# Crystal structure of 1,3-dialkyldiazolium bromides*

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Systematic X-ray diffraction study of the crystal structures of 1,3-dialkylimidazole-based ionic liquids containing the $Br^-$ anion was performed. Analysis of the influence of the nature of the cation on the formation of a hydrogen bond system and the supramolecular arrangement of ions demonstrated that not only CH···Br contacts but also anion—π-system and CH—π-system interactions exist in the crystalline state. Conclusions were drawn on the character of changes in the melting point in a series of bromide ionic liquids containing the imidazolium cation.

**Key words:** ionic liquids, imidazolium salts, cation—anion contacts, melting point, packing, X-ray diffraction study.

Solvents used in chemical synthesis have a strong, sometimes decisive, influence on the reaction kinetics and mechanism and the electronic and geometric structures of the resulting compounds. However, most solvents traditionally used in chemistry are flammable, volatile, highly toxic, and environmentally dangerous. In this connection, a search for new reaction media with controlled physicochemical properties is an urgent problem.

The use of supercritical solvents (carbon dioxide) or ionic liquids instead of usual solvents is one of approaches to environmentally sound technologies, which is actively developed in recent years.[1] Ionic liquids (IL) are low-melting salts (m.p. < 150 °C) consisting of a bulky organic cation and an organic or inorganic anion. These salts are characterized by low melting points (below –96 °C, Table 1), low vapor pressure, and good dissolving ability for various classes of compounds,[2,3] as well as by high chemical and thermal stability and low toxicity.[4] In addition, IL are characterized as promising solvents, because they can stabilize systems unstable in usual organic solvents[5] and exhibit catalytic activity in different reactions.[6]

In spite of the fact that IL hold considerable promise as solvents and catalytic systems, the structures of these salts are poorly known. Based on IR spectroscopic data, it was assumed that the imidazole ring is substantially distorted with attendant loss of aromaticity, and the possible systems of hydrogen bonds between ions in the crystalline state were discussed.[7] The IR spectra of IL containing halogen atoms as anions show an absorption band at 3050 $cm^{-1}$, which was assigned to strong CH···$Cl^-$ hydrogen bonds. The absence of this band in the spectra of salts containing the $UCl_6^{2-}$ and $UO_2Cl_4^{2-}$ anions was, on the contrary, attributed to the absence of hydrogen bonding.[7] A structural model of IL was proposed.[8] According to this model, the ions are organized to form oligomeric chains so that the anions are located above and below the plane of the imidazole ring. In terms of this model, hydrogen bonds are absent, and contacts between ions are assigned only to Coulomb interactions between the ions. First reliable information on the structures of IL in the crystalline state was obtained for 1-ethyl-3-methylimidazolium iodide ((Emim)I).[9] The IR spectrum of this compound shows an absorption band at 3080 $cm^{-1}$ both in the liquid and solid states, which is consistent with the results of the study.[7] The ionic liquid (Emim)I crystallizes in the mono-

**Table 1.** Melting points of selected inorganic salts, organic salts, and alloys

| Salt* | M.p./°C | Reference |
|---|---|---|
| $[C_2NH_3]NO_3$ | 12 | 1b |
| $[C_6(C_2)_3N]Br$ | 108 | 1c |
| $[C_6(C_2)_3N](CF_3SO_2)_2N$ | –81 | 1c |
| [Mmim]Cl | 125 | 1d |
| [Emim]Cl | 87 | 1d |
| [Bmim]Cl | 65 | 1d |
| [Bmim]Cl/$AlCl_3$ (0.33/0.67) | –96 | 1e |
| [Bmim]$(CF_3SO_2)_2N$ | –4 | 1f |
| [Hpy]Br | 200 (decomp.) | 1g |
| [Hpy]Cl | 145 | 1g |
| [Hpy]$(CF_3SO_3)$ | 221 | 1g |
| [Ppy]Br | 76 | 1g |

* Mmim is 1,3-dimethylimidazolium, Emim is 1-ethyl-3-methylimidazolium, Bmim is 1-butyl-3-methylimidazolium, Hpy is pyridinium, and Ppy is *N*-propylpyridinium.

* Dedicated to Academician O. M. Nefedov on the occasion of his 75th birthday.

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clinic space group with one ionic pair per asymmetric unit. An analysis of the crystal packing demonstrated that the anion is not located above the plane of the imidazole ring; instead, it forms CH···I contacts, the strongest interaction being observed for the hydrogen atom at position 2 of the imidazole ring (H···I, 2.9 Å). In addition, the mass spectrum of this compound has intense peaks corresponding to the $[Emim]^+$ and $[(Emim)_2I]^+$ ions, which was attributed[7] to hydrogen bonding in the gas phase.

Further studies demonstrated that the crystal structures and properties of IL are determined by the nature of the constituent cations and anions.[10] Initially, studies of these salts were aimed at lowering the melting point. As a result, we formulated general rules relating the structure and composition of IL to the melting point. A lowering of the symmetry of the cation, the presence of long alkyl substituents, and a strong charge delocalization lead to a decrease in the melting point, whereas methylation of the cation at any position causes an increase in the melting point. More recently, it has been found[1e] that there are about $10^{18}$ possible combinations of cations and anions involved in IL with a rather wide range of properties. Taking into account general tendencies to use solvents in different chemical reactions, the requirements to the necessary set of physicochemical properties of IL presently include thermal stability (>200 °C), a low melting point, and good dissolving ability for various organic, organometallic, and inorganic compounds.

According to the published data,[1e] phosphine and pyridine hydrochlorides are the most easily prepared IL. However, the high melting points of these compounds (Tables 1 and 2) and their tendency to undergo deprotonation in the presence of bases limit their use in chemical reactions. Ammonium salts also belong to IL. The melting points of these salts vary in a broad range;

**Table 2.** Thermal stability of selected ionic liquids

| Salt | $T_d$/°C[a] | Reference |
|---|---|---|
| [Hpy]Br | 200[b] | 1g |
| $[Hpy]ClCrO_3$ | 205[b] | 1g |
| $[C_{14}H_{29}Et_3N]Br$ | 170 | 1h |
| $[C_{16}H_{33}EtMe_2N]Br$ | 180 | 1h |
| [Bpy]Cl[c] | 190 | — |
| $[Emim](CF_3SO_2)_2N$ | 440 | 1f |

[a] $T_d$ is the temperature at which decomposition begins and corresponds to the 10% weight loss calculated from dynamic TGA in air.
[b] $T_d$ is the melting point.
[c] Bpy is *N*-butylpyridinium.

however, these IL are thermally less stable. Thermally more stable salts of 1,3-dialkyl-substituted imidazole and *N*-substituted pyridine (see Tables 1 and 2) belong to another known class of IL, which is often used in organic synthesis. Since the structure of the imidazolium cation can be widely varied, it is possible to prepare IL with lower melting points compared to the corresponding pyridinium salts (see Table 1) and with a wider range of properties.[1d]

Both small stable anions, such as $Hal^-$, $PF_6^-$, $BF_4^-$, and $MHal_4^-$, and more complex anions, such as $CF_3SO_3$, $(CF_3CF_2)_3PF_3$, *etc.*, are used in IL. The physicochemical properties of ionic solvents can be varied over a wide range by varying the nature of anions.[1] Taking into account the fact that most of anions are generated by ion-exchange reactions from bromide or chloride IL and the fact that imidazole-containing IL are most promising solvents for practical use, we chose 1,3-dialkylimidazolium bromides as objects of investigation (Fig. 1). The use of the bromide anion bearing a localized charge makes it

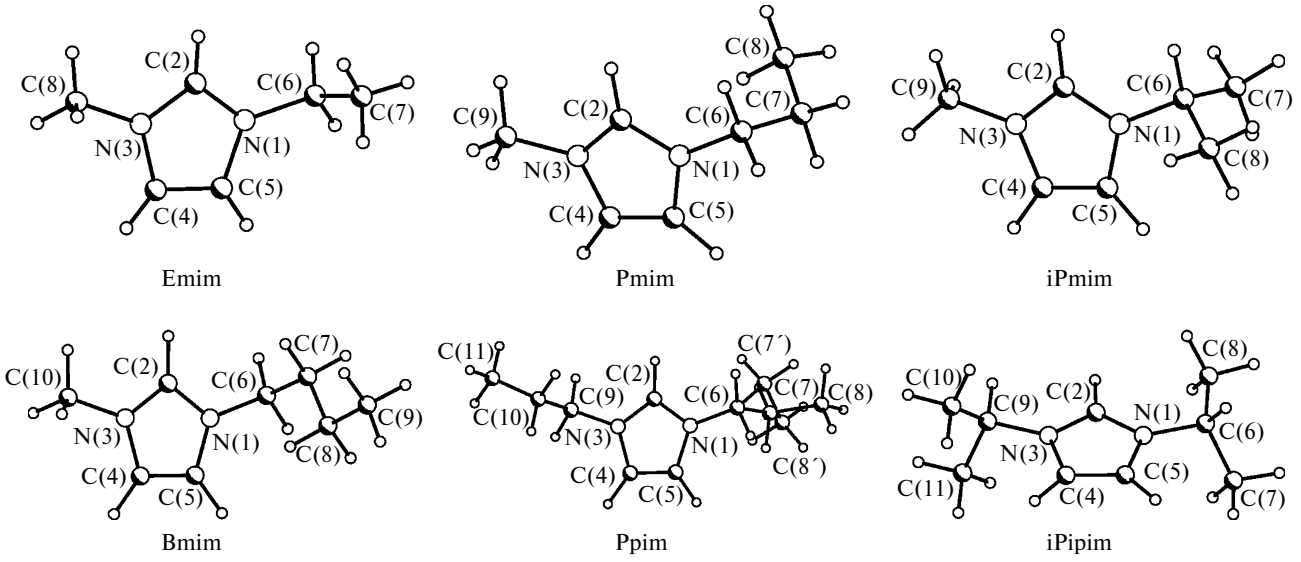


**Fig. 1.** Structures of the imidazolium cations in the crystals of bromide ionic liquids.

possible to exclude additional coordination centers typical of $PF_6^-$ or $BF_4^-$.

In spite of a high interest in IL, a systematic analysis of the structures of series of these compounds and their properties is lacking in the literature. As part of systematic studies of the structures of IL in the crystalline state, we made an attempt to relate the molecular structures of cations in IL to the types of crystal packings and the melting points of the salts.

## Experimental

X-ray diffraction studies were carried out at 120 K on a SMART 1000 CCD diffractometer (λ(Mo-Kα) = 0.71072 Å, ω-scanning technique). The X-ray data were processed and merged using the SAINT Plus[11] and SADABS program packages.[12]

The structures were solved by direct methods and with the use of successive electron density maps. The refinement was carried out against $F^2_{hkl}$ with anisotropic displacement parameters for all nonhydrogen atoms and isotropic displacement parameters for hydrogen atoms. All calculations were performed with the use of the SHELXTL 5.10 program package.[13a] Principal crystallographic parameters and the structure refinement statistics are given in Table 3. The contacts were analyzed based on the atomic radii.[13b]

Quantum chemical calculations were performed by density functional theory (DFT) with the use of the B3PW91 hybrid functional and the 6-311G* all-electron triple-zeta basis set taking into account the polarization functions on nonhydrogen atoms. The geometry optimization was carried out with the use of the Gaussian98 program package.[14] The electron density topology was analyzed and the atomic charges were calculated in terms of Bader's Atoms in Molecules theory[15] using the MORPHY98 program.[16]

## Results and Discussion

We chose the 1-ethyl-3-methylimidazolium cation as a model compound, because, on the one hand, it con-

**Table 3.** Crystallographic parameters and the X-ray data collection and refinement statistics

| Parameter | Emim | Pmim | iPmim | Bmim | Ppim | iPipim |
|---|---|---|---|---|---|---|
| Molecular formula | $C_6H_{11}BrN_2$ | $C_7H_{13}BrN_2$ | $C_7H_{13}BrN_2$ | $C_8H_{15}BrN_2$ | $C_9H_{17}BrN_2$ | $C_9H_{17}BrN_2$ |
| Molecular weight | 191.08 | 205.10 | 205.10 | 219.13 | 233.16 | 233.16 |
| Color, crystal shape | Colorless prisms | | | | | |
| Diffractometer | «SMART 1000 CCD» | | | | | |
| Scanning mode | ω | | | | | |
| $T$/K | 110 | | | | | |
| Crystal dimensions/mm$^3$ | 0.27×0.26×0.21 | 0.28×0.23×0.22 | 0.32×0.29×0.28 | 0.31×0.27×0.18 | 0.27×0.24×0.18 | 0.30×0.29×0.24 |
| Crystal system | Monoclinic | | Orthorhombic | | | Monoclinic |
| Space group | $P2_1/c$ | $Pca2_1$ | $P2_12_12_1$ | $Pna2_1$ | $P2_1/c$ | $P2_1/n$ |
| Unit cell parameters | | | | | | |
| $a$/Å | 8.698(2) | 11.076(3) | 7.5865(5) | 10.034(4) | 8.738(4) | 8.033(4) |
| $b$/Å | 7.903(1) | 6.897(2) | 10.7364(7) | 11.784(4) | 9.057(3) | 9.962(5) |
| $c$/Å | 12.465(2) | 11.661(3) | 11.1846(7) | 8.386(3) | 14.888(5) | 14.235(7) |
| β/deg | 109.257(3) | 90 | 95.45(1) | 106.328(9) | | |
| $V$/Å$^3$ | 808.9(2) | 890.8(4) | 911.0(1) | 991.5(6) | 1172.9(8) | 1093.2(10) |
| $Z$ ($Z'$) | 4 (1) | | | | | |
| $F$(000) | 384 | 416 | 416 | 448 | 480 | 480 |
| $\rho_{calc}$/g cm$^{-3}$ | 1.569 | 1.529 | 1.495 | 1.468 | 1.320 | 1.417 |
| Absorption coefficient, μ/cm$^{-1}$ | 50.02 | 45.48 | 44.47 | 40.91 | 34.63 | 37.15 |
| $T_{min}/T_{max}$ | 0.2823/0.3501 | 0.2963/0.3681 | 0.2633/0.2881 | 0.2933/0.4791 | 0.4083/0.5361 | 0.2733/0.3281 |
| θ Angle range | 2.48—30.00 | 3.48—30.02 | 2.63—30.00 | 2.67—26.01 | 2.64—27.12 | 2.7—28.20 |
| Number of observed reflections | 4672 | 5199 | 10841 | 2996 | 4842 | 12538 |
| Number of independent reflections | 2266 | 2414 | 2646 | 1223 | 2511 | 3173 |
| Number of reflections with $I > 2s(I)$ | 1575 | 2052 | 2313 | 965 | 1698 | 2651 |
| Number of parameters | 84 | 144 | 144 | 101 | 135 | 177 |
| $R_1$ | 5.72 | 2.84 | 2.88 | 3.30 | 5.22 | 2.63 |
| $wR_2$ | 14.76 | 6.26 | 6.32 | 7.57 | 12.83 | 6.03 |
| GOOF | 0.815 | 0.996 | 0.978 | 0.976 | 1.074 | 1.068 |
| Residual electron density/e Å$^{-3}$, $\rho_{max}/\rho_{min}$ | −1.082/0.176 | −0.599/0.096 | −0.360/0.078 | −0.732/0.101 | −0.980/0.107 | −0.374/0.076 |

**Table 4.** Bond lengths (*d*) in the imidazole ring in the compounds under consideration

| Bond | *d*/Å | | | | | |
|---|---|---|---|---|---|---|
| | Emim | Pmim | iPmim | Bmim | Ppim | iPipim |
| N(1)—C(2) | 1.317(6) | 1.336(4) | 1.326(3) | 1.323(6) | 1.331(5) | 1.331(2) |
| C(2)—N(3) | 1.328(6) | 1.326(4) | 1.323(4) | 1.335(7) | 1.310(5) | 1.331(2) |
| N(3)—C(4) | 1.376(6) | 1.378(4) | 1.381(3) | 1.380(5) | 1.388(5) | 1.382(2) |
| C(4)—C(5) | 1.362(7) | 1.352(5) | 1.348(4) | 1.353(8) | 1.353(7) | 1.352(2) |
| C(5)—N(1) | 1.389(6) | 1.380(4) | 1.389(3) | 1.367(5) | 1.380(5) | 1.383(2) |

tains different substituents at the nitrogen atoms and, on the other hand, the use of the ethyl substituent substantially simplifies calculations and analysis of the results.

## Molecular structure

X-ray diffraction study demonstrated that the C—C and C—N bond lengths are in the ranges typical of this class of compounds[17] (Table 4). The imidazole ring is aromatic and planar. It should be noted that the C(2)—N(1) and C(2)—N(3) bonds are substantially shorter than the N(1)—C(5) and N(3)—C(4) bonds. Besides, the C(2)—N(1) and C(2)—N(3) bonds are nonequivalent, which is observed in all cations except for 1,3-diisopropylimidazolium (iPipim). For example, the difference between the C(2)—N(1) and C(2)—N(3) bond lengths in 1-ethyl-3-methylimidazolium (Emim) and 3-methyl-1-propylimidazolium (Pmim) is 0.02 Å. The observed difference in the bond length cannot be attributed exclusively to the influence of the alkyl substituents at the nitrogen atoms. For example, the shorter N—C bond in the Pmim molecule is observed for the nitrogen atom bound to the propyl substituent, whereas the N—C bond with the nitrogen atom bearing the Me substituent (1.323(6) Å) is, on the contrary, shortened in 1-butyl-3-methylimidazolium (Bmim). An analogous situation is observed for pairs of the N(1)—C(5) and N(3)—C(4) bonds, for which the effect of the substituents on the bond length distribution is indistinguishable.

To estimate the influence of substituents at the nitrogen atoms on the bond length distribution in the imidazole ring, we performed quantum chemical calculations for the Emim cation. The calculations showed that the bond lengths in the isolated cation are equalized. The N(1)—C(2) and N(1)—C(5) bonds are only slightly shorter than the N(3)—C(2) and N(3)—C(4) bonds (Table 5). As can be seen, the calculations perfectly reproduce the C(2)—N(3), N(3)—C(4), and C(4)—C(5) bond lengths, the error being at most 0.005 Å, which is within experimental error. The largest difference is observed for the N(1)—C(2) and C(5)—N(1) bond lengths. According to the quantum chemical calculations, the N(1)—C(2) bond in Emim is 0.015 Å longer, whereas the C(5)—N(1) bond is 0.011 Å shorter compared to the experimental values.

**Table 5.** Experimental and calculated (B3PW91/6-311G*) bond lengths (*d*) in the imidazole ring in the cation of Emim

| Bond | *d*/Å | | Δ*d*/Å |
|---|---|---|---|
| | Experiment | Calculations | |
| N(1)—C(2) | 1.317(6) | 1.332 | −0.015 |
| C(2)—N(3) | 1.328(6) | 1.333 | −0.005 |
| N(3)—C(4) | 1.376(6) | 1.379 | −0.003 |
| C(4)—C(5) | 1.362(7) | 1.358 | 0.004 |
| C(5)—N(1) | 1.389(6) | 1.378 | 0.011 |

Apparently, the experimental difference in the bond lengths in the imidazole ring is due to the influence of the crystal environment, in particular, to the cation—anion contacts in the crystalline state.

The cations of IL under study differ both in the length and conformation of the alkyl substituents at the nitrogen atoms. In the 1,3-dipropylimidazolium salt (Ppim), one of the propyl substituent is disordered (see Fig. 1). In the Emim and Bmim cations, the substituents at the N(1) atom are in a synclinal conformation with respect to the plane of the imidazole ring; the C(2)N(1)C(6)C(7) torsion angle (ϕ) is 80.0 and 76.2°, respectively. In IL with Pmim, the propyl substituent is in an anticlinal orientation; the torsion angle ϕ = 109.2°. In Ppim, the substituent at the N(3) atom is perpendicular to the plane of the imidazole ring. The substituent at the N(1) atom is disordered over two positions with equal occupancies; the C(2)N(1)C(6)C(7) and C(2)N(1)C(6)C(7′) torsion angles are 94.6° and 61.2°, respectively. In the case of compounds containing the isopropyl substituent, it is convenient to describe the conformations with the use of the C(2)N(1)C(6)H(6) (ω) or C(2)N(3)C(9)H(9) (ω′) torsion angles, because the positions of the hydrogen atoms at the C(6) and C(9) atoms are strictly fixed by two methyl substituents. In the iPipim cation, the substituents at the nitrogen atoms adopt different conformations. The alkyl fragment at the N(1) atom is anticlinal with respect to the plane of the imidazole ring with the angle ω = 122.9°, whereas the substituent at the N(3) atom is characterized

by the torsion angle ω′ = 12.4° similar to the ω angle in iPmim.

Therefore, the substituents at the nitrogen atoms of the imidazole ring are characterized by high conformational flexibility. Consequently, the preference of a particular conformation in the crystalline state is determined primarily by interionic contacts in the crystal (see below).

## Crystal structure

An analysis of the data from the Cambridge Structural Database[13c] demonstrated that the crystal structures of IL are stabilized primarily by CH—anion contacts.

It should be noted that strong contacts are formed with the involvement of only the H atoms of the imidazole ring and the H atoms at the α-carbon atoms of the substituents. The strongest contact is formed by the H(2) atom; the smallest length of this contact is observed in Bmim (2.46 Å) (Table 6). The H···Br contacts formed by the H(4) and H(5) atoms are elongated, on the average, by 0.05 Å compared to the shortened distances for the H(2) atom (see Table 4), whereas most of the other interactions with the α-carbon atoms of the substituents are at the limit of the van der Waals radii.

The observed character of changes in the strength of contacts formed by the hydrogen atoms of the imidazole ring is primarily associated with the electronic effects, to be more precise, with the charges of hydrogen atoms. To study the electron density distribution in the imidazolium cation, we performed the topological analysis of the electron density distribution and calculated the atomic charges in terms of the Atoms in Molecules theory.[15] The calculations demonstrated that the hydrogen atom at position 2 of the imidazole ring bears the highest positive charge (0.182 e), whereas the charges of the H(4) and H(5) atoms are lower and are virtually identical (0.167 and 0.169 e). For comparison, the charges of the hydrogen atoms of the methyl and ethyl substituents are in the ranges of 0.104—0.113 and 0.062—0.096 e, respectively.

Apparently, the observed charge distribution is attributed to the difference in the electronegativity of the nitrogen and carbon atoms. The C(2) atom bears the highest positive charge (0.983 e), whereas the charges of the C(4) and C(5) atoms are substantially lower (0.374 and 0.371 e, respectively) and are similar to the charges of the C(8) atom of the Me group (0.237 e) and the C(6) atom of the Et group (0.265 e). In the Et group, the C(7) atom bound to the C(6) atom bears a negative charge (−0.076 e). In turn, the highest negative charges are located on the N(1) and N(3) atoms (−1.920 and −1.923 e, respectively) due to higher electronegativity of the nitrogen atoms.

**Table 6.** The CH···Br contacts formed by the hydrogen atoms of the imidazole ring in the crystals of the ionic liquids

| Contact | *d*/Å | | | | | |
|---|---|---|---|---|---|---|
| | Emim | Pmim | iPmim | Bmim | Ppim | iPipim |
| C(2)H(2)···Br(1) | 2.65 | 2.62 | 2.50 | 2.46 | 2.62 | 2.96 |
| C(4)H(4)···Br(1) | 2.72 | 2.75 | — | 2.95 | 2.81 | 2.76 |
| C(5)H(5)···Br(1) | 2.92 | 2.69 | 2.69 | 2.99—3.00 | 2.73 | 2.92 |

In addition to the electronic factors, the steric factors also have an effect on the formation of contacts. For example, the weakest contact in iPipim is C(2)H(2)···Br(1) (2.96 Å) due apparently to the steric effect of two isopropyl groups at the nitrogen atoms.

An analysis of the crystal packings of the compounds under study showed that the number of contacts in the crystals depends on the length of the alkyl substituent. For example, the number of anions in the nearest environment of the cation gradually increases in the series of Emim, Pmim, and Bmim. However, the number of contacts formed by the cation is not directly dependent on the length of the alkyl substituent. In particular, the cation in the structure of Pmim is involved in eight contacts, whereas the cations in the structures of Emim and Bmim form seven contacts each (Fig. 2, *a*—*c*). The crystal structure of Bmim is characterized by the presence of a bifurcated contact between the H(4) atom and two bromide anions (see Fig. 2, *c*). The introduction of the sterically overcrowded substituents of the $Pr^i$ groups into the cations leads to a decrease in the number of the bromide anions and the number of contacts formed by the cation (see Fig. 2).

In the crystalline state of IL Ppim, the propyl substituent at the N(1) atom is disordered over two positions with equal occupancies (see Fig. 2, *f*). Although the nearest environment of this cation is formed by the smallest number of anions of all the structures under consideration, the cation is involved in the formation of six contacts. The ordered substituent at the N(3) atom forms two CH···Br contacts with the H(9A) and H(9B) atoms (2.95 and 2.90 Å, respectively). In turn, the disordered substituent forms only one contact with the H(6B) atom (2.89 Å). Therefore, the presence of only one CH···Br contact and the absence of additional interactions are apparently responsible for the disorder of the alkyl substituent at the N(1) atom.

In addition to the cation—anion contacts, the cation—cation contacts were also described in the literature.[18] In our study, we found the latter contacts only in the crystal structures of Emim and Ppim (Fig. 3). In Emim, there is a shortened distance between the C(4) atom and the H(8CA) atom of the Me group (C···H, 2.78 Å). An analogous situation is observed in the crystal structure of Ppim, in which the H(11E) atom of the ordered propyl substituent forms contacts with the C(4) and N(3) atoms of the imidazole ring. The C(4)···H(11E) distance (2.76 Å) is substantially longer than the N(3)···H(11E) contact

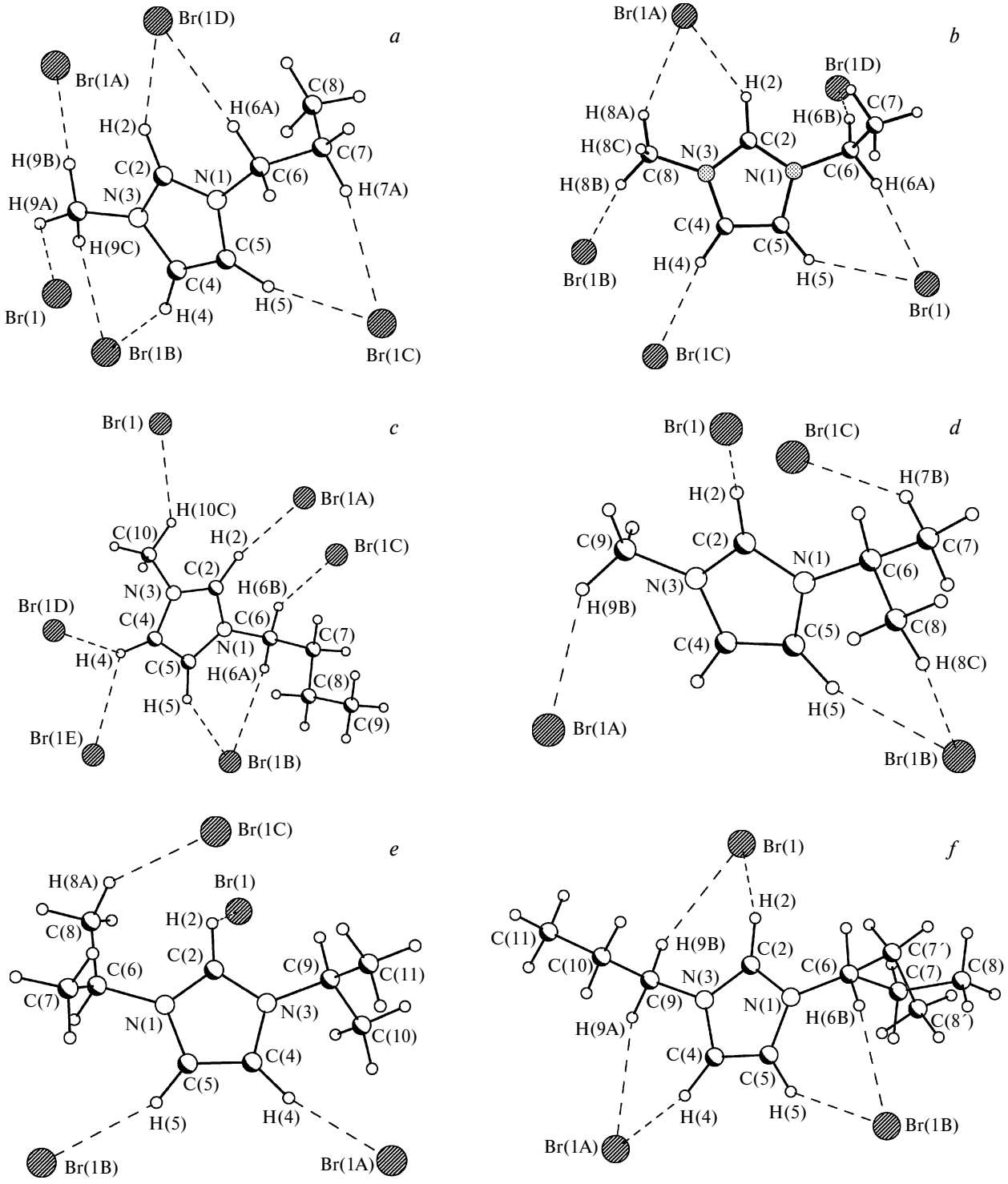


**Fig. 2.** The CH···Br contacts in the crystal structures of iPmim (*a*), Pmim (*b*), Emim (*c*), Bmim (*d*), iPipim (*e*), and Ppim (*f*).

(2.59 Å). Therefore, in addition to the above-mentioned CH···Br interactions, cation—cation contacts can also play role in stabilization of a particular conformation of the alkyl substituent.

In the crystals of iPmim and Pmim, there are interactions between the anion and the π system of the imidazole ring (Fig. 4). Earlier, this coordination mode of the anion has been found only in IL containing polyhalide anions. For example, in the structures containing a polybromide anion,[17,19] the bromine atom is located above the plane of the imidazole ring (C···Br distances are in the range of 3.36—3.53 Å).

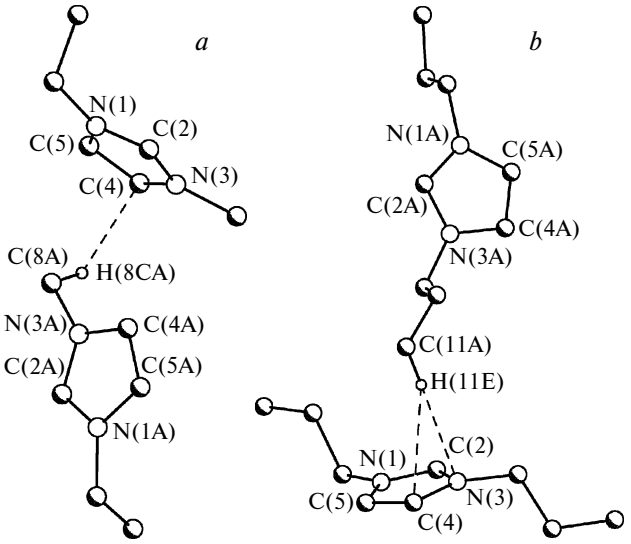


**Fig. 3.** The CH···π contacts in the crystal structures of Emim (*a*) and Ppim (*b*). Only hydrogen atoms involved in contacts are shown for simplicity. For the structure of Ppim, one position of the disordered fragment is shown.

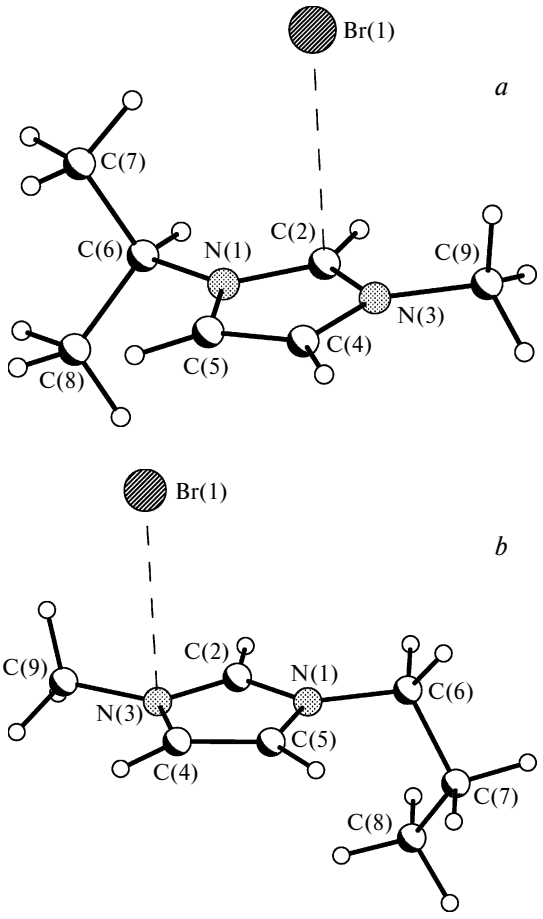


**Fig. 4.** The Br···π contacts in the crystal structures of iPmim (*a*) and Pmim (*b*).

In the crystal structure of iPmim, the bromide anion is above the C(2) atom of the imidazole ring (Br···C, 3.34 Å). This arrangement of the anion is quite understandable. As mentioned above, the C(2) atom bears the highest positive charge and, consequently, this interaction is apparently predominantly electrostatic. However, the bromide anion in the crystal structure of Pmim is located above the N(3) atom (see Fig. 4, *b*). The Br···N distance is 3.48 Å. Therefore, in addition to the influence of the crystal environment, exchange interactions stabilizing specific interactions between anions and cations make a substantial contribution to the formation of such interactions between the anion and the π system of the imidazole cation.

In spite of the fact that in most cases, the CH···π and Br···π interactions are apparently forced and are a consequence of the presence of stronger C—H···Br interactions and a small size of the cation, they undoubtedly make an additional stabilizing contribution to the crystal structure formation.

Therefore, the analysis of interionic interactions in the crystalline state demonstrated that there is no pronounced dependence of the formation of particular contacts on the molecular structure of the cation. The analysis of the crystal packings revealed the following three main types of the supramolecular arrangement of the ions in the crystalline state: chains, layers, and three-dimensional frameworks.

The crystal structure of iPipim consists of chains (Fig. 5). The isopropyl substituents of the cation are not involved in the formation of contacts with the anions. Therefore, the chains are formed through the CH···Br contacts with the hydrogen atoms of the imidazole ring, the hydrophobic alkyl substituents forming the outer surface of the chains. In the crystal structure, the chains run along the $2_1$ screw axis and are directed perpendicular to the *001* crystallographic plane. The coordination polyhedron of the anion is not completely filled by contacts with the cation (see Fig. 5). Consequently, this polyhedron on the crystal surface of the corresponding face can be additionally coordinated by external solvent molecules. Taking into account that competing interactions with water molecules undoubtedly lead to a weakening of C—H···Br contacts, this crystal packing accounts for high hydrophilicity of IL[1].

The crystal packing consisting of layers was found in the crystals of the ionic liquids Emim and Ppim (Fig. 6). Earlier, the isostructural bromide and iodide salts with the Emim cation have been studied by X-ray diffraction.[17a] These salts have a layer structure. However, since the ionic radius of the $I^-$ anion is substantially larger than that of the $Br^-$ anion, the structure of the iodide salt cannot be reliably assigned to layer structures. In the crystal structure of Ppim, the propyl substituent at the N(1) atom is disordered and forms only one contact with the anion and, therefore, the crystal packing is stabilized

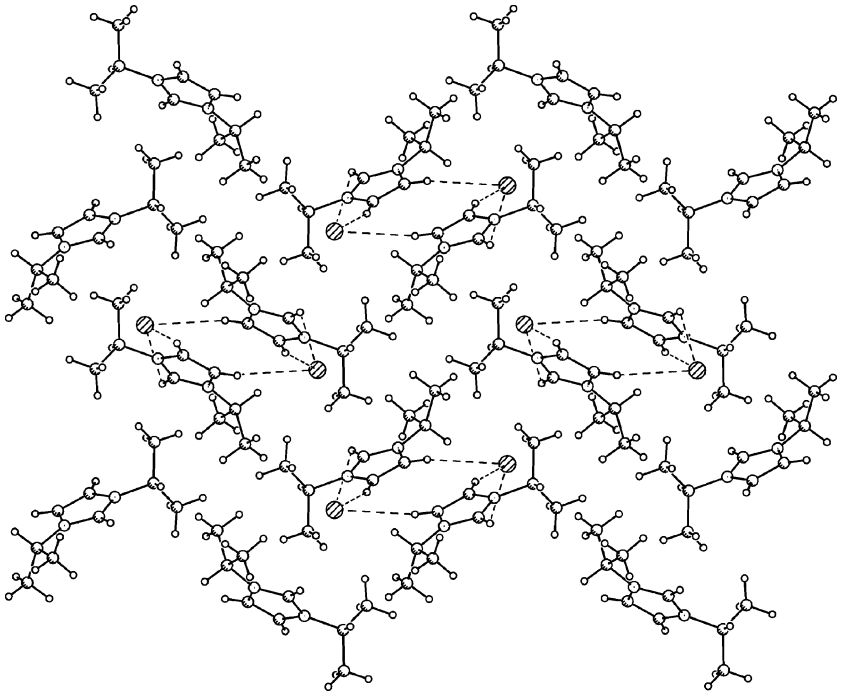

**Fig. 5.** Crystal packing of IL iPiPim illustrating the supramolecular arrangement of molecules in the crystal.

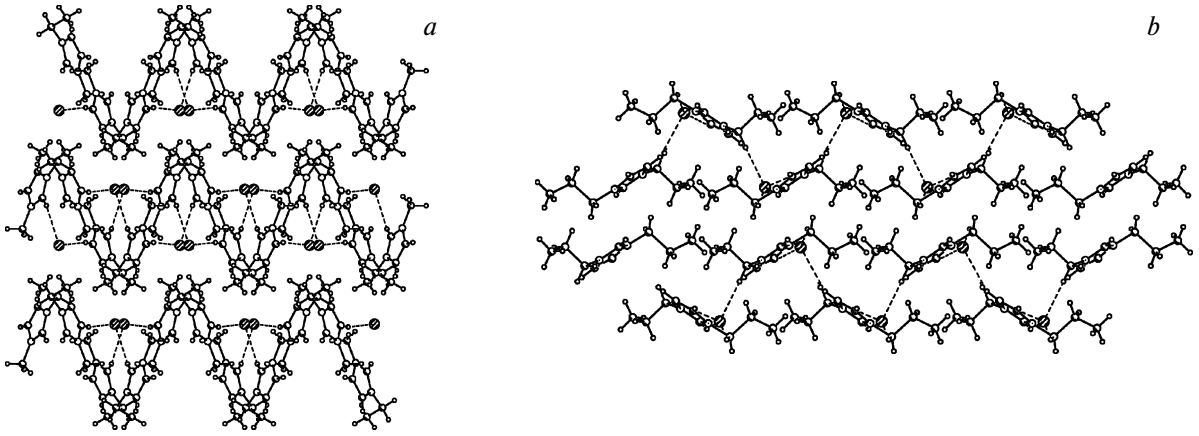


**Fig. 6.** Crystal packings of IL Emim (*a*) and Ppim (*b*) illustrating the supramolecular arrangement of molecules as layers.

primarily by contacts between the bromide anion and the hydrogen atoms of the propyl substituent at the N(3) atom and the hydrogen atoms of the imidazole ring. As opposed to the packing of Emim, the alkyl substituents in the crystal structure of Ppim occupy a substantially larger space and adopt the *E*,*E* conformation. Taking into account a small number of structure-forming contacts of the disordered substituent and the above-mentioned high conformational flexibility of the alkyl fragments, several polymorphs associated with changes in the conformation of the substituent would be expected to exist. The formation of co-crystals with small organic molecules, which can be coordinated to the anion, is also possible, which we have exemplified earlier by co-crystals of Bmim with *p*-phenylenediamine.[6f]

The third type of the supramolecular arrangement in crystals includes compounds containing the bulkiest alkyl substituents and cations characterized by the highest asymmetry of the substituent (Pmim, iPmim, and Bmim) (Fig. 7). The crystal structures of these salts are stabilized primarily by CH···Br interactions. However, as mentioned above, there are interactions between the anion and the π system of the imidazole ring in Pmim and iPmim. These crystal structures are characterized by the presence of infinite channels filled by the alkyl substituents, which are clearly seen in the crystal structure of Bmim.

Therefore, based on the analysis of the crystal packings, it can be concluded that cations, which contain the longest alkyl substituents and are characterized by the highest asymmetry, preferably crystallize to form a three-dimen-

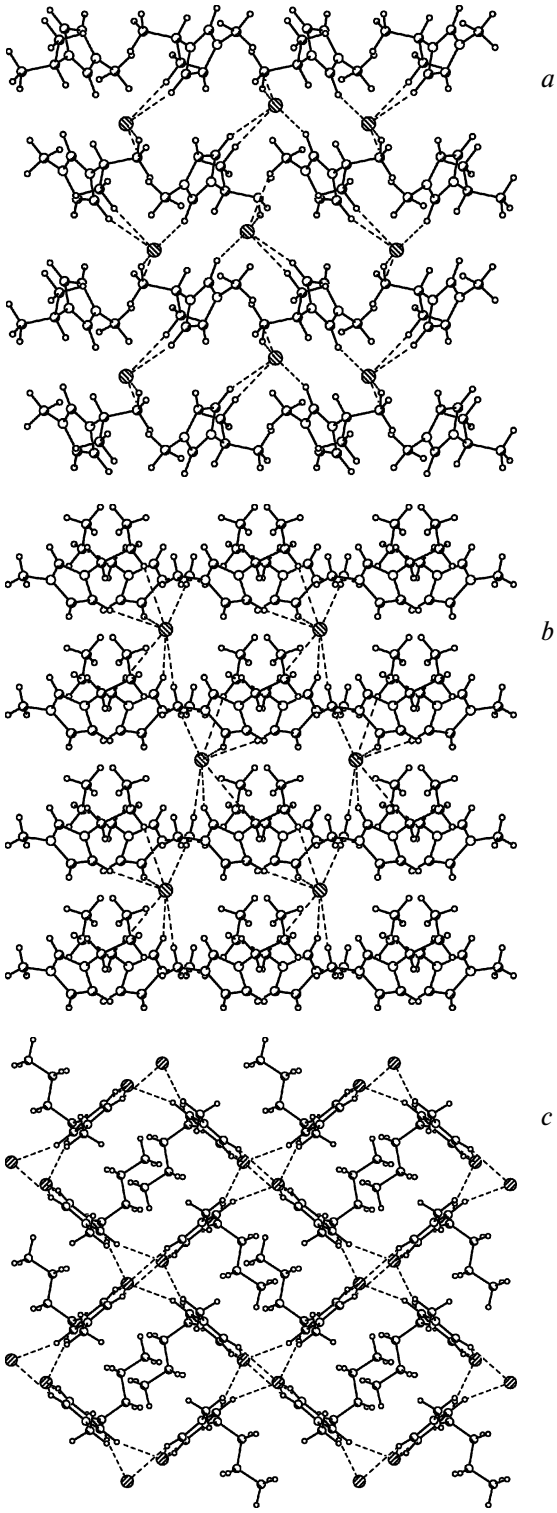


**Fig. 7.** Crystal packings of IL iPmim (*a*), Pmim (*b*), and Bmim (*c*) illustrating the supramolecular arrangement of molecules as a three-dimensional framework.

sional framework containing channels filled by alkyl substituents, whereas the most symmetric cations with small substituents crystallize to form chain or layer packings. Interestingly, the melting point of IL is defined by an empirical rule related to the structure of the cation. In particular, the melting points of the salts sharply decrease with increasing size of the substituents and decreasing symmetry of the cation.[1,10]

Apparently, the melting point of IL is determined primarily by the crystal structure, to be more precise, by both the interactions between the ions and the supramolecular arrangement in the crystal.

Table 7 gives the melting points of IL under study, the numbers of contacts formed by the anions, and the numbers of bromide anions in the nearest environment of the cations. As can be seen from Table 7, the number of contacts formed by the anion decreases as the melting point increases in the series of the salts. Since the melting point is determined by a combination of the energy and entropy factors, it cannot be estimated based only on the data on the strength of interactions in the crystalline state. Nevertheless, the strength of the contacts is controlled primarily by the thermodynamic contribution to the energy of the system. The contribution of electrostatic interactions to changes in the energy is more diminished due to the nondirectional character of interactions and the similar nature of the ions involved in the system. The presence of a larger number of contacts leads to a decrease in the strength of interactions between the ions. A weakening or cleavage of one of the contacts would not lead to a sharp change in the energy of the system. In turn, the smaller the number of contacts formed by the anion, the higher the probability of strong directed interactions (see Table 4). Consequently, the cleavage of one of these contacts would lead to a substantial change in the energy of the system. The strength of the contacts is primarily determined by the sublimation energy,[20] whereas the kinetic factor is also of importance in the case of melting. Recent studies[21] have demonstrated that modern methods for estimation of the crystal lattice energy and the solvation energy provide adequate estimates of the melting points of IL. However, such approximations ignore the

**Table 7.** Dependence of the melting point on the number of contacts in the crystals of the salts

| Cation | M.p./°C | $N_c$ | $N_a$ |
|---|---|---|---|
| Pmim | 36.2 | 8 | 5 |
| Ppim | 67.2 | 6 | 3 |
| Emim | 76.9 | 7 | 5 |
| Bmim | 79.2 | 7 | 6 |
| iPmim | 110.5 | 5 | 4 |
| iPipim | 132.0 | 4 | 4 |

*Note.* $N_c$ is the number of contacts formed by the anion, and $N_a$ is the number of anions in the nearest environment of the cation.

specificity of interactions between the ions in crystals. Indirectly, the number of contacts and their strength provide an estimate of the entropy contribution to the melting points of salts: the larger the number of contacts in the system, the easier the dynamic equilibrium, which involves the hydrogen bond cleavage and formation in melts, is achieved, whereas a decrease in the strength of interactions leads to a decrease in the activation energy of bond cleavage. Therefore, the above-mentioned factors account for the changes in the melting point in the series of IL under study.

An analysis of the crystal structures demonstrated that the CH···Br contacts are primarily responsible for the formation of the crystal structures of IL. In spite of the fact that the bromide anion in all the above-considered salts is involved in a large number of interactions with cations, the coordination polyhedron of the anion is substantially distorted. As a result, there are regions, which are not shielded by contacts. This, in turn, is manifested in high hydrophilicity of these compounds. The crystal structure formation is determined primarily by the nature of substituents at the nitrogen atoms. The analysis of interactions in the crystalline state explained the character of changes in the melting point of IL.

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