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Effect of alkali metal ions on the pyrrole and pyridine π-electron systems in pyrrole-2-carboxylate and pyridine-2-carboxylate molecules: FT-IR, FT-Raman, NMR and theoretical studies

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ABSTRACT

The FT-IR, FT-Raman and ^1H and ^{13}C NMR spectra of pyrrole-2-carboxylic acid (PCA) and lithium, sodium, potassium, rubidium and caesium pyrrole-2-carboxylates were recorded, assigned and compared in the Li → Na → K → Rb → Cs salt series. The effect of alkali metal ions on the electronic system of ligands was discussed. The obtained results were compared with previously reported ones for pyridine-2-carboxylic acid and alkali metal pyridine-2-carboxylates. Calculations for pyrrole-2-carboxylic acid and Li, Na, K pyrrole-2-carboxylates in B3LYP/6-311++G** level and Møller–Plesset method in MP2/6-311++G** level were made. Bond lengths, angles and dipole moments as well as aromaticity indices (HOMA, EN, GEO, I_6) for the optimized structures of pyrrole-2-carboxylic acid (PCA) and lithium, sodium, potassium pyrrole-2-carboxylates were also calculated. The degree of perturbation of the aromatic system of ligand under the influence of metals in the Li → Cs series was investigated with the use of statistical methods (linear correlation), calculated aromaticity indices and Mulliken, NBO and ChelpG population analysis method. Additionally, the Bader theory (AIM) was applied to setting the characteristic of the bond critical points what confirmed the influence of alkali metals on the pyrrole ring.

1. Introduction

Pyrrole-2-carboxylic acid (PCA) and pyridine-2-carboxylic acid (PA, picolinic acid) are interesting models since they are biologically important ligands incorporated into larger biomolecular systems. The structures, chemical properties and biological activities of pyridine-2-carboxylic acid and metal complexes of pyridine-2-carboxylates have been widely investigated [1–4]. PA is the body's prime natural chelator of vital trace elements: chromium, zinc, manganese, copper, iron and molybdenum. Biosynthesized in the liver and kidneys from the amino acid tryptophan, and stored in the pancreas during digestion, PA is secreted into the intestine. PA is present in dietary additives as a carrier of the divalent zinc or chromium cation and these compounds are widely distributed and consumed. The spectroscopic study of pyrrole is important since it is a parent compound of hemoglobin, chlorophyll, the corrin ring of vitamin B12 and many other complexes that are biologically active substances [5–9].

In this study we used spectroscopic (FT-IR, FT-Raman, NMR) and theoretical (AIM, DFT, MP2) methods. The spectroscopic studies enabled us to estimate the effect of metal ions on the electronic charge distribution of pyrrole-2-carboxylic acid. Experimental and theoretical study of pyridine-2-carboxylic acid and its alkali metal salts was reported previously [10]. In this paper some of this published data were compared with experimentally and theoretically obtained results for PCA and its salts. An estimation of electronic charge distribution makes possible prediction of properties of a molecule, for example: its reactivity, durability of complex compounds, kinship to enzymes. In the evaluation of electronic charge perturbation several criterions, coming from different complementary measurement methods, were used. The evidences of an increase in the disturbance of the aromatic system were [11–16]:

a. In the IR and Raman spectra, a decrease in the number, wavenumber and/or intensities of the bands for metal complexes in comparison to the appropriate bands in the spectra of ligands. It is caused by a decrease in the force constants of the bonds and polarization of the bonds in the ring.
b. In the NMR spectra, a decrease in the chemical shifts for metal complexes in comparison to the appropriate chemical shifts in the spectra of ligands. It points at an increase in the screening of aromatic protons as a consequence of the circular current weakening.

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c. In the UV spectra, hipsochromic shifts of $\pi \rightarrow \pi^*$ bands of metal complexes in comparison to the spectra of ligands. This is caused by an increase in the energy gap between bonding and antibonding orbitals and a decrease in the delocalization energy in the ring.
d. An increase in the alternation of bond length and angles between carbon atoms in the ring, observed by X-ray analysis.

2. Experimental methods

The pyrrole-2-carboxylates were prepared by dissolving in high temperature (95 °C) the appropriate weighed amount of pyrrole-2-carboxylic acid in the aqueous solution of alkali metal hydroxides in a stoichiometric ratio 1:1. The anhydrous compounds were obtained after the evaporation of solutions on the vapour bath and drying at 110 °C in a dryer under reduced pressure.

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 were obtained with hydraulic press under 739 MPa pressure. Samples in water solutions were recorded by the use of ATR accessory. Raman spectra of solid samples in capillary tubes were recorded in the range of 400–4000 cm^{-1} with a FT-Raman accessory of Perkin–Elmer system 2000. The resolution of spectrometer was 1 cm^{-1}. The NMR spectra of D_2O saturated solution were recorded with Bruker unit at room temperature. DSS (sodium salt of 3-(trimethylsilyl)-1-propanesulphonic acid) was used as an internal reference.

To calculate optimized geometrical structures of pyrrole-2-carboxylic acid and lithium, sodium and potassium pyrrole-2-carboxylates a few quantum-mechanical methods were used: (i) density functional (DFT) hybrid method B3LYP with non-local correlation provided by Lee–Young–Parr expression, (ii) Møller-Plesset method (MP2). Optimized geometric structures for pyridine-2-carboxylic acid and its salts were calculated [10] at the density functional theory (DFT) hybrid method B3PW91 which uses the Becke's three-parameter functional with non-local correlation provided by the Perdew–Wang 91 expression. All calculations were carried out with functional base 6-311++G**. With regard to the limitation of 311++G** basis to H–Kr atoms, it was not possible to calculate the structure of Cs and Rb pyrrole-2-carboxylates. Calculations were performed using the GAUSSIAN 2003 package of programs [17] running on a SGI 2800 Supercomputer. Experimental spectra were interpreted in terms of calculated ones at Møller–Plesset method in MP2/6-311++G** level and literature data [18,19]. The vibrational bands of studied compounds were assigned according to the normal vibrations for pyrrole calculated in the MP2 level [20]. Theoretical wavenumbers were scaled according to the formula: $\nu_{scaled} = 0.955\nu_{calculated} + 25.7$ for MP2/6-311++G** level method [21] and $\nu_{scaled} = 0.98\nu_{calculated}$ for B3LYP/6-311++G** level method [19]. The chemical shifts were calculated using GIAO (gauge including atomic orbitals) method in the B3LYP/6-311++G** and MP2/6-311++G** level. Chemical shifts (δ_i) were calculated by subtracting the appropriate isotopic part of the shielding tensor (σ_i) from that of TMS (σ_{TMS}): $\delta_i = \sigma_{TMS} - \sigma_i$ (ppm). The isotropic shielding constants for TMS calculated by using the same basis set were equal to 31.8201 and 31.8945 ppm for the ^1H nuclei and 182.4485 and 198.5698 ppm for the ^{13}C nuclei, as calculated at the B3LYP and MP2 levels, respectively [17]. The electronic charge distribution were calculated by Natural Bond Orbital (NBO) [22] and Charges from Electrostatic Potentials using a Grid based method (CHelpG) [23] methods in B3LYP/6-311++G** and MP2/6-311++G** levels. Additionally the AIM theory of Bader [24] was used to localize bond critical points and to calculate their properties: electron densities at bond critical points ($\rho_{RCP}S$) and electron densities at ring critical points ($\rho_{RCP}S$). All AIM calculations [25,26] were performed using AIM2000 program [27]. The aromaticity indices (HOMA, I_6/I_5, pEDA) were calculated for optimal geometrical structures of pyrrole-2-carboxylates [28–33].

The **HOMA** (harmonic oscillator model of aromaticity) index differs from all other geometry-based ones by assuming another

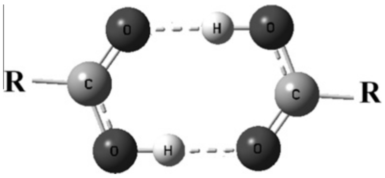


Fig. 1. The scheme of carboxylic acid dimer.

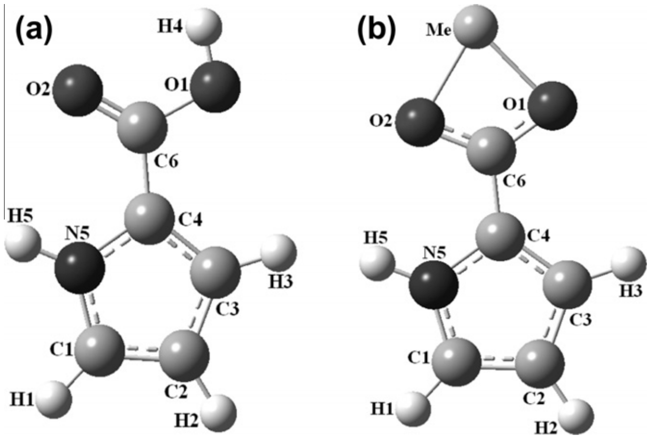
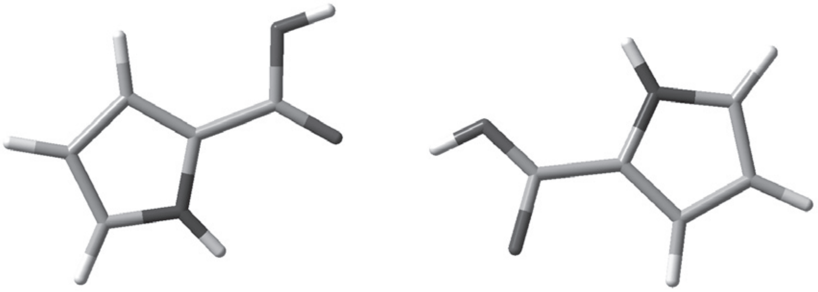


Fig. 3. Atom assignment for PCA (a) and pyrrole-2-carboxylates (b).



s-cis (*syn*) s-trans (*anti*)

Fig. 2. The structures of pyrrole-2-carboxylic acid monomer (*syn* and *anti* conformer).