Theoretical and experimental studies on selected 1,3-diazolium salts

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Abstract

An analysis of the molecular structures of the benzyl and adamantyl derivatives of 1,3-diazolium salts in solid state was carried out based on the detailed interpretation of their vibrational spectra. The description of IR and Raman spectra was supported by DFT (B3LYP) calculations of the unsubstituted and substituted imidazolium cations as models. These results allowed finding markers bands originated mainly from the stretching, rocking and wagging vibrations of the C2–H bond. Additionally, calculations of the heteroaromaticity (HOMA index) showed that cation formation causes dearomaticity of the imidazole ring. However, the substitution of the cationic species by the benzyl and adamantyl groups increases aromatic nature of the heterocyclic moiety. Moreover, the electron distribution performed using the GAPT method indicated the positive charge delocalization in the ring.

Keywords: Imidazolium salts; IR and Raman spectra; DFT calculation; Aromaticity; Atomic charges

1. Introduction

The 1,3-diazolium salts are widely used in many chemical processes and technologies. For example, they serve as ionic liquids in organic reactions, catalytic processes, and separation technologies [1]. Due to their biological activity group of them is applied as herbicides [2]. The most famous are the azolium derivatives that have been synthesized predominantly as
precursors of N-heterocyclic carbens in organometallic chemistry, ruthenium-mediated olefin metathesis and palladium cross-coupling chemistry [3]. Until now, studies on such molecular systems have been focused on synthesis of ligands and their metallocomplexes followed by crystallographic determination of their structures [4]. Only few papers of diazolium salts have reported some general remarks on conformational analysis, cycloaddition reactions or aromaticity of the unsubstituted azolium cations [5]. According to our best knowledge, there has been no explanation of experimental data, including spectroscopic analysis, by using quantum-chemical calculations [6].

Thus, as the subject of this work the following imidazolium salts were chosen: 1,3-dibenzylimidazolium chlorate(VII) ([Im(CH2C6H5)2]ClO4 and 1,3-di-1-adamantylimidazolium chlorate(VII) ([Im(Ad)2]ClO4 (see Scheme 1). These compounds possess different chemically and geometrically substituents.

To study the influence of the steric and electronic factors on the imidazolium cation and to afford a direct comparison between the different derivatives, we carried out the DFT calculations. The cationic forms were applied as a model structures for the unsubstituted diazolium ring ([ImH2]+) as well as the mentioned-above derivatives ([Im(CH2C6H5)2]+ and [Im(Ad)2]+). We performed simulation of vibrational spectra and calculated geometrical parameters, aromaticity and atomic charges. Theoretical results were compared to the available experimental data. It allowed us to determine molecular structure of both compounds and discuss the substituent effect on imidazolium cation.

2. Experimental

The synthesis of the compounds studied was performed as described elsewhere [7]. The elemental analysis for [Im(CH2C6H5)2]ClO4 is: C, 58.5%; H, 4.8%; N, 7.9%, found; and C, 58.5%; H, 4.9%; N, 8.0%, calculated. For [Im(Ad)2]-ClO4 is: C, 63.6%; H, 8.1%; N, 6.9%, found, and C, 63.2%; H, 7.6%; N, 6.4%, calculated.

For FT-Raman measurements, a few milligrams of the compound was placed in capillary tube and measured directly; 200 scans were collected (with a resolution of 4 cm⁻¹) for both compounds. Fourier transform mid-infrared (FT-MIR, 512 scans) and Fourier transform far-infrared (FT-FIR, 512 scans) spectra were run in KBr and low molecular weight polyethylene discs, respectively. Resolution was set at 4 cm⁻¹ (MIR) and 2 cm⁻¹ (FIR). FT-Raman spectra were recorded on a Bio-Rad step-scan spectrometer (FTS 6000) combined with a Bio-Rad Raman Accessory (FTS 40). Excitation at 1064 nm was made by a Spectra-Physics Topaz T10-106c cw Nd:YAG laser. FT-IR spectra were measured on Bruker (IFS 48) and Bio-Rad (FTS 60 V) spectrometers in the mid and far IR regions, respectively. The accuracy of the readings was ±1 cm⁻¹.

3. Computational methods

All calculations were performed using the Gaussian 03 set of programs [8]. The geometries and harmonic frequencies with their IR and Raman intensities were obtained by using the DFT method employing the hybrid B3LYP functional [9]. No imaginary frequencies for all structures proved that the applied models are at their potential energy minima. The 6-31G basis set was used in computations, with one additional set of polarization as well as diffusion function on the heavy atoms [6-31+G(d)]. To adjust for anharmonicity effects, the computed frequencies were scaled by the factor of 0.96 for the stretching modes of C–H and N–H bonds [10]. The modes in the 0–2000 cm⁻¹ region of the IR and Raman spectra were scaled by the factor of 0.98. Since only Raman scattering activities are obtained from the Gaussian outputs, the following expression [11] was used to determine the theoretical Raman intensities: 

\[ I_i = \left(10^{-12}(\nu_0 - \nu_i)\right)^4 / (\nu_i R_{A_G}) \]

where: \(I_i\) — Raman intensity, \(R_{A_G}\) — Raman scattering activities, \(\nu_i\) — wavenumber of the normal modes; \(\nu_0\) — wavenumber of the excitation laser. Program Gar2ped [12] was used for calculation of potential energy distribution (PED) of normal modes in terms of natural internal coordinates evaluated by Pulay and Fogarasi [13]. The PED calculations were carried out for [ImH2]+ and [Im(CH2C6H5)2]+ only. Due to limitation of the internal coordinates for fused rings present in the adamantane molecule, the description of the vibrational spectra of [Im(Ad)2]+ was based on visualization (Molekel program [14]). Atomic charges were obtained using Generalized Atomic Polar Tensors (GAPT) elaborated by Cioslowski [15]. This method, similarly to the other quantum methods, distributes the electron density among atoms in a molecule. Furthermore, the GAPT method sums charges up to the total charge of a molecule and reflects its symmetry. The most popular in aromaticity studies is the Harmonic Oscillator Model of Aromaticity (HOMA) index [16]. It is computed according to the following equation:

\[ \text{HOMA} = 1 - \left[ (\alpha(R_{\text{opt}} - R_{\text{ave}})^2 - \alpha) / (n\sum(R_{\text{ave}} - R_i)^2) \right] = 1 - \text{EN} - \text{GEO}, \]

where \(\alpha\) is an empirical factor and \(R_{\text{opt}}, R_i\) and \(R_{\text{ave}}\) are optimal bond lengths, bond lengths in a real system and average bond lengths, respectively, and \(n\) is the number of bonds. Two effects can decrease aromaticity of a molecule, e.g. bond length alternation (GEO factor) and bond length elongation (EN factor). For the aromaticity determination,
experimental as well as theoretical bond lengths can be used. In the case of the diazolium salts studied here, crystallographic data are not available. Therefore, the calculated geometrical parameters were applied to evaluate their HOMA index.

4. Results and discussion

4.1. Geometries

The elemental analysis did not show the presence of the other species than the diazolium and chlorate(VII) ions. For this reason and because of the steric bulk of the adamantyl and benzyl substituents, the presence of strong electrostatic interaction (H-bonding, π-stacking) between cation and anion can be excluded. Moreover, the available crystallographic data for other diazolium salts indicate that the distance cation–anion is in the range of 3–4 Å [17–19]. Therefore, the interactions between ions are neglected and cationic species are used as models in calculations (Fig. 1). Symmetry Cs is imposed for [ImH₂]⁺ and [Im(CH₂C₆H₅)₂]⁺ and C₂ for [Im(Ad)₂]⁺ during the optimization process. The values of bond lengths and valence angles of the imidazolium cation are given in Table 1 and the atom numbering in Fig. 1.

Calculated structural parameters show that introduction of two different chemically substituent groups on the imidazolium cation causes insignificant changes in bond distances (0.001–0.005 Å) as well as in angles (1–3°). It indicates that only steric effect of the benzyl and adamantyl groups on the imidazolium ring may play role in any changes of the cation structure.

4.2. GAPT charge distribution

Table 2 shows the atomic charges of the imidazolium cation (the complete data for all atoms are given in Table I in Supplementary Materials). The C₂ atom, which is a potential site of the carbene center or metal coordination, shows a strong positive charge (+0.225 a.u. for [ImH₂]⁺) that increases by ~0.8 a.u. in the substituted derivatives. Similarly to the discussed geometry, the same increase of the charge on this atom does not indicate an effect of the chemical character of the substituents. On the other hand, the charge of the hydrogen atom adjacent to C₂ is close to charges of the other hydrogen atoms of the heterocyclic ring. The charge values on C₄ and C₅ are typical for organic molecules (close to zero). The negative charge on the nitrogen atoms (~0.239 a.u.) causes the relatively high decrease of the electron distribution on their hydrogen atoms (+0.325). After substitution, the nitrogen charge increases significantly to ~0.425 a.u. for the benzyl, and...
−0.432 a.u. for adamantyl derivatives. Simultaneously, the electron density on adjacent carbon atoms of the substituents falls down to ca. +0.58 and +0.45 a.u. from 0.1 a.u., for [Im(CH₂C₆H₅)₂]⁺ and [Im(Ad)₂]⁺, respectively. Despite those atoms bonded to the ring nitrogen atoms, the electron density on the other atoms of the substituent molecules remains unchanged. Moreover, the electron distribution indicates delocalization of the positive charge in the diazolium cations between C₂ and the carbon atoms of the substituents attached to the ring nitrogen atoms.

4.3. HOMA aromaticity

As mentioned above, the aromaticity of the heterocyclic and aromatic rings were determined by using the HOMA index and can be calculated using the available experimental as well as theoretical bond distances. Table 3 shows the values of HOMA, GEO and EN terms for the compounds studied here. To compare, the experimental data are used to compute the heteroaromaticity of the unsubstituted imidazole [18] and imidazolium cation [19]. These results indicate dearomaticity (by 0.09) of the heterocyclic ring to cation formation. On the other hand, the discrepancy (0.07 unit) between the HOMA values of the “neat” cation obtained by using computed and experimental geometries [19] is due to the fact that the latter refers to the imidazolium cation surrounded by the H-bonded sulfate anions and the first refers to a single cation molecule. Upon substitution, aromaticity of compounds studied here increases by factor of 0.01 for the benzyl derivative and remains almost unchanged for the adamantyl one. These changes are caused mainly by decrease of the bond length alternation (GEO factor). The larger change of aromaticity in [Im(CH₂C₆H₅)₂]⁺ in comparison to [Im(Ad)₂]⁺ can also result from the close vicinity of phenyl π-electrons to the imidazolium ring. The HOMA index was calculated also for the phenyl rings in [Im(CH₂C₆H₅)₂]⁺. Their aromaticity decrease slightly by 0.03 unit comparing to the benzene molecule (HOMA = 1).

4.4. IR and Raman spectra

Infrared and Raman spectra of [Im(CH₂C₆H₅)₂]ClO₄ and [Im(Ad)₂]ClO₄ are presented in Figs. 2 and 3, respectively. The theoretical spectra (B3LYP/6-31+G(d)) for the models are also given for comparison. The analysis of the most characteristic normal modes of the studied compounds is presented in Table 4 (the full description of the spectra with the internal coordinates’ definitions is given in the Supplementary Materials, Tables II–V).

The match between the theoretical and experimental spectra for both compounds is fairly good. It shows that the applied model structure neglecting the cation–anion interaction can be
used for the cationic organic compounds. The analysis of the
normal modes allows proposing marker bands that can be
useful in the further examination of the diazolium salts.

4.4.1. The C2–H vibrations

The most interesting modes are those related with the C2–H
bond (see the numbering in Fig. 1) which should vanish in
vibrational spectra of diazolium carbens and metallocom-
plexes. Therefore, the stretching [\(\nu(C2–H)\)], rocking [\(\rho(C2–H)\)]
and wagging [\(\omega(C2–H)\)] are discussed below. The calculation
for the imidazolium cation [\(\text{Im}(\text{H})_2^+\)] clearly indicates that
\(\nu(C2–H)\) is an isolated vibration (97\% PED) expected at
3179 cm\(^{-1}\) as a weak and a medium intensity band in IR and
Raman spectra, respectively. The DFT results predict that the
substitution of the benzyl group shifts this mode slightly by
8 cm\(^{-1}\) to the lower wavenumber range, while the effect of the
adamantyl group is more significant (the blue-shift by
47 cm\(^{-1}\)). However, the IR and Raman intensities of \(\nu(C2–H)\)
for both compounds decrease substantially preventing from
their unambiguous identification in the experimental spectra,
especially for [\(\text{Im}(\text{Ad})_2\)]\(^+\). Thus, \(\nu(C2–H)\) is assigned only
to FT-IR and FT-Raman bands of \(\text{Im}(\text{CH}_2\text{C}_6\text{H}_5)_2\)]\(^+\) at
3142 cm\(^{-1}\). As can be seen from Table 4, the rocking [\(\rho(C2–H)\)]
and wagging [\(\omega(C2–H)\)] vibrations of the derivatives studied
here are also shifted in comparison to “the neat” diazolium
ring. Among them, only \(\rho(C2–H)\) of [\(\text{Im}(\text{Ad})_2\)]\(^+\) occurs as a

Fig. 3. IR and Raman spectra of [\(\text{Im}(\text{Ad})\text{ClO}_4\): (A) Theoretical Raman spectrum; (B) Experimental Raman spectrum; (C) Experimental IR spectrum; (D) Theoretical
IR spectrum. (\(^*\)) Denotes \(\text{ClO}_4^−\) vibrations; (\(^**\)) band originates from water in KBr.

Table 4

<table>
<thead>
<tr>
<th>[(\text{H}_2\text{Im})](^+)</th>
<th>[(\text{Im}(\text{CH}_2\text{C}_6\text{H}_5)_2)](^+)</th>
<th>[(\text{Im}(\text{Ad})_2)](^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_{\text{calc}}) (%PED)</td>
<td>(\rho_{\text{IR}})</td>
<td>(\rho_{\text{R}})</td>
</tr>
<tr>
<td>3179(97)</td>
<td>14.9</td>
<td>35.2</td>
</tr>
<tr>
<td>1178(49)</td>
<td>vvw</td>
<td>4.4</td>
</tr>
<tr>
<td>833(59)</td>
<td>vvw</td>
<td>vvw</td>
</tr>
<tr>
<td>716(30)</td>
<td>43.0</td>
<td>vvw</td>
</tr>
<tr>
<td>1603(38)</td>
<td>15.7</td>
<td>1.9</td>
</tr>
<tr>
<td>1537(60)</td>
<td>2.7</td>
<td>vvw</td>
</tr>
<tr>
<td>1110(36)</td>
<td>7.4</td>
<td>vvw</td>
</tr>
<tr>
<td>1049(48)</td>
<td>11.1</td>
<td>vvw</td>
</tr>
<tr>
<td>919(83)</td>
<td>vvw</td>
<td>1.3</td>
</tr>
<tr>
<td>902(89)</td>
<td>vvw</td>
<td>2.1</td>
</tr>
<tr>
<td>612(80)</td>
<td>vvw</td>
<td>vvw</td>
</tr>
<tr>
<td>611(70)</td>
<td>14.7</td>
<td>vvw</td>
</tr>
</tbody>
</table>

\(\rho_{\text{IR}}\) and \(\rho_{\text{R}}\) indicate the relative intensity (in \%) of theoretical bands in respect with the strongest one.
very intense IR band (1155 cm\(^{-1}\)) what is consistent with our calculation (1122 cm\(^{-1}\)). On the other hand, \(\omega(C_2-H)\) is assigned to the medium-intense IR band at ca. 820 cm\(^{-1}\) for both imidazolium derivatives. Again, calculations predict this frequency very well (801 and 802 cm\(^{-1}\) for [Im(CH\(_2\)C\(_6\)H\(_5\))\(_2\)]\(^+\) and [Im(Ad)\(_2\)]\(^+\), respectively).

4.4.2. The imidazolium ring vibrations

According to the Pulay’s and Fogarasi’s definition of the internal coordinates, the motions of the 5-membered ring are as follows: the stretching modes of its bonds \((\nu)\), two deformations in-plane \([\beta_1(R_3), \beta_2(R_3)]\) and two deformations out-of-plane \([\gamma_1(R_3), \gamma_2(R_3)]\). The characteristic vibration of the heterocyclic ring is stretching mode of the \(C\equiv C_3\) bond \([\nu(C_4\equiv C_3)]\). For both studied compounds, \(\nu(C_4\equiv C_3)\) is observed at the same wavenumber (\(~1560 \text{ cm}^{-1}\)) in IR and Raman spectra. It is found to be in excellent agreement with DFT calculations that predict the same frequency and intensity of this mode (\(1564 \text{ cm}^{-1}\)) for both compounds. Upon substitution, this vibration is red-shifted by ca. 40 cm\(^{-1}\) with reduction in intensity. For the benzylic derivative, the out-of-phase stretching of the \(\text{N}_1\text{C}_2\text{N}_3\) fragment (PED: 50\%) is assigned to the same bands as \(\nu(C_4\equiv C_3)\) (FT-IR: 1558 cm\(^{-1}\); FT-Raman: 1560 cm\(^{-1}\)). It is consistent with our calculations that predict frequency of \(\nu(C_2\equiv N_1)\) and \(\nu(C_2\equiv N_3)\) red-shifted by 4 cm\(^{-1}\) comparing to \(\nu(C_4\equiv C_3)\). However, for [Im(Ad)\(_2\)]\(^-\)ClO\(_4\), the out-of-phase \(\nu(C_2\equiv N_1)\) and \(\nu(C_2\equiv N_3)\) are present as a single IR medium band at 1539 cm\(^{-1}\) (calc. 1541 cm\(^{-1}\)). Calculation for [ImH\(_2\)]\(^+\) suggests that these modes should be found at 1537 cm\(^{-1}\). This slight shift can imply an increase of the “double” character of \(C_2\equiv N\) bonds after the substitution. Smaller contribution (\(~15\%) of \(\nu(C_2\equiv N_1)\) is also observed for several experimental bands in the range 1340–1460 cm\(^{-1}\). The strong-intensity bands at 1149 and 1155 cm\(^{-1}\) in the experimental spectra of [Im(CH\(_2\)C\(_6\)H\(_5\))\(_2\)]ClO\(_4\) and [Im(Ad)\(_2\)]-ClO\(_4\), respectively, are assigned to the out-of-phase stretches of the \(C_2\equiv N_1\) and \(C_2\equiv N_3\) bonds (calc. 1128 and 1122, respectively). Their contribution to these normal modes is small (\(~20\%) PED). It is worth noting that DFT calculations predict these bands as the most intense in the theoretical IR spectra and it is consistent with the experimental spectra. On the other hand, the in-phase counterparts are observed in Raman spectra as strong and weak-intensity bands at 1028 (\([\text{Im}_4(\text{CH}_2\text{CH}_4\text{H}_5)_2]\text{ClO}_4\)) and 1079 cm\(^{-1}\) (\([\text{Im}(\text{Ad})_2]\text{ClO}_4\)). The next characteristic modes of the imidazolium ring are those representing its bending motions. Our calculations indicate that all of them \([\beta_1(R_3), \beta_2(R_3)], \gamma_1(R_3), \gamma_2(R_3)]\) should be observed in vibrational spectra as very weak bands. Those with the greatest contribution in potential energy of the normal modes are predicted at: 919 \([\beta_1(R_3), 83\%], 902 \([\beta_2(R_3), 89\%], 612 \[\gamma_1(R_3), 80\%], \text{and } 611 \text{ cm}^{-1} \[\gamma_2(R_3), 70\%], \text{for } [\text{ImH}_2]^+\). Magnitude and direction of the wavenumber shifts of those vibrations is similar for both compounds in respect with the “ neat” imidazolium cation (see Table 4). The greatest change in the positions of bands is observed rather for the in-plane deformation of the ring than for its out-of-plane bend.

4.4.3. The substituents’ vibrations

In the studied [Im(CH\(_2\)C\(_6\)H\(_5\))\(_2\)]ClO\(_4\), the phenyl rings are bonded to the imidazolium cation through the methylene groups. According to DFT calculations, the stretching modes of the \(CH_2\) group (asymmetric, symmetric, in-phase and out-of phase) are observed as the broad IR band with maximum at 2924 cm\(^{-1}\) and as weak- and medium-intensity Raman bands at 3003 and 2968 cm\(^{-1}\). On the other hand, the methylene scissoring vibrations \([\nu(CH_2)]\) are present in IR and Raman spectra at 1496 cm\(^{-1}\) (calc. 1484 (in-phase) and 1480 cm\(^{-1}\) (out-of-phase)).

Typical range for the stretches of the phenyl \(C-H\) bonds is 3100–3000 cm\(^{-1}\). As calculated, these vibrations are responsible for the strong and broad Raman band with maximum at 3067 cm\(^{-1}\) and the weak IR band at 3084 cm\(^{-1}\). Moreover, the wagging mode \([\omega(C-H)_{R6}]\) is sensitive to substitution of benzene. For the mono-substituted benzene, \([\omega(C-H)_{R6}]\) is expected to be at ca. 750 and 700 cm\(^{-1}\). Calculations show that this vibration is observed as IR bands at 697 and 752 cm\(^{-1}\) (calculated: 703 cm\(^{-1}\), 36\% PED and 736 cm\(^{-1}\), 36\% PED, respectively). Still, the agreement is considered to be fairly good with the relative differences in experimental and calculated frequencies by ca. 2\%. On the basis of the theoretical data, the stretches of the \(C-C\) bonds appears clearly as bands in Raman spectrum of [Im(CH\(_2\)C\(_6\)H\(_5\))\(_2\)]ClO\(_4\) at 1605 and 1587 cm\(^{-1}\) (DFT: 1621 and 1606 cm\(^{-1}\), respectively). The former corresponds to the symmetric stretching of \(C_2\equiv C_3\) and \(C_5\equiv C_6\) bonds (numbering as follows: \(C_1\) is a carbon atom of the phenyl ring substituted by the \(CH_2\) group). According to PED, the band at 1605 cm\(^{-1}\) originates from two normal modes with the same frequency but different phase motion (see Table IV in Supplementary Materials). The mode at 1587 cm\(^{-1}\) is represented by the asymmetric stretching of the other \(C-C\) bonds than \(C_2\equiv C_3\) and \(C_5\equiv C_6\) (68\% PED). Similarly, the breathing vibration of the phenyl ring is predicted as two normal modes with the same energy but different phase of movement. It is present as an isolated mode (over 60\% PED) at 1003 cm\(^{-1}\) in Raman spectrum (calc. 997 cm\(^{-1}\)). The out-of-plane deformations of the ring (ca. 30\% PED) are observed mainly in IR lower-frequency range (483–413 cm\(^{-1}\)) and are assigned to the experimental weak-intensity bands at 476 and 460 cm\(^{-1}\).

As was mentioned above, it is impossible to define internal coordinates of [Im(Ad)\(_2\)]\(^+\). Moreover, the adamantyl group is a complex polycyclic hydrocarbon for which 72 normal modes are expected. To identify vibrations of this substituent in [Im(Ad)\(_2\)]ClO\(_4\), the B3LYP calculation (6-31+G(d) basis set) was performed for the adamantane molecule itself. Theoretical spectra with assignment of calculated bands are shown in Fig. 4. Based on this, experimental strong-intensity and broad bands with maxima at 2913 (IR) and 2926 cm\(^{-1}\) (Raman) are assigned to the asymmetric \(-CH_2-\) stretches \([\nu(CH_2)_{\text{as}}]\) and \(>CH-\) stretches \([\nu(CH)_{\text{as}}]\) (calc. range: 2963–2944 cm\(^{-1}\)). \(\nu(CH)_{\text{as}}\) is observed as IR and Raman medium bands at 2853 cm\(^{-1}\) (calc. range: 2921–2902 cm\(^{-1}\)). Comparison of calculation for [Im(Ad)\(_2\)]\(^+\) and adamantane indicates that the stretching \(C-H\) vibrations are shifted to the lower frequencies by ca. 40 and
20 cm\(^{-1}\) in the [Im(Ad)\(_2\)]\(^+\) spectra. Bands observed at 1454 (Raman) and 1439 cm\(^{-1}\) (IR) are attributed to in-phase scissoring mode of the CH\(_2\) groups (calculated: 1486 and 1473 cm\(^{-1}\), respectively). They are insensitive to the substitution of adamantane for that DFT calculation predicts these vibrations at 1488 and 1474 cm\(^{-1}\). Vibrations of –CH\(_2–\) groups appear also in range 1391–1271 cm\(^{-1}\). In this region of vibrational spectra, the rocking \[ r(CH_2) \] and wagging \[ v(CH_2) \] modes of the adamantyl group are also expected. Our calculations indicate that they couple with \( r \) and \( v \) of the imidazolium ring. The most characteristic mode of the adamantyl moiety is skeletal stretching vibration \[ n(C–C)_{Ad} \] found in the theoretical Raman spectrum at 739 and 752 cm\(^{-1}\), for adamantane and [Im(Ad)\(_2\)]\(^+\), respectively. In the experimental spectrum of [Im(Ad)\(_2\)]ClO\(_4\), this mode is observed at 770 cm\(^{-1}\). Several weak intensity bands below 684 cm\(^{-1}\) (Raman spectrum) include chiefly skeletal deformation of the adamantyl rings \[ \beta(C=C–C)_{Ad} \].

5. Summary

B3LYP method is showed to be an effective tool for interpreting and predicting IR and Raman spectra of such large molecular systems as studied here. Our DFT-based analysis reproduces the experimental vibrational spectra of the imidazolium derivatives with the error less than 5%. Moreover, we present the detailed description of these spectra and discuss changes of characteristic modes frequencies of the imidazolium ring upon substitution. Our studies indicate also that the most useful range is the mid-infrared region of the spectra (presence of marker bands). Comparison of the calculated vibrational spectra of [Im(CH\(_2\)C\(_6\)H\(_5\))\(_2\)]\(^+\) and [Im(Ad)\(_2\)]\(^+\) to the results obtained for the unsubstituted imidazolium cation indicate significant shifts of the ring vibrations. For instance: 23 cm\(^{-1}\) for \( v(C=C–C) \) and ca. 40 cm\(^{-1}\) for the out-of-phase stretching of the N\(_1–C_2–N_3\) fragment. Moreover, these shifts of the ring mode frequencies are very similar for both compounds, except \( v(C_2–H) \) (55 cm\(^{-1}\) of difference between [Im(CH\(_2\)C\(_6\)H\(_5\))\(_2\)]\(^+\) and [Im(Ad)\(_2\)]\(^+\)). Geometrical parameters show only small effect of the benzyl and adamantyl substituents on structure of the imidazolium cation. The bonds in N\(_1–C_2–N_3\) moiety are equal to each other and shorter than N\(_1–C_3\) and N\(_3–C_4\). It is consistent with proposed electron delocalization over the imidazolium moiety. According to the HOMA calculations, the aromaticity of the imidazolium ring is 0.87 and 0.88 units for the adamantyl and benzyl derivatives, respectively. It shows that this heterocyclic ring belongs to aromatic compounds. The larger increase of the heteroaromaticity for [Im(CH\(_2\)C\(_6\)H\(_5\))\(_2\)]\(^+\) is due to presence of \( \pi \)-electron system (phenyl ring) bonded to the imidazolium ring. In the case of atomic charges, the influence of the substituted groups is negligible. Our GAPT calculations indicate also that positive charge of the imidazolium ring is delocalized between the C\(_2\) and carbon atoms of the substituents attached to the imidazolium nitrogen atoms.

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Appendix A. Supplementary data

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