THE ELECTROSTATIC ENERGY IN IODIDE SALTS
OF MONO-NITROGEN ORGANIC BASES

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ABSTRACT

The electrostatic part of the lattice energy in iodide salts of mono-nitrogen organic bases was evaluated by adopting the Ewald method. The calculations were performed for compounds for which a complete or at least a partial crystal structure is known. In the case of incomplete structures the modified neglect of diatomic overlap (MNDO) optimization procedure was applied to find the unknown positions of atoms. The electrostatic energy calculations were carried out with the assumption that the negative (-1) charge is localized at the iodine atom and the positive $(+1)$ charge is located on the N atom or distributed between all the atoms in the cation. The charge distribution in the isolated cation was evaluated by applying CNDO/2, INDO and MNDO quantum chemistry methods. The electrostatic energy values thus derived were compared with values reported in the literature for the crystal lattice energy determined either theoretically or experimentally. The agreement between these characteristics appeared to be very satisfactory, indicating that, in the compounds studied, the main contribution to the cohesive forces is brought by electrostatic (Coulombic) interactions.

INTRODUCTION

The last two decades have been a period of tremendous increase in the number of works concerning the application of theoretical methods for the determination of various physicochemical characteristics, even for very complex systems. This advance has become feasible due to the accessibility of fast computers. A great contribution to developments in this area has been made by quantum chemistry methods, which have been widely applied either to verify the experimental results or to predict physicochemical characteristics not accessible experimentally. Theoretical methods have also been developed in other fields of chemistry. One group of such methods comprises those enabling the evaluation of the magnitude of cohesive forces in the solid phase. This work is primarily devoted to this problem.

For ionic substance of general formula $K_m A_n$, the crystal lattice energy (E_c) is defined as the energy change for the process

$$K_m A_n(c) \rightarrow m K^{\alpha n+}(g) + n A^{\alpha m-}(g) \tag{1}$$

where α is the multiplier accounting for the actual valence of both ions. This quantity can, in general, be expressed by the equation [1–3]

$$E_c = -E_{el} + E_r - E_d + E_0 \tag{2}$$

where E_{el} is the term accounting for the electrostatic interactions between ions, E_r represents the repulsive interactions, E_d the van der Waals interactions and E_0 is the zero point energy. The determination of E_c requires, therefore, the knowledge of contributions brought by all four terms of the right hand side of eqn. (2). A knowledge of the charge distribution between ions, and between atoms in complex ions, enables the precise calculation of the electrostatic energy on the basis of the Coulomb equation [4,5]. The relationship for the evaluation of E_r contains constants which can be derived from certain experimental data [6–12]. The approximate values of both E_d and E_0 terms can be also obtained theoretically [4,6]. The above discussion implies that the theoretical evaluation of E_c values should be possible. In reality, complete calculations of the lattice energy have so far been carried out only for simple inorganic ionic substances [13,14] and for compounds composed of complex ions of high symmetry [2,15], as well as for some organic ionic substances [16,17]. Such calculations do not seem to be feasible for salts composed of complex, unsymmetrical ions. Therefore, the approximate methods of lattice energy calculation which are restricted only to the E_{el} term acquire a special significance. Such an approximation is justifiable since the contribution from the sum $E_r - E_d + E_0$ is small enough to be neglected. This results from the fact that the terms E_r and E_d are roughly equal to one another in magnitude and have the opposite sign, and the E_0 term is negligibly small in comparison with the values of the other terms in eqn. (2).

The iodide salts of mono-nitrogen organic bases contain rather complex and, in many cases, highly unsymmetrical cations. Thus, the theoretical evaluation of the lattice energy, or electrostatic energy, presents a rather difficult problem. Such calculations have been carried out only in the case of two simple representatives of this group of compounds [16–18]. For several salts of this series, E_c values have, however, been derived on the basis of calorimetric measurements [19–22], thermoanalytical studies [23], and by applying other methods [24], or have been estimated using the phenomenological Kapustinskii–Yatsimirskii equation [22,23].

In this work we made an effort to evaluate the electrostatic energy in iodide salts of nitrogen bases for which structural data are available. By undertaking these studies we hoped to gather information on the nature of the cohesive forces keeping molecules of the compounds in the solid phase,

and we also anticipated obtaining an insight into the properties of salts composed of complex and highly unsymmetrical ions.

ELECTROSTATIC LATTICE ENERGY CALCULATION

General problems

The electrostatic energy of 1 mol of ionic substance composed of structural units $(K^{\alpha n+})_m (A^{\alpha m-})_n$ (corresponding to the simplest formula unit of the molecule) is given by the equation [4,5]

$$E_{el} = 1/2 N_A \left[m E_p^{(\alpha n+)} - n E_p^{(\alpha m-)} \right] \tag{3}$$

where N_A is Avogadro's number, and the factor $1/2$ eliminates the double counting of electrostatic interactions. $E_p^{(\alpha n+)}$ and $E_p^{(\alpha m-)}$ express the potential energy of a single cation and anion, respectively, as a result of their interactions with all other ions. The mathematical expressions for these latter two quantities result from the Coulomb law and are shown in eqns. (4) and (5), viz

$$E_p^{(\alpha n+)} = \left[(\alpha n +) e^2 / (4\pi\epsilon_0 R_0) \right] \sum_j z_j / \rho_{\alpha n+, j} \tag{4}$$

$$E_p^{(\alpha m-)} = \left[(\alpha m -) e^2 / (4\pi\epsilon_0 R_0) \right] \sum_j z_j / \rho_{\alpha m-, j} \tag{5}$$

In eqns. (4) and (5) e denotes the absolute electron charge, ϵ_0 is the permittivity of free space, R_0 represents a unit of length on the molecular level (usually this quantity is equal to the shortest cation–anion distance or distance between two other characteristic points in the lattice; sometimes it is related to the dimensions of the unit cell), z_i represents the relative charges of all other ions interacting with the cation (of relative charge = $\alpha n +$) and anion (of relative charge = $\alpha m -$) and $\rho_{\alpha n+, j}$ and $\rho_{\alpha m-, j}$ denote distances in the crystal, from a given ion ($\alpha n +$ or $\alpha m -$) to the ion j, expressed in R_0 units (real distance = ρR_0). The summations in eqns. (4) and (5) are sometimes named the lattice sums.

Combining eqns. (3)–(5), one obtains an equation often recommended for the evaluation of the electrostatic energy of ionic crystals, namely

$$E_{el} = aM/R_0 \tag{6}$$

where a is a constant equal to

$$a = N_A (\alpha n +)(\alpha m -) e^2 / (4\pi\epsilon_0) \tag{7}$$

and M is the Madelung constant

$$M = 1/2 \sum_j \left[m(z_j / \alpha m -) / \rho_{\alpha n+, j} + n(z_j / \alpha n +) / \rho_{\alpha m-, j} \right] \tag{8}$$

The Madelung constant is always positive and depends on the type of lattice. On the other hand, constant a is always negative because of the opposite signs of $(an+)$ and $(am-)$. Therefore, E_{el} is also negative, and this is in accord with the fact that electrostatic interactions cause stabilization of ions in the lattice. The value of constant a is easy to obtain for a given substance. The real problem, however, is posed by the calculation of the Madelung constant. This problem, as well as the problem of direct evaluation of E_{el} values, will be discussed in the next section.

Principles of the Ewald method

A well-known method for the evaluation of $E_p^{(an+)}$ and $E_p^{(am-)}$, and thus E_{el} and M, was developed by Ewald [25]. The method utilizes the effect of the periodical location of atoms in the lattice. It further assumes that the density of a charge localized at each atom is well represented by the Gaussian distribution. Taking the above into account, Ewald derived the relationship for the potential (V) at a site r_i in an ionic lattice, taken as an origin of the coordinate system, due to the monopoles at sites r_j. For the cation and anion in our case, this relationship assumes the forms given by eqns. (9) and (10), respectively:

$$V^{(an+)} = 1/(4\pi\epsilon_0)\left[1/(\pi v) \sum_{h=0} F(h)/h^2 \exp(-\pi h^2/K^2) - 2Ke(an+)\right.$$

$$\left. + \sum_{j\neq i} ez_j/r_{ij}ERFC\left(\pi^{1/2}Kr_{ij}\right)\right] \qquad (9)$$

$$V^{(am-)} = 1/(4\pi\epsilon_0)\left[1/(\pi v) \sum_{h=0} F(h)/h^2 \exp(-\pi h^2/K^2) - 2Ke(am-)\right.$$

$$\left. + \sum_{j\neq i} ez_j/r_{ij}ERFC\left(\pi^{1/2}Kr_{ij}\right)\right] \qquad (10)$$

In eqns. (9) and (10) v represents the volume of the unit cell, h is a vector in the reciprocal space, $F(h) = \sum_s ez_s \cos(2\pi h r_{is})$ represents the Coulombic structure factor with s running over a unit cell with origin site r_i, K is the convergence parameter to obtain the optimal convergence of series (in this work we assumed $K = v^{1/3}$), r_{ij} (r_{is}) is the distance vector between the origin site $r_i = 0$ and the site r_j (r_s) with charge ez_j (ez_s), and $ERFC(x) = 2/\pi^{1/2}\int_x^\infty e^{-t^2} dt$ represents the complementary error function. In eqns. (9) and (10) the symbol $\sum_{h=0}$ indicates summation over the reciprocal space, whereas $\sum_{j\neq i}$ ($\sum_s$) indicates summation over the real lattice omitting $r_{ij} = 0$. The meaning of the other symbols was given earlier.

The value of E_{el} for a given compound is obtained by substituting in eqn. (3) the expressions $(an+)eV^{(an+)}$ and $(am-)eV^{(am-)}$ for $E_p^{(an+)}$ and $E_p^{(am-)}$ respectively. The calculations in this work were performed on an IBM PC computer.

TABLE 1

Structural data for iodide salts of mono-nitrogen organic bases

Substance [a]		Space group	Number of structural units in the elementary cell	N–I minimal distance in the lattice (Å)	Reference
No.	Formula [b]				
1	NH_4I	$Fm3m$	4	3.62	[3]
2	$[(CH_3)_3NH]I$	$P2_1/m$	2	3.49	[30]
3	$[(CH_3)_4N]I$	$P4/nmm$	2	4.58	[31–33]
4	$[(C_2H_5)_3NH]I$	$P6_3mc$	2	3.60	[34]
5	$[(C_2H_5)_4N]I$	$I\bar{4}$	2	4.76	[35]
6	$[(CH_3)C_5H_8CH_2N(CH_3)_3]I$	$Pna2_1$	4	3.87	[36]
7	$[(C_6H_5)_2CH(CH_2)_2N(CH_3)_3]I$	$P\bar{1}$	4	4.74	[37]
8	$[(C_6H_5)CH_2(CH_3)NC_3H_4(CH_3)_2]I$	$Pbca$	8	4.33	[38]
9	$\{(CH_3)[(C_6H_5)_2CH(CH_2)_2]NC_5H_{10}\}I$	Pn	2	4.57	[39]
10	$[C_9H_{18}N]I$	$Pna2_1$	4	4.76	[40]
11	$[C_6H_5NH_3]I$	$P2_1/c$	4	3.52	[41]
12	$\{(CH_3)[(CH_3)_3C]_2NC_5H_3\}I$	$P2_1/c$	4	4.16	[42]
13	$[(C_2H_5)(CH_3)NC_9H_6]I$	$P2_1/c$	4	4.83	[43]

[a] 1: Ammonium iodide; 2: *N,N*-dimethylmethanaminium iodide; 3: *N,N,N*-trimethylmethanaminium iodide; 4: *N,N*-diethylethanaminium iodide; 5: *N,N,N*-triethylethanaminium iodide; 6: *N,N,N*-trimethyl-(*cis*-3-methylcyclopentyl)ethanaminium iodide; 7: *N,N,N*-trimethyl-3,3-diphenylpropanaminium iodide; 8: 1-phenylmethyl-1,3,3-trimethylazetidinium iodide; 9: 1-(3,3-diphenylpropyl)-1-methylpiperidinium iodide; 10: 8,8-dimethyl-8-azoniabicyclo[5.1.0]octane iodide; 11: benzenaminium iodide; 12: 2,6-bis-(1,1-dimethylethyl)-1-methylpyridinium iodide; 13: 1-ethyl-2-methylquinolinium iodide.

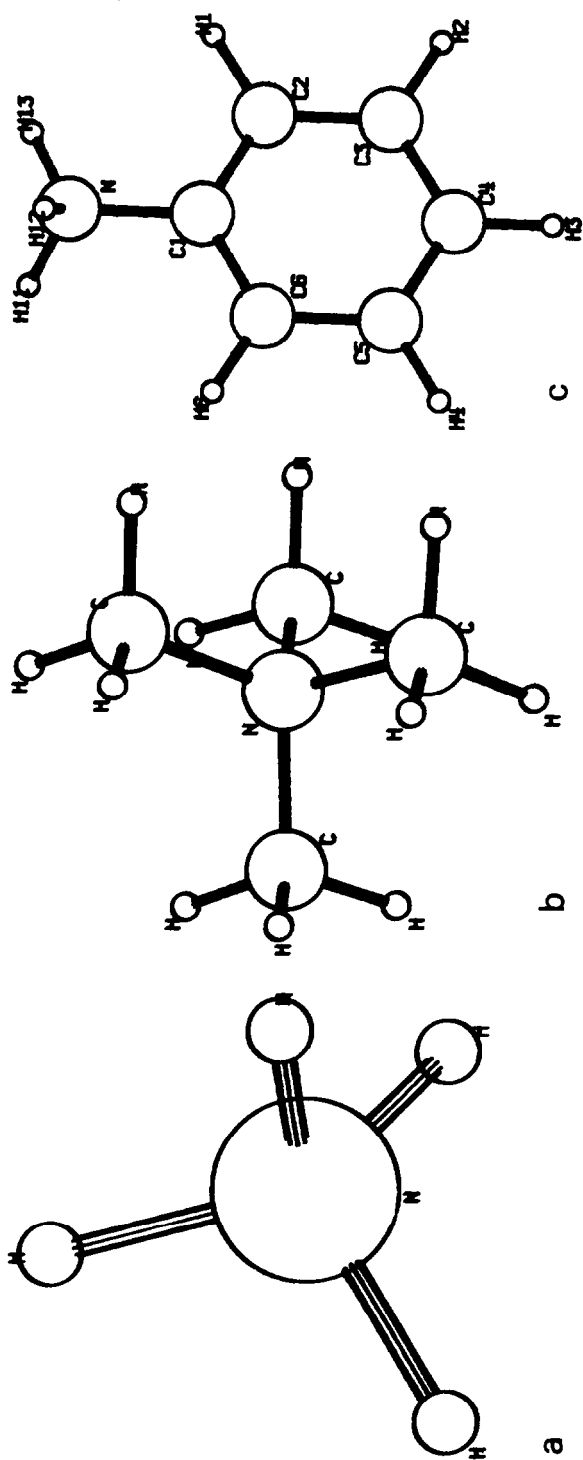[b] For structures of cations see Figs. 1 and 2.

Fig. 1. Structures of NH_4^+ (a), $[N(CH_3)_4]^+$ (b) and $[C_6H_5NH_3]^+$ (c).

The problem of the evaluation of E_{el} is often considered in the category of lattice sum calculation. Such sums for example occur in eqns. (4) and (5). The evaluation of lattice sums using the Ewald method is not affected by the type of lattice or the type of charge distribution. Bertaut derived general equations, analogous to eqns. (9) and (10), for various functions describing charge distribution, including the Gaussian charge distribution function [26]. Jenkins and Pratt found, however, that lattice sums obtained using Gaussian charge distribution profiles are characterized by high convergence [27].

One question requires some comment. Ewald made an assumption that charge density distribution is spherical around the atom in a lattice. Such an assumption is well justified for lattices composed of simple monoatomic ions, e.g. in the NaCl lattice [28,29]. In lattices containing complex poly-atomic ions, e.g. cations of mono-nitrogen organic bases, this assumption seems also to be justified. This conclusion results from the examination of the crystallographic electron density maps of various complex ionic substances.

Structural information

To calculate the electrostatic energy in the lattice of an ionic substance one has to know the distribution of interacting charges. It seems justifiable to assume that certain point charges are localized on all or on certain chosen atoms in the lattice. Therefore, to perform calculations, a knowledge of the crystal structure, which provides exact positions of atoms in the lattice, is necessary. Such information is available from diffraction measurements. Unfortunately, only for a few compounds among the iodide salts of mono-nitrogen bases are the crystallographic data sufficient to enable lattice energy calculations. The structural information is compiled in Table 1. The search for crystal structures was carried out on the basis of the Cambridge Structural Database System [44] and other available sources. We believe that in this way most of the structures have been established.

For compounds No. 4, 11 and 12 the complete crystal structures are available. In the case of compound No. 11 the crystal structure has been derived for the partially deuterated hydriodide, i.e. $[C_6D_5NH_3]I$ [41]. In lattice energy calculations for this compound we substituted deuterium atoms attached to the benzene ring with H atoms. For ammonium iodide the location of H atoms was assumed following the work of Raghurama and Narayan (Ref. 3 and references cited therein). The structures of the remaining compounds listed in Table 1 appeared to be incomplete. For compounds No. 3, 5, 6, 8, 10 and 13 the positions of hydrogen atoms attached to carbon atoms have not been determined. These structures were completed by placing H atoms at the standard distance from C atoms [45] (1.11 Å in the case of the aliphatic C–H bond and 1.08 Å for the aromatic C–H bond). The most probable location of these atoms was subsequently established by

optimization of the appropriate valence and torsion angles using the semi-empirical MNDO method together with the minimum energy criterion [46]. The H atom involved in the $\equiv$N–H $\cdots$ I hydrogen bond was located in the N–I direction and was moved 1.02 Å apart from the nitrogen atom [47]. Its position was not further optimized. This also had to be done in the case of compounds No. 1 and 2, for which only the N–I distance in the lattice has been established. For compounds No. 7 and 9 it was not adequate to complete the structures in the above described manner owing to their complexity. The lattice energy calculations for these last two compounds were carried out only on the basis of known positions of N and I atoms.

Charge distribution

In crystal lattice energy calculations, we assumed that a point negative charge (-1) is always located on the iodine atom. The complexity of the cations in the salts examined may cause that unit positive charge to be

TABLE 2

Charge distribution in cationic forms of simple mono-nitrogen bases calculated by quantum chemistry methods

Method Cation[a]		CNDO/2[b]		INDO[b]		MNDO
Formula	Atom	A	B	A	B	
NH_4^+	N	-0.0768	-0.4482	0.0005	-0.3588	0.0672
	H	0.2692	0.3620	0.2499	0.3397	0.2332
$[N(CH_3)_4]^+$	N	0.0778	-0.1082	0.0983	-0.0799	-0.7113
	C	0.0547	-0.0477	0.1209	0.0320	0.1194
	H	0.0587	0.1082	0.0348	0.0793	0.0578
$[C_6H_5NH_3]^+$	N	-0.0170	-0.3364	0.0508	-0.2562	0.0976
	C_1	0.0903	0.0937	0.0872	0.0963	-0.1328
	C_2	0.0051	-0.0115	0.0237	0.0092	-0.0191
	C_3	0.0356	0.0142	0.0556	0.0377	-0.0298
	C_4	0.0338	0.0010	0.0515	0.0226	0.0167
	C_5	0.0338	0.0114	0.0536	0.0346	-0.0300
	C_6	0.0015	-0.0161	0.0204	0.0053	-0.0206
	H_1	0.0294	0.0640	0.0080	0.0373	0.0855
	H_2	0.0396	0.0796	0.0180	0.0523	0.1022
	H_3	0.0398	0.0813	0.0187	0.0544	0.1012
	H_4	0.0405	0.0815	0.0192	0.0543	0.1026
	H_5	0.0310	0.0672	0.0098	0.0406	0.0867
	H_{11}	0.2142	0.2906	0.1961	0.2707	0.2137
	H_{12}	0.2118	0.2886	0.1941	0.2695	0.2138
	H_{13}	0.2106	0.2909	0.1933	0.2715	0.2124

[a] For structure and numbering of atoms see Fig. 1.
[b] Quantum chemistry method was used with orthogonalized (A) and deorthogonalized (B) orbitals.
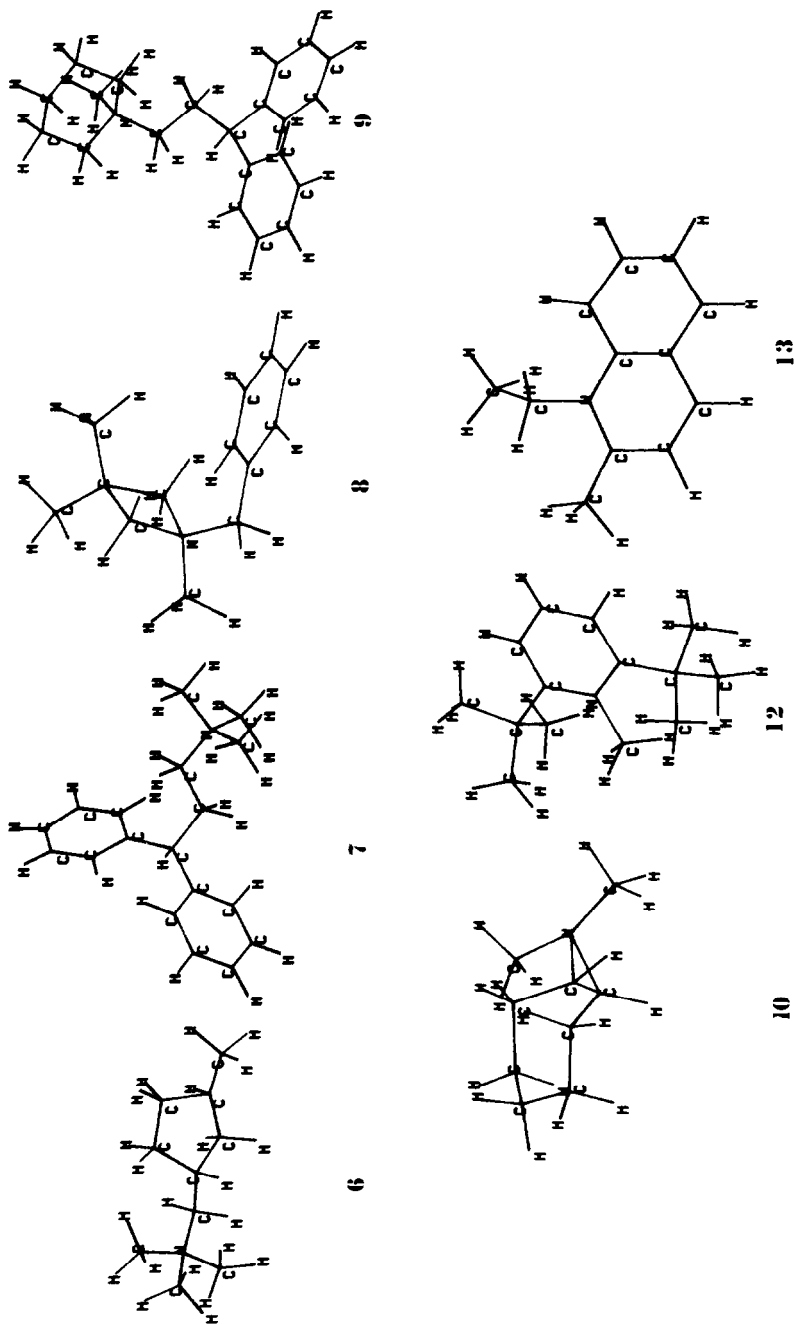
Fig. 2. Bonding geometry (structure) of cations of compounds 6–10, 12 and 13 (see Table 1) in the crystal lattices used in E_{el} calculations.

TABLE 3

Crystal lattice energy (in kJ mol^{-1}) of iodide salts of mono-nitrogen organic bases

Substance[a]		Theoretical					Experimental (From the literature)	
		From this work				From the literature		
No.	Formula	CNDO/2[b]	INDO[b]	MNDO	$N(+)-I(-)$[c]		From ref. 23[d]	Other
1	NH$_4$I	673 674*	673 674*	673	671	594 [54] 603 [55] 609 [56] 619, 621 [57]	631$^+$ 631^{++}	628 [19] 634 [58] 637 [24]
2	[(CH$_3$)$_3$NH]I	536 533*	538 534*	535	551		539$^+$ 547^{++}	565 [19]
3	[(CH$_3$)$_4$N]I	506 509*	505 507*	505	506	477 [17] 506 [18] 518 [16]	531^{++}	498 [20] 544 [19]
4	[(C$_2$H$_5$)$_3$NH]I	495 477*	498 483*	493	537		510$^+$ 549^{++}	558, 601 [21]
5	[(C$_2$H$_5$)$_4$N]I	484 481*	481 479*	481	478	448 [17] 459 [16] 478 [18]	530^{++}	396 [22] 449 [20] 583 [21]

No.	Compound				
6	$[(CH_3)C_5H_8CH_2N(CH_3)_3]I$	456	462	456	497
		443*	450*		
7	$[(C_6H_5)_2CH(CH_2)_2N(CH_3)_3]I$	439	439		470
8	$[(C_6H_5)CH_2(CH_3)NC_3H_4(CH_3)_2]I$	428*	430*	439	482
9	$\{(CH_3)[(C_6H_5)_2CH(CH_2)_2]NC_5H_{10}\}I$				427
10	$[C_9H_{18}N]I$	470	475	466	514
		455*	461		
11	$[C_6H_5NH_3]I$	553	554	563	620
		544*	546*		
12	$\{(CH_3)[(CH_3)_3C]_2NC_5H_3\}I$	420	427	401	492
		394*	405*		
13	$[(C_2H_5)(CH_3)NC_9H_6]I$	411	401	437	448
		426*	415*		

[a] For names of compounds see Table 1.

[b] Asterisks indicate values obtained when the quantum chemistry method used involved deorthogonalized orbitals.

[c] Values obtained when total positive charge was located on nitrogen atom.

[d] Plus sign shows values evaluated on the basis of thermoanalytical studies and thermochemical cycle; double plus sign shows values estimated on the basis of the Kapustinskii–Yatsimirskii equation [52,53].

located on a certain atom in the cation or on all the atoms forming this ion. In the simplified approach we assumed that a $+1$ charge is located on the N atom. In more advanced calculations the distribution of the unit positive charge between all the atoms in the cation, giving fractional charges (net charges), was derived by applying the semiempirical CNDO/2 [48,49], INDO [48–51] and MNDO [46] methods. Some examples are shown in Table 2.

Undoubtedly, none of the methods described above gives an exact representation of the charge distribution in the lattice. This is because the assumed or evaluated charge distribution concerns isolated ions, and neglects the influence of neighbouring ions in the lattice. Nevertheless, these charge distributions form a necessary basis for electrostatic lattice energy calculations.

RESULTS AND DISCUSSION

The derived electrostatic energy values, together with literature values of the crystal lattice energy for 13 iodide salts of mono-nitrogen organic bases, are shown in Table 3. Only for the first five compounds listed in the table can the evaluated Coulombic energies be compared with the literature values of E_c or E_{el}. Generally, the trend of changes in E_{el} values calculated in this work applies also in the case of E_c values determined by other methods. This trend is seen in the decrease of both E_c and E_{el} values with an increase in the number and size of substituents at the N atom. The trend discussed above is also observed for the remaining compounds studied. In the case of NH_4I, all values of the lattice energy reported in the literature are lower than the values of E_{el} determined in this work. For the tertiary and quaternary alkanaminium iodides studied the derived E_{el} values compare well with the values of lattice energy reported in the literature.

The values of E_{el} calculated in this work depend on the method of evaluation of the charge distribution in the cation. The values of the electrostatic energy are, however, rather scattered, and no regular influence of the quantum chemistry method applied to the values of E_{el} can be observed. The MNDO method leads to values of E_{el} which are comparable with those obtained via CNDO/2 and INDO methods. Also of interest are the values of E_{el} calculated assuming that point positive ($+1$) and negative (-1) charges are located at the nitrogen and iodine atoms, respectively. Using this latter approximation, the calculated values of the Coulombic energy in the case of quaternary salts are comparable with those obtained when the precise charge distribution in the cation was derived by advanced quantum chemistry methods. However, discrepancies between values of the above discussed characteristics are observed for salts containing complex, highly unsymmetrical cations. The assumption as to the location of negative

(-1) and positive $(+1)$ charges at N and I atoms, respectively, does not seem to reflect the true charge distribution in the lattice, although it leads to E_{el} values which fit very well to the experimental lattice energy values. This might mean that, by using this simple model, one can obtain very easily the approximate values of E_{el}. One would expect that the observed regularity would be general for all salts of mono-nitrogen organic bases with simple monatomic anions. To support this suggestion, extension of the experimental and theoretical bases is necessary. Indeed, our recent calculations have revealed that the above discussed regularity is observed in the case of chloride [59] and bromide [60] salts of mono-nitrogen bases.

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