acid}G$ for benzoic acid and 16 meta- and para-substituted benzoic acids, along with experimental values, are presented in Table IV.

Critically compiled experimental gas-phase Brønsted acidities in Table IV were taken from the NIST data base[28]. At first glance, it appears that calculated and experimental $\Delta_{acid}H$ and $\Delta_{acid}G$ values (298 K) agree rather well, but are somewhat systematically lower for $\Delta_{acid}G$ (this small discrepancy comes from the difference between the DFT-calculated entropy term and the estimated value in ref.[28]). As a result, these thermochemical acidity parameters $\Delta_{acid}H$, $\Delta_{acid}G$ correlate rather accurately with the experimental values,

TABLE IV
Calculated and experimental gas-phase Brønsted acidity parameters $\Delta_{acid}H$ and $\Delta_{acid}G$ (in kJ/mol at 298.15 K) for 3- and 4-substituted benzoic acids

Substituent	Calculated (DFT)		Experimental[a]	
	$\Delta_{acid}H$	$\Delta_{acid}G$	$\Delta_{acid}H$	$\Delta_{acid}G$
H	1419.6	1385.7	1423	1393
3-F	1401.8	1368.1	1406	1377
4-F	1406.5	1372.6	1410	1381
3-CF$_3$	1387.7	1354.4	1390	1361
4-CF$_3$	1384.7	1349.6	1390	1361
3-NH$_2$	1426.7	1392.6	1429	1400
4-NH$_2$	1437.9	1403.5	1437	1407
3-CN	1376.6	1342.9	1374	1345
4-CN	1373.3	1339.3	1372	1342
3-NO$_2$	1372.1	1338.3	1377	1347
4-NO$_2$	1364.7	1330.6	1373	1343
3-OH	1409.8	1376.5	1417	1387
4-OH	1424.0	1389.6	1405[b]	1376[b]
3-COOH	1395.4	1361.4		
4-COOH	1390.7	1356.5		
3-CH$_3$	1423.2	1387.9	1425	1396
4-CH$_3$	1425.2	1388.7	1427	1397

[a] Uncertainties for absolute values are in the range ±8–9 kJ/mol, but relative values are more accurate (±1–2 kJ/mol). [b] Ionization of the phenolic OH [27].

with the exception of 4-hydroxybenzoic acid, for which it was shown that the acid site is the phenolic hydroxy group instead of the carboxyl group[27]. When this substituent is excluded from the set (n = 14; experimental values for the 3- and 4-COOH derivatives are not available), the correlation equations become (in kJ/mol; the indicated uncertainties are standard deviations, s is standard deviation of the regression, r is correlation coefficient):

$$\Delta_{acid}H(exp) = (0.975 \pm 0.037)\ \Delta_{acid}H(DFT) + (37.5 \pm 51.3) \qquad (3)$$

$$s = 3.17;\ r^2 = 0.9834$$

$$\Delta_{acid}G(exp) = (0.987 \pm 0.037)\ \Delta_{acid}G(DFT) + (25.1 \pm 50.8) \qquad (4)$$

$$s = 3.18;\ r^2 = 0.9833.$$

The slopes are close to unity and the intercepts are not significant (the large standard deviations on the intercepts are due to long extrapolations). The correlation with the more homogeneous relative values $\delta\Delta_{acid}G$, from the Taft laboratory[17c], gives an even better correlation. These relationships allow to propose values for the acidity parameters of the carboxyl group of 4-hydroxybenzoic acid $\Delta_{acid}H(COOH)$ = 1428 kJ/mol, $\Delta_{acid}G(COOH)$ = 1398 kJ/mol.

Another conclusion that can be reasonably drawn from the good fit of Eqs (*3*) and (*4*) is that the energetics of the benzoate anions are adequately described by the level of calculation, and that the subsequent calculations on the Cs$^+$ adducts with anions will be effective, at least for the anionic groups. Three kinds of Cs$^+$ adduct formation (or dissociation) were considered in our study – (i) of AH and Cs$^+$, (ii) of A$^-$ and Cs$^+$, and (iii) of [Cs$^+$A$^-$] and Cs$^+$ – leading to cesium cation affinities (CsCA) and basicities (CsCB) of the ligands AH, A$^-$, and [Cs$^+$A$^-$]. The differences between CsCA and CsCB arise from the entropy associated with complexation. To a first approximation, this term may be considered as constant, and the two basicity scales may be considered as equivalent (or parallel) in general discussion. In fact, it is expected that different adduct structures will bring small variations of the entropy term. The Cs$^+$ adducts may show different calculated stable structures, as described in the preceding section. The most stable structure generates the largest calculated CsCA and CsCB, corresponding to the strongest Cs$^+$ basic site. We considered also less stable structures, giving smaller CsCA and CsCB, as they may also contribute to basic properties.

Moreover, for a given species, different binding sites may not have the same basicity order (depending on whether CsCA or CsCB values are considered) because of entropy effects. Accordingly, we have considered as significant the possible adduct structures of a given species as long as the calculated CsCA or CsCB were not too far from the maximum value. The CsCA and CsCB data for different structures of Cs^+ adducts of AH, A^- and $[Cs^+A^-]$, are listed in Table V.

For the Cs^+/AH adducts, the complex formation with COOH and the substituent was considered. It appears that complex formation with CN and NO_2 groups, either in meta- or para-position, is highly favored as regards the carboxyl function. The difference between CsCA and CsCB is rather constant and close to 25 kJ/mol. The other groups have much smaller CsCA and CsCB values than the carboxyl group. There are unfortunately few experimental data on the thermochemistry of Cs^+/neutral molecules (CsCA or CsCB) for comparison. In our recent review[1], the listed CsCAs for dimethyl ether and acetonitrile are close to 57 and 80 kJ/mol, respectively, i.e. close to our calculated CsCAs for neutral AH. For complexation with the carboxyl group, the order of electronic effects is observed on both basicity parameters, with a variation of 42 kJ/mol when going from $4-NO_2$ to $4-NH_2$ substituent. The relatively high Cs^+ basicity of isophthalic acid (substituent 3-COOH) is attributed to the chelation of Cs^+ by the two carboxylate groups. Although the meta groups are distant, the long interaction range of Cs^+ renders the chelation energetically favorable. When excluding these data, the substituent effect follows roughly the order of classical Hammett substituent constants σ_m and σ_p (refs[17a,17b]), but this correlation is not analyzed further because (i) several deviations are due to special structures, in particular for some meta groups, (ii) σ_m and σ_p are influenced by solvation, and (iii) polarizability is not accounted for by these constants[17c]. Application of the Taft–Topsom three-parameter (field, resonance, polarizability) equation, specially designed for describing gas-phase substituent effects, would require a larger array of substituents.

Variations in the Cs–O bond length were discussed in the above section as a possible measure of the basic strength of the carboxyl function. Hence, a relationship between the bond lengths and CsCA or CsCB was sought. In fact, general correlations are rather poor. It was shown that the adduct of isophthalic acid possesses a special structure, and that other groups in meta-position seem to exert a long-distance influence on the Cs^+ bonding. A reasonable linearity ($r^2 > 0.97$) is found between the Cs-O distances and CsCAs (and similarly with CsCBs) of AH only if most of the meta substituents are excluded.

TABLE V
Calculated CsCA and CsCB (in kJ/mol at 298.15 K) for the undissociated substituted benzoic acids AH, anion A⁻, and ion pair [Cs⁺A⁻][a]

	Cs⁺/RCOOH				Cs⁺/RCOO⁻		Cs⁺/[RCOO·Cs⁺]					
Subst.	on C=O		on substituent		on COO⁻		in-out[b]		propeller[b]		on substituent	
	CsCA	CsCB	CsCA	CsCB	CsCA	CsCB	CsCA	CsCB	CsCA	CsCB	CsCA	CsCB
H	74.4	48.7	–	–	462.4	432.7	125.1	97.6	123.1	91.1		
3-F	68.5	43.1	39.7	18.8	451.7	421.9	116.8	89.4	114.4	93.2	78.2	55.0
4-F	67.9	42.5	c	c	453.6	424.1	114.3	86.7	112.7	90.3	77.3	36.7
3-CF₃	65.1	37.8	43.1	17.6	442.4	413.0	114.8	86.2	110.8	87.3	75.1	48.8
4-CF₃	59.1	33.1	36.7	15.4	439.7	410.6	105.9	77.2	105.8	80.1	72.8	52.2
3-NH₂	77.4	52.1	49.9	24.1	465.6	436.0	137.9	110.1	c	c		
4-NH₂	91.6	67.0	c	c	471.4	441.3	137.6	108.9	131.6	99.2		
3-CN	60.0	34.9	81.5	57.7	435.5	405.8	104.2	77.8	104.8	82.2	115.1	89.4
4-CN	54.1	28.6	77.6	53.1	431.9	402.4	97.6	71.5	99.5	78.4	113.4	95.7
3-NO₂	63.1	37.5	80.5	53.5	432.8	402.8	112.3	83.8	109.1	86.0	120.5	92.9
4-NO₂	50.7	25.2	77.1	51.1	426.5	396.8	94.4	67.9	97.5	73.5	119.5	94.6
3-OH	79.5	54.0	c	c	456.5	426.9	127.9	100.0	122.1	102.6		
4-OH	80.3	54.6	36.6	12.1	463.8	433.8	127.3	98.8	121.1	99.5		
3-COOH	80.7	54.1	–	–	446.5	416.7	133.4	104.1	125.6	102.7	108.1	82.8
4-COOH	65.8	40.2	–	–	443.0	413.3	113.4	85.9	111.3	87.4	105.0	79.1
3-CH₃	77.8	52.5			463.9	435.5	129.2	98.2	122.0	99.3		
4-CH₃	79.7	55.3			464.9	433.5	129.2	101.4	128.7	89.1		

[a] For the different adduct forms of [Cs⁺A⁻Cs⁺], see text and Fig. 1 for illustration. [b] See text and Fig. 1 for description of the structures and Fig. 1 for illustration. [c] No such stable structure found.

The Cs^+/A^- interaction, occurring on the carboxylate function, corresponds to the affinity (CsCA) in the range 427 to 471 kJ/mol. Note that corresponding CsCB are systematically about 30 kJ/mol smaller. The small anions F^- and OH^- exhibit somewhat larger affinities (above ~550 kJ/mol), but larger anions, like Br^- and I^-, display similar affinities (~445 and ~415 kJ/mol, respectively)[1]. The limits of the CsCA and CsCB ranges in this series are again for the two substituents $4\text{-}NO_2$ and $4\text{-}NH_2$. The variation within the series (44 kJ/mol) is almost the same as for the CsCA of neutral AH. A plot versus σ_m and σ_p (not shown) produces some scatter, but the linearity is improved when excluding meta substituents. The restricted significance of such correlations may come from the structure of the adducts, but also from the Hammett constants, as mentioned above. Meaningful relationships are expected between different thermochemical properties pertaining to the carboxylate function. A property, well established experimentally and computationally, is the gas-phase Brønsted acidity, parameters $\Delta_{acid}H(COOH)$ and $\Delta_{acid}G(COOH)$ (Eq. (*1*)), equivalent to the Brønsted basicity of COO^-, to be compared, respectively, with CsCA and CsCB of COO^- (Eq. (*2*), L = substituted benzoate anion). There are indeed excellent linear relationships between these parameters, using either experimental or calculated $\Delta_{acid}H(COOH)$ and $\Delta_{acid}G(COOH)$. The results involving experimental or calculated Brønsted parameters should be equivalent, because Eqs (*3*) and (*4*) show that experimental and calculated parameters are accurately proportional. Using the calculated values allows including all 17 data points (units and symbols as for Eqs (*3*) and (*4*)):

$$CsCA(A^-, DFT) = (0.6183 \pm 0.0088)\, \Delta_{acid}H(DFT) - (416.2 \pm 12.4) \qquad (5)$$

$$s = 0.80;\ r^2 = 0.9970$$

$$CsCB(A^-, DFT) = (0.6206 \pm 0.0105)\, \Delta_{acid}G(DFT) - (427.9 \pm 14.3) \qquad (6)$$

$$s = 0.94;\ r^2 = 0.9957.$$

Thus, a unique descriptor emerges from Eqs (*5*) and (*6*) for the substituent effect on the basicity of benzoate anions toward Cs^+ and H^+, even though CsCA values are by a factor of ~3 smaller than $\Delta_{acid}H$. It is noteworthy that the relative sensitivity of CsCA and CsCB to the substituent effect (slopes = 0.62) is still relatively high.

The Cs–O bond length was also considered a basicity indicator in this case of anion/cation interaction and compared with the thermochemical basicity. It is immediately apparent that the two Cs–O bonds in the adducts of meta-substituted anions (Table II) have different lengths and cannot be correlated independently. Using the mean Cs–O bond length, a reasonable correlation ($r^2 = 0.965$) is found, which can be improved to $r^2 = 0.990$ by removing the data for meta substituents. The link between the Cs–O bond length and energetics of complexation exists, but cannot be considered quantitative unless restricted to para substituents.

The energetics of the system $Cs^+/[Cs^+A^-]$ (adding a second Cs^+ to the ion pair) is interesting because the system can be approached by mass spectrometry techniques[16a,16b]. The strength of the interaction may be thought as occurring with the charge of the anion, with attenuation due to Coulomb repulsion between the two Cs^+. As shown in Table V, the range is well below that calculated for the Cs^+/anion interaction. The two major structures correspond to the in plane-out of plane and the propeller adducts described before (see Figs 1a and 1b). These two structures exhibit close values of CsCA and CsCB, indicating that they may coexist at room temperature and interconvert if the transition state(s) is (are) not too high in energy. In the case of the benzoates bearing NO_2 and CN, the complexation with these substituents is much favored relatively to that of the carboxylate function. These dipolar groups show a strong affinity (and basicity) to Cs^+, as seen for the neutral benzoic acids, for which Cs^+ preferred NO_2 and CN to COOH. Additionally, positioning of the second Cs^+ on the remote substituent minimizes the Coulomb repulsion with the first cation.

The analysis of the Cs–O distance vs basicity is obscured by the number of possible bonds and structures to be considered. The above examination of the in-out structure showed that the shortest bonds (Table III, shortest for in-plane Cs^+ and out-of-plane Cs^+) do not exhibit significant variations. On the contrary, the trend was logical for the longest Cs–O bond in this structure. Nevertheless, the meta-substituted compounds bearing electron-withdrawing groups (COOH, NO_2, CN, CF_3) must be excluded to obtain a reasonably quantitative correlation with CsCA, $r^2 = 0.965$. This rather stringent limitation is the same as mentioned for other cases. As seen in the structural part, the propeller structure is not likely to give a reasonable correlation.

Finally, the different scales may be compared. Again, the correlations are not accurate unless several meta compounds are excluded from the set. For example, the correlation CsCA of $[Cs^+A^-]$ (in-out form) vs CsCA of A^- gives $r^2 = 0.788$ with 17 points, and $r^2 = 0.971$ without 8 meta compounds.

Similarly, CsCA of [AH] vs CsCA of A$^-$ gives $r^2 = 0.813$ and $r^2 = 0.947$ with the exclusion of meta compounds. Correlations of CsCB values give a similar pattern, but in general with a reduced accuracy.

It emerges from the correlation analysis of the bond lengths and thermochemical basicities that the meta substituents often give rise to unexpected deviations: in several cases, the meta groups were seen to bring additional long-distance interaction with the large cesium cation.

Mass Spectrometry

The method and data treatment in this work is similar to that used previously[16b], except that cesium iodide was used for the complex formation instead of cesium nitrate. Therefore, only a brief description will be given. Positively charged clusters $[Cs^+A^-]_nCs^+[Cs^+I^-]_m$ containing the ion pairs $[Cs^+I^-]$ and $[Cs^+A^-]$, bound by Cs^+, are generated by electrospray ionization (ESI) from a water/methanol solution of cesium iodide and carboxylic acid, and injected into the ion-trap mass analyzer. The simplest cluster $[Cs^+A^-]Cs^+[Cs^+I^-]$ is isolated, subjected to collisional activation with the helium buffer gas, and the fragment ions are measured. The fragments $[Cs^+A^-]Cs^+$ and $[Cs^+I^-]Cs^+$, arising from the breaking of the weakest (non-covalent) bonds, are in general the most abundant. The ratio of the two first-order rate constants k_1 and k_0 for the two bond breakings is equal to the intensity ratio for the two product ions $L_1Cs^+ = [Cs^+A^-]Cs^+$ and $L_0Cs^+ = [Cs^+I^-]Cs^+$, as shown in Scheme 1.

$$[L_1CsL_0]^+ \quad \overset{k_1}{\nearrow} \quad [L_1Cs]^+ + L_0$$
$$\underset{k_0}{\searrow} \quad [L_0Cs]^+ + L_1$$
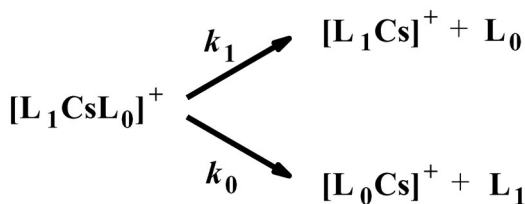
SCHEME 1

Using the kinetic (or Cooks) method[29], based on the transition state theory and several assumptions on the structure and bonding of the dissociating cluster, thermochemical quantities regarding the broken bonds are obtained:

$$\ln(k_1/k_0) \cong \ln(I_1/I_0) \cong \Delta\Delta H/RT_{eff} \cong \Delta\Delta G/RT_{eff}. \tag{7}$$

In our case, one ligand [Cs$^+$I$^-$] is kept the same, and the thermodynamic parameters in Eq. (7) are CsCA and CsCB, respectively, relative to [Cs$^+$I$^-$]. The "effective" temperature, T_{eff}, in this equation is actually an adjustable parameter that reflects the extent of collisional excitation of the dissociating cluster ion. Most of the underlying assumptions are fulfilled when the structures of the fragment ions are similar. The limitations and extent of the validity of the kinetic method for proton and metal ion affinities were discussed in commentaries[30]. The results of the collision-induced dissociation of the clusters [Cs$^+$A$^-$]Cs$^+$[Cs$^+$I$^-$], along with the selected CsCA and CsCB values are reported in Table VI. "Selected" means that the largest values, corresponding to the strongest bonding in terms of enthalpy or Gibbs energy, were chosen, because we assume that the strongest bonding is assumed to occur in the observed ion fragments.

Therefore, the experimental ln (I_1/I_0) values are relative CsCA or CsCB, but unscaled, as T_{eff} is not known. There is no experimental value that may be used for calibration. However, calculated CsCA and CsCB values may be used in Eq. (7); the corresponding plot is shown in Fig. 2.

The points pertaining to the 3- and 4-hydroxybenzoic acids are obvious outliers. The origin of the deviation is attributed, at least for the 4-OH substituent, to the differences in stability of the anion in solution and in the gas phase. The first pK_a values of 4-hydroxybenzoic acid (about 4.3 in water at room temperature)[31] belongs to the carboxyl function, but the favored acid dissociation in the gas phase correspond to the phenolic hy-

TABLE VI
Collision-induced dissociation of the clusters [Cs$^+$A$^-$]Cs$^+$[Cs$^+$I$^-$] (A$^-$ = substituted benzoate anion)[a]

Substituent	ln (I/I_0)	CsCA	CsCB
H	−1.840	125.1	97.6
4-NH$_2$	1.271	137.6	108.7
3-NO$_2$	−2.393	120.5	92.9
4-NO$_2$	−3.126	119.5	94.6
3-OH	−2.067	127.9	100.0
4-OH	−2.483	127.3	98.8
3-CH$_3$	−0.647	129.2	98.2
4-CH$_3$	−0.333	129.2	101.4

[a] Selected CsCA and CsCB values are from Table V.

droxy group, as mentioned above. The pK_a values of the phenolic OH and carboxyl groups in methanol are actually different from those in water, and can be estimated using appropriate relationships[32]. Nevertheless, the difference between the pK_a's of the two groups remains approximately the same, and the most easily ionized function in aqueous methanol is still COOH. It is hypothesized that a change in the Cs$^+$ binding site occurs in the formation, or during the dissociation, of the cluster for the 4-hydroxybenzoic acid (and possibly for the 3-substituted isomer as well). Further experiments and calculations are under way for testing this proposition. For the remaining series of closely related compounds, the correlation is quite precise (see the legend to Fig. 2). The value of the slope (1/RT_{eff} = 0.236 ± 0.018) is comparable with that obtained previously for a less homogeneous series of acids (0.160 ± 0.016)[16b]. The relationship with CsCB is less precise. This difference with CsCA is attributable to variable entropy effects, due either to artifacts of the DFT methodology or to some actual (but small) changes in the flexibility (degrees of freedom) going from one structure to another. The DFT thermochemical data and the experimental relative CsCA and CsCB of the ion pairs appear consistent, adding credence to the whole set of calculated structural and energetic parameters reported in this work.
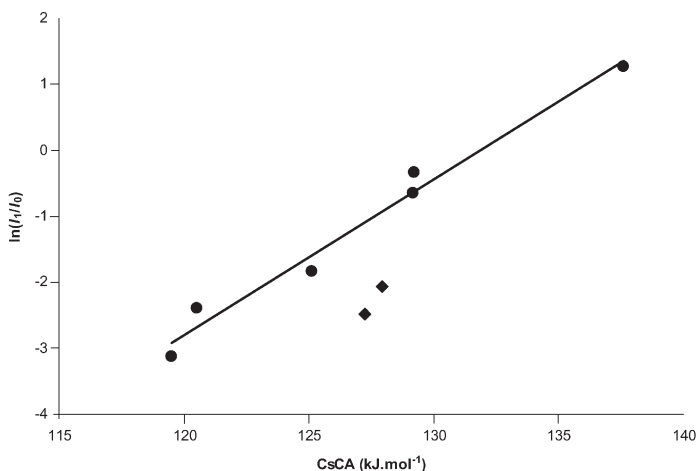

FIG. 2
Application of the kinetic method to the relative cesium cation affinity CsCA (Table IV) of the [Cs$^+$A$^-$] ion pairs. The data points for the 3-OH and 4-OH compounds (◆) are excluded from the least-square line. Least-square fit for the six remaining data points (●): ln (I_1/I_0) = (0.236 ± 0.018) CsCA(DFT) – (31.08 ± 2.26); s = 0.26; r^2 = 0.978

CONCLUSION

The interaction between the cesium cation and organic functionalities need to be better characterized, and this work was designed to obtain a better knowledge of the primary effects that may influence the interaction between Cs^+ and the neutral and anionic carboxyl function. By choosing a homogeneous series of 17 benzoic acids substituted in the 3- and 4-position with archetypal groups, we followed the seminal concepts of Louis P. Hammett, Robert W. Taft and Otto Exner in the characterization of electronic effects acting on a given functionality. The density functional theory was applied to the adducts formed from Cs^+ and neutral acids AH, the corresponding anions A^- and ion pairs $[Cs^+A^-]$, leading to structural and energetic aspects of the complexation. The Cs^+–oxygen bond distances in the adducts proved to be useful as a first approach to the interaction, but of limited generality as a quantitative measure of the bond strength. The calculated enthalpy (affinity) and Gibbs energy (basicity) of interaction of the cesium cation and neutral benzoic acids, the corresponding anions, and the cesium benzoate ion pairs (salts) provide the ranges of such intrinsic interactions, but also characterize the substituent electronic effects in the series. The general picture of the Cs^+ adduct structures and of their bonding energetics given by the DFT calculations are supported by mass spectrometry measurements on cesium clusters. Some unusual features in the domain of metal cation complexation, due to the long bonds formed with Cs^+, in particular when meta-substituted compounds are involved, emerged from the correlation analysis of the data.

Our previous experimental and theoretical studies of the Cs^+/carboxylic acids interactions involved molecules intended to mimic building blocks of humic substances. The series of acids examined in this work is more restricted in terms of structural variation, and bear less similarity to molecules modeling fulvic and humic acids. Nevertheless, the present results constitute a step forward to a better understanding of electronic effects operating in the interaction of carboxylic acids and carboxylates with the cesium cation. We hope that this knowledge will help improving our understanding of the cesium complexation by natural organic matter.

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