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CRYSTAL STRUCTURE OF 9(10-METHYL)-ACRIDINIMINE HYDRIODIDE. LATTICE ENERGETICS OF THIS COMPOUND AND HALIDE SALTS OF NITROGEN ORGANIC BASES

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Abstract The crystal structure of hydriodide of 9(10-methyl)-acridinimine, the cation of which originates from the imino tautomeric form of 9-acridinamine, was determined by X-ray analysis (monoclinic; space group $P2_1/c$; Z=4; R=0.0368 for 1651 observed reflections). The bond between the egzocyclic N atom and the acridine moiety retains a length typical for double bonds, while lengths of adjacent C-C bonds are contained between those characteristic for single and aromatic bonds. The central ring system is strongly conjugated with the side rings through bonds at the endocyclic N atom which results in the acridine skeleton being almost planar. For this molecule and fifteen halide salts of simple nitrogen organic bases, the electrostatic, dispersive and repulsive contributions to the lattice energy were evaluated, boiling down the problem of intermolecular interactions to atom - atom interactions. Coulombic energies arising from charges fitted to the molecular electrostatic potential on the DFT level, compare well with experimental values of the crystal lattice energy and show a decreasing tendency with growth of dimensions (volume of a stoichiometric unit) of interacting ions.

INTRODUCTION

Discussions as to whether 9-acridinamine exists in one or two (amino or imino) tautomeric forms (Figure 1), which can occur as a result of migration of the H atom between egzocyclic and endocyclic N atom (prototropic tautomerism) have been conducted for many years.[1] While some investigations seemed to support the existence of this phenomenon,[2-6] others did not.[7-12] The results of experimental[13] and

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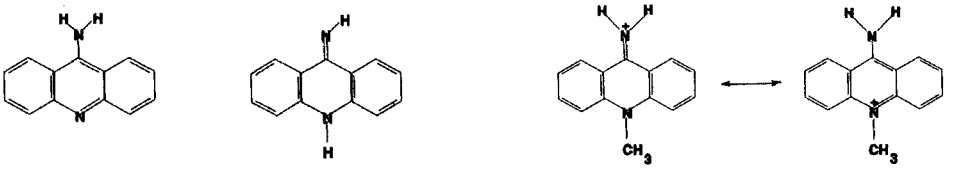
theoretical[1,13] studies already published by us, as well as recent theoretical calculations (which will be published soon) revealed that the phenomenon actually exists and to prove this we have synthesized and determined the structure of the hydriodide of the methyl derivative of 9-acridinamine with fixed imino structure.



9-acridinamine 9(10-H)-acridinimine mesomeric structure of cation

FIGURE 1 Canonic structures of tautomeric forms of 9-acridinamine and its methylated cation.

Another problem on which our attention was concentrated is the crystal lattice energetics of this compound and halides of nitrogen organic bases. These salts are the simplest ionic derivatives remaining on the boundary between organic and inorganic matter. In our previous works we presented a theoretical prediction (for the first time) of the energies of Coulombic interactions of several such salts whose structures in the solid phase were established.[14-16] Here we demonstrate the possibilities of evaluation of electrostatic, dispersive and repulsive contributions to the lattice energy on the basis of a model which boils down the problem of intermolecular interactions to atom - atom interactions. The results of these calculations are compared with available literature data in order to reveal which of the theoretical methods provide characteristics closest to the experimental ones. Furthermore, the influence of dimensions (volume of a stoichiometric unit) of interacting fragments on the energy of the crystal lattice is considered in brief.

MATERIALS AND METHODS

9(10-methyl)-acridinimine hydriodide was formed as the result of the reaction of methyl iodide with 9-acridinamine.[17] Crystals, purple needles, suitable for X-ray analysis were grown from ethanol solution.

Details concerning data collection are given in Table I. The structure was solved by conventional heavy atom method using SHELXS-86 program.[18] The anisotropic displacement coefficients were applied to all non-hydrogen atoms. The hydrogen atoms were treated as 'riding' at a fixed distance of 1.00 Å from the carbon atom and 0.97 Å from the nitrogen atom and included in the refinement with individual isotropic

temperature factors. Neither the absorption corrections nor extinction ones were used. The structure refinement was carried out using the SHELX-76 program[19] and converged at R=3.68%. The atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1974). Illustrations concerning the crystalline phase were drawn using the ORTEP program.[20]

STRUCTURE OF 9(10-METHYL)-ACRIDINIMINE HYDRIODIDE

The summary of crystallographic data is given in Table I. Table II contains the non-hydrogen atom coordinates, while Table III supplies information on the molecular geometry. Tables of H-atom positions, anisotropic thermal parameters, and F_0, F_c structure factors are available from the authors. The ORTEP[20] view of the stoichiometric unit of 9(10-methyl)-acridinimine hydriodide, with labelling sequence, is shown in Figure 2. On the other hand, Figure 3 demonstrates the arrangement of molecules in the solid phase.

The cationic fragment is almost planar within the acridine moiety and $H_2N(15)$ group containing the egzocyclic N atom. The C(9)-N(15) bond maintains the length (1.308 Å) typical for double bonds, while lengths of adjacent to C(9) the C-C bonds are contained between values characteristic of single and aromatic bonds.[21] The central ring system is strongly conjugated with the side rings through bonds at the endocyclic N atom. All these facts clearly demonstrate that cationic fragment retains the structure originating from the imino tautomeric form of 9-acridinamine (Figure 1).

Two 9(10-methyl)-acridiniminium fragments are engaged in hydrogen bonds with iodine (Figure 3). The latter entity presumably also participates in weak non-specific interactions with hydrogen atoms of side rings, since the sum of van der Waals radii of atoms involved in these exceeds their separation (three such interactions are shown in Figure 3). Both hydrogen bonding and non-specific interactions seem to be the main cohesive forces maintaining molecules in the solid phase.

CRYSTAL LATTICE ENERGY OF HALIDE SALTS OF NITROGEN ORGANIC BASES

It is generally recognized that there are four contributions to the lattice energy (E_c) of molecular crystals, namely, electrostatic (E_{el}), dispersive (E_d) and repulsive (E_r) interactions, as well as the term of zero point energy (E_0), which makes[22]

$$E_c = E_{el} + E_d + E_r + E_0 \qquad (1)$$

TABLE I Crystallographic data for 9(10-methyl)-acridinimine hydriodide.

Crystal data		*Data collection*	
Chemical formula	$[C_{14}H_{13}N_2]I$	Diffractometer	Kuma KM-4
Formula weight	336.2	Radiation	MoK_α (λ=0.71069)
Crystal system	monoclinic	Temperature	293 K
Space group	$P2_1/c$	Absorption coefficient	2.430
		sin Θ/λ	0.049-1.322
Unit cell dimensions		Independent reflections	2455
a = 10.356(2) (Å)		Reflections observed	1651
b = 17.784(4) (Å)		Index range	0-14, 0-12, -13-14
c = 7.280(1) (Å)			
β = 105.64(3) (deg)			
Volume	V = 1291.1(5) (Å^3)		
Molecules/unit cell	Z = 4		
Density	D_x = 1.728 g/cm^3		
Refinement			
Solution	Heavy atom method	R =3.68%	
Refinement	full-matrix least-squares	wR = 6.38%	
Weighting scheme	$w^{-1} = \sigma^2+0.001\ F^2$	GOOF = 0.97	
Largest and mean Δ/σ	0.270, 0.043	$\Delta_r$max = 0.34	(0.70 close to I)
Data to parameter ratio	10:1	$\Delta_r$min = 0.41	

TABLE II Fractional atomic coordinates (x10^4) and equivalent isotropic temperature factors (Å^{2}x10^3) with e.s.d.'s in parentheses for 9(10-methyl)-acridinimine hydriodide.

Atom	x/a	y/b	z/c	Ueq[a]
I	7256(0)	605(0)	6858(1)	51(0)
C(1)	1061(6)	1390(3)	2713(10)	58(1)
C(2)	-244(6)	1463(4)	1601(9)	52(1)
C(3)	-767(6)	2172(4)	1158(10)	55(1)
C(4)	-31(6)	2820(4)	1749(9)	45(1)
C(5)	4125(8)	4000(3)	5290(9)	49(1)
C(6)	5407(8)	3945(3)	6443(10)	66(1)
C(7)	6009(7)	3242(4)	6975(10)	54(1)
C(8)	5326(6)	2601(3)	6331(9)	38(1)
C(9)	3254(5)	1958(3)	4479(8)	34(1)
N(10)	2070(6)	3398(3)	3503(8)	41(1)
C(11)	1862(6)	2037(3)	3380(8)	32(1)
C(12)	1318(6)	2763(3)	2905(8)	34(1)
C(13)	3388(6)	3347(3)	4633(9)	36(1)
C(14)	3976(6)	2632(3)	5173(8)	34(1)
N(15)	3793(5)	1293(3)	4898(8)	50(1)
C(16)	1497(9)	4148(4)	2929(12)	77(1)

[a] $Ueq = (U_{11}(a^*a)^2 + U_{22}(b^*b)^2 + U_{33}(c^*c)^2 + 2(U_{12}a^*b^*abcos\gamma + U_{13}a^*c^*accos\beta + U_{23}b^*c^*bccos\alpha))/3$.

TABLE III Molecular geometry of 9(10-methyl)-acridinimine hydriodide.

Bond lengths (Å) in the cation (with e.s.d.'s in parentheses)

C(1)-C(2)	1.382(8)	C(8)-C(14)	1.426(8)
C(1)-C(11)	1.425(8)	C(9)-C(11)	1.455(7)
C(2)-C(3)	1.376(10)	C(9)-C(14)	1.431(7)
C(3)-C(4)	1.385(9)	C(9)-N(15)	1.308(7)
C(4)-C(12)	1.427(8)	N(10)-C(12)	1.374(8)
C(5)-C(6)	1.370(10)	N(10)-C(13)	1.394(8)
C(5)-C(13)	1.401(8)	N(10)-C(16)	1.474(9)
C(6)-C(7)	1.404(9)	C(11)-C(12)	1.414(8)
C(7)-C(8)	1.357(9)	C(13)-C(14)	1.419(8)

Bond angles in the cation (deg) (with e.s.d.'s in parentheses)

C(2)-C(1)-C(11)	120.8(6)	C(13)-N(10)-C(16)	118.8(6)
C(1)-C(2)-C(3)	119.0(6)	C(1)-C(11)-C(9)	120.6(5)
C(2)-C(3)-C(4)	122.8(6)	C(1)-C(11)-C(12)	119.8(5)
C(3)-C(4)-C(12)	119.6(6)	C(9)-C(11)-C(12)	119.6(5)
C(6)-C(5)-C(13)	119.9(6)	C(4)-C(12)-N(10)	120.6(5)
C(5)-C(6)-C(7)	121.2(7)	N(10)-C(13)-C(14)	120.0(5)
C(6)-C(7)-C(8)	120.1(6)	C(4)-C(12)-C(11)	118.1(5)
C(7)-C(8)-C(14)	120.6(6)	N(10)-C(12)-C(11)	121.2(5)
C(11)-C(9)-C(14)	117.4(5)	C(5)-C(13)-N(10)	120.3(6)
C(11)-C(9)-N(15)	120.9(5)	C(5)-C(13)-C(14)	119.6(6)
C(14)-C(9)-N(15)	121.7(5)	C(8)-C(14)-C(9)	120.8(5)
C(12)-N(10)-C(13)	121.0(5)	C(8)-C(14)-C(13)	118.5(5)
C(12)-N(10)-C(16)	120.2(6)	C(9)-C(14)-C(13)	120.6(5)

Dihedral angles in the cation (deg) (with e.s.d.'s in parentheses)

C(1)-C(2)-C(3)-C(4)	1.3(10)	C(6)-C(5)-C(13)-N(10)	178.2(6)
C(1)-C(11)-C(9)-C(14)	-177.2(5)	C(6)-C(5)-C(13)-C(14)	0.2(10)
C(1)-C(11)-C(9)-N(15)	-0.9(9)	C(6)-C(7)-C(8)-C(14)	-2.5(10)
C(1)-C(11)-C(12)-C(4)	-0.3(9)	C(7)-C(6)-C(5)-C(13)	0.5(11)
C(1)-C(11)-C(12)-N(10)	-179.1(6)	C(7)-C(8)-C(14)-C(9)	179.6(6)
C(2)-C(1)-C(11)-C(9)	-177.3(6)	C(7)-C(8)-C(14)-C(13)	3.1(9)
C(2)-C(1)-C(11)-C(12)	0.1(9)	C(8)-C(14)-C(9)-C(11)	177.3(5)
C(2)-C(3)-C(4)-C(12)	-1.5(10)	C(8)-C(14)-C(9)-N(15)	1.0(9)
C(3)-C(2)-C(1)-C(11)	-0.6(10)	C(8)-C(14)-C(13)-N(10)	-180.0(6)
C(3)-C(4)-C(12)-N(10)	179.8(6)	C(9)-C(11)-C(12)-N(10)	-1.7(9)
C(3)-C(4)-C(12)-C(11)	1.0(9)	C(9)-C(14)-C(13)-N(10)	3.6(9)
C(4)-C(12)-N(10)-C(13)	180.0(6)	C(1)-C(9)-C(14)-C(13)	-6.3(8)
C(4)-C(12)-N(10)-C(16)	-1.0(9)	C(1)-C(12)-N(10)-C(13)	-1.3(9)
C(4)-C(12)-C(11)-C(9)	177.1(5)	C(1)-C(12)-N(10)-C(16)	177.7(6)
C(5)-C(6)-C(7)-C(8)	0.7(11)	C(12)-N(10)-C(13)-C(14)	0.4(9)
C(5)-C(13)-N(10)-C(12)	-177.6(6)	C(12)-C(11)-C(9)-C(14)	5.4(8)
C(5)-C(13)-N(10)-C(16)	3.3(9)	C(12)-C(11)-C(9)-N(15)	-178.3(5)
C(5)-C(13)-C(14)-C(8)	-1.9(9)	C(13)-C(14)-C(9)-N(15)	177.4(6)
C(5)-C(13)-C(14)-C(9)	-178.4(6)	C(14)-C(13)-N(10)-C(16)	-178.6(6)

Possible hydrogen bonds in the crystal (with e.s.d.'s in parentheses)

		distance (Å)		angle (deg)	symm 1.
-HN - H...I	-HN-H	H...I	-HN...I	-HN-H...I	OP.
N(15)-H(15a)...I[b]	0.971(7)	2.733(3)	3.669(5)	162.1(7)	1-X,-Y,1-Z
N(15)-H(15b)...I[c]	0.971(10)	2.735(9)	3.693(5)	169.0(7)	X,Y,Z

TABLE III (continuation)

Van der Waals contacts with I anion		
	distance	symm1.OP.
I..H(1a)	3.133(8)	X,Y,Z
I..H(4a)	2.990(5)	1-X,1/2+Y,3/2-Z
I..H(8a)	3.102(5)	1+X,3/2-Y,1/2+Z

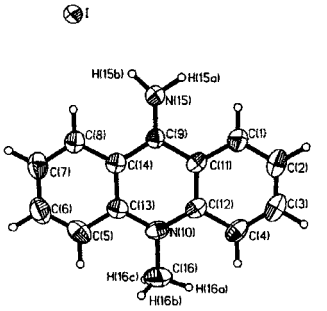


FIGURE 2 The ORTEP view of the stoichiometric unit of 9(10-methyl)-acridinimine hydriodide.

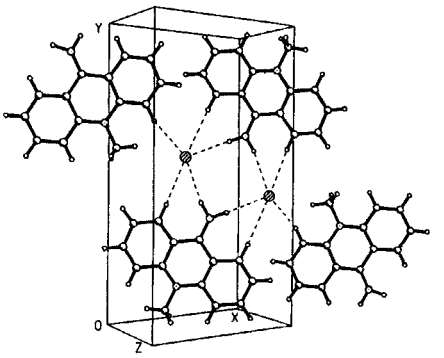


FIGURE 3 The molecular arrangement of 9(10-methyl)-acridinimine hydriodide in the solid phase (dashed lines indicate possible hydrogen bonding (-HN-H···I) and non-bonding (C-H···I) interactions).

Values of the electrostatic term result from the summing up of Coulombic interactions,[23]

$$E_{el} = \frac{1}{2} \sum_{i} \sum_{j \neq i} \frac{Ne^2}{4\pi\epsilon_0} \frac{Q_i Q_j}{R_{ij}} \qquad (2)$$

The magnitude of the dispersive (attractive) term can be evaluated considering the problem in the category of the van der Waals interactions,[23-25]

$$E_d = -\frac{1}{2}\sum_i \sum_{j \neq i} \frac{D_i D_j}{R_{ij}^6} \quad (3)$$

while repulsive interactions can be estimated using the relevant fragments of the Lennard-Jones,[23-25]

$$E_r = \frac{1}{2}\sum_i \sum_{j \neq i} \frac{A_i A_j}{R_{ij}^{12}} \quad (4)$$

or Buckingham[23,24]

$$E_r = \frac{1}{2}\sum_i \sum_{j \neq i} B_i B_j \exp(-C_i C_j R_{ij}) \quad (5)$$

equations. In Equations (2)-(5) N is the Avogadro number, e the elementary charge and ϵ_0 the permittivity of free space; Q_i (Q_j) represent the relative partial charges at atoms, D_i (D_j), B_i (B_j) and C_i (C_j) denote atomic parameters, while R_{ij} the distance between interacting centres; all summations extend over all pairwise interactions between each atom of the basic stoichiometric unit (denoted as i) and all atoms from its surroundings (denoted as j). We neglected the E_0 term since it is insignificant in the case of ionic crystals.[22]

The evaluation of the crystal lattice energy requires knowledge of the solid phase structures. The search for these structures has been carried out in the *Cambridge Structural Database System*[26] and information concerning the compounds examined in this work is given in Table IV.

The energy of electrostatic interactions was calculated assuming that halide anions and organic cations gain 1- and 1+ charges, respectively, and that the charge in a complex cation is spread over all atoms. The relevant partial charges were derived on the ab initio Hartree-Fock (HF)[41] or density functional theory (DFT)[42] level, as Mulliken charges,[43] or those fitted so as to reproduce the molecular electrostatic potential (MEP fit).[44] These charges were derived using the 6-31G** basis sets included in GAUSSIAN 94 program package.[45] Table V shows such charges in ammonium and 9(10-methyl)-acridiniminium cation. The excess of a negative charge is usually predicted at more electronegative atoms, *i.e.* on nitrogen or carbon atoms, whereas the defficiency of a negative charge at hydrogen atoms. This does not correspond to our traditional belief that deficiency of a charge imparted to the proton is shared by the nitrogen atom of the base molecule upon its attachment.

Parameters for evaluating the energy of dispersive interactions between the same

entities (atoms or monoatomic ions) were obtained following the London[46] or Slater-Kirkwood[47] approach. Relevant parameters of repulsive terms were found taking into account that the energy of short-range (dispersive and repulsive) interactions attains minimum at a distance equal to the sum of van der Waals radii of interacting entities.[48] This fact enables parameters of repulsive interactions in relation to dispersive ones to be expressed. In evaluation of parameters of dispersive and repulsive interactions we assumed that halogens retain 1- charge and atoms of organic cations are devoid of a charge. Details regarding the manner of evaluating atomic parameters are given elsewhere,[49] while Table VI provides those used in this work.

TABLE IV Structural data for halide salts of nitrogen organic bases.

Compound[a]		Space group	Z[b]	V/Z[c] (Å^3)	Ref.
No.	Formula				
1	$[NH_4]Cl$	*Pm3m*	1	57.8	27,28
2	$[(CH_3)_2NH_2]Cl$	*Ibam*	8	131.5	29
3	$[(CH_3)_3NH]Cl$	$P2_1/m$	2	149.8	30
4	$[(CH_3)_4N]Cl$	*P4/nmm*	2	157.4	31,32
5	$[C_5H_{10}NH_2]Cl$	*Pcmb*	4	170.8	33
6	$[C_6H_5NH_3]Cl$	*Cc*	4	177.8	34
7	$[C_5H_5NH]Cl$	$P2_1/c$	8	149.8	35
7'		$P\bar{1}$	2	143.5	36
8	$[NH_4]Br$	*Pm3m*	1	66.3	27,28
9	$[(CH_3)_4N]Br$	*P4/nmm*	2	163.3	31,32
10	$[C_2H_5NH_3]Br$	$P2_1/m$	2	121.0	37
11	$[(n\text{-}C_3H_7)_4N]Br$	$I\bar{4}$	2.	370.7	38
12	$[NH_4]I$	*Fm3m*	4	83.5	28
13	$[(CH_3)_3NH]I$	$P2_1/m$	2	161.4	39
14	$[(CH_3)_4N]I$	*P4/nmm*	2	181.8	31,32
15	$[(C_2H_5)_4N]I$	$I\bar{4}$	2	272.1	40
16	$[C_{14}H_{13}N_2]I$	$P2_1/c$	4	320.2	this work

[a] **5** - piperidinium chloride; **6** - benzenaminium chloride; **7** - pyridinium chloride; **16** - 9(10-methyl)-acridiniminium chloride.
[b] Number of stoichiometric units in the unit cell.
[c] Ratio of volume of the unit cell to the number of stoichiometric units in the cell.

All three contributions to the crystal lattice energy were evaluated using the PCK 83 program.[52] This program requires knowledge of individual atomic partial charges (see Table V for example), as well as parameters of dispersive and repulsive interactions for each pair of interacting entities. These latter parameters were obtained multiplying relevant atomic parameters (shown in Table VI) in the manner described by Equations (3)-(5). The results of calculations are compiled in Table VII. The sum of relevant E_d and E_r contributions is negative in the majority of cases which would

TABLE V Atomic partial charges (Q) in ammonium (compound **12**) and 9(10-methyl)-acridiniminium (compound **16**) cations.

Atom(s)[a]	Method			
	HF		DFT	
	Mulliken	MEP fit	Mulliken	MEP fit
		$[NH_4]^+$		
N	-0.664	-0.892	-0.592	-0.795
H	0.416	0.473	0.398	0.449
		$[C_{14}H_{13}N_2]^+$		
C(1)	-0.071	-0.025	-0.099	-0.076
C(2)	-0.151	-0.246	-0.055	-0.139
C(3)	-0.088	0.073	-0.059	-0.002
C(4)	-0.184	-0.409	-0.101	-0.269
C(5)	-0.177	-0.344	-0.088	-0.207
C(6)	-0.085	0.061	-0.061	-0.018
C(7)	-0.160	-0.254	-0.061	-0.145
C(8)	-0.058	-0.029	-0.084	-0.078
C(9)	0.554	0.715	0.366	0.455
N(10)	-0.924	-0.156	-0.687	-0.014
C(11)	-0.152	-0.329	0.075	-0.158
C(12)	0.451	0.342	0.323	0.183
C(13)	0.446	0.307	0.316	0.145
C(14)	-0.147	-0.290	0.076	-0.119
N(15)	-0.790	-0.955	-0.666	-0.772
C(16)	-0.111	-0.163	-0.179	-0.200
H(1)	0.159	0.149	0.087	0.128
H(2)	0.189	0.193	0.121	0.161
H(3)	0.191	0.155	0.123	0.142
H(4)	0.190	0.233	0.121	0.189
H(5)	0.188	0.197	0.114	0.157
H(6)	0.196	0.162	0.126	0.149
H(7)	0.187	0.194	0.120	0.162
H(8)	0.166	0.155	0.091	0.134
H(15a)	0.339	0.442	0.295	0.398
H(15b)	0.347	0.462	0.298	0.416
H(16a)	0.152	0.116	0.148	0.119
H(16b)	0.171	0.125	0.169	0.130
H(16c)	0.172	0.120	0.170	0.126

[a] For numbering of atoms, see Figure 2.

imply that dispersive (attractive) interactions dominate over repulsive ones and would cause thermodynamic stabilization of the crystal lattice. However, if ($E_d + E_r$) residues are combined with any of E_{el} values predicted, one obtains E_c values much lower than those determined experimentally (Table VII). Actually, very good conformity between E_{el} values originating from charges fitted to molecular electrostatic potential-calculated

on the DFT level (DFT/MEP fit), and experimental E_c values can be noted. It is thus evident that Coulombic energy predicted on this latter level of theory reflects very soundly the energy of cohesion in crystals of halide salts of nitrogen organic bases.

TABLE VI Atomic (ionic) parameters for evaluating the energy of dispersive and repulsive interactions.[49]

Entity	Parameter[a]						
	Originating from the London equation[46]			Originating from the Slater-Kirkwood equation[47]			C[b]
	D	A	B	D	A	B	
H	20.9	204.3	37.1	20.3	198.4	36.1	1.64
C	50.2	1395.2	522.4	50.0	1389.6	520.3	1.94
N	35.7	752.0	193.9	39.2	825.8	213.0	1.86
Cl^-	53.6	1265.4	185.7	105.0	2478.8	363.9	1.76
Br^-	71.8	2139.7	307.4	134.0	3993.3	573.8	1.78
I^-	104.1	4168.0	665.4	182.9	7323.1	1169.1	1.81

[a] D in $(kJ/mol)^{1/2}Å^3$; A in $(kJ/mol)^{1/2}Å^6$; B in $(kJ/mol)^{1/2}$; and C in $(Å)^{-1/2}$.
[b] Values for H, C, N originate from ref. 50 and for Cl^-, Br^-, I^- - from ref. 51.

The electrostatic lattice energies gradually decrease with the increase of dimensions of ionic fragments (Table VII). This tendency is clearly seen in Figure 4 where $-E_{el}$ values (originating from DFT/MEP fit) are plotted against the volume of a basic stoichiometric unit of the compounds, and is in accordance with the well-known empirical rules.[65]

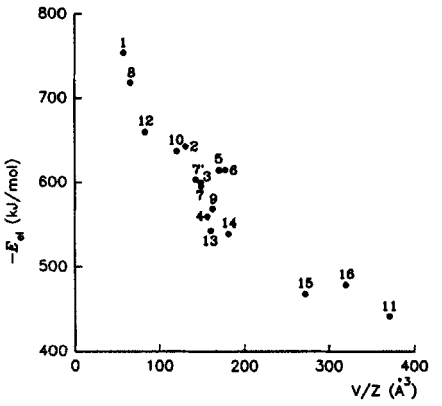


FIGURE 4 Electrostatic lattice energy (values relevant to DFT/MEP fit, Table VII; compound numbers are given at points) versus volume of a basic stiochiometric unit (Table IV).

TABLE VII Electrostatic, dispersive and repulsive terms of the crystal lattice energy of halide salts of nitrogen organic bases (in kJ/mol).

Compd.	E_{el}				E_d		E_r				E_c	
No.	HF[a]		DFT[a]		London[b]	Slater-Kirkwood[b]	London[b]		Slater-Kirkwood[b]		(experimental)	
(Table IV)	Mulliken	MEP fit	Mulliken	MEP fit			Eqn(4)	Eqn(5)	Eqn(4)	Eqn(5)	Value[c]	Ref.
1	-752.3	-753.8	-751.4	-754.0	-110.9	-205.9	60.5	66.6	116.1	122.9	-695	53,54
2	-619.4	-640.9	-623.5	-642.8	-95.2	-157.5	48.5	44.9	91.7	80.9	-626	53,55
3	-568.6	-598.6	-574.4	-600.4	-113.9	-175.1	47.6	47.2	88.4	79.8	-596	53,55
4	-561.3	-560.3	-563.3	-559.1	-160.0	-252.3	83.8	69.7	156.3	120.0	-571	53,55
5	-590.3	-612.8	-593.1	-614.9	-169.6	-258.3	75.8	76.3	132.4	126.9	-626	55
6	-601.6	-618.0	-595.7	-615.2	-115.4	-149.0	20.7	38.2	30.5	52.3	-661	56
7	-606.0	-600.9	-581.3	-595.3	-135.1	-204.4	65.6	61.3	117.6	101.1	-603	57
7'	-612.0	-607.5	-600.4	-603.5	-150.7	-248.0	128.7	67.7	240.8	122.2		
8	-716.5	-717.9	-715.7	-718.1	-97.5	-179.8	45.2	57.9	84.1	104.5	-667	53,58,59
9	-561.7	-565.8	-563.0	-568.5	-188.4	-297.8	193.1	108.3	347.2	184.3	-554	53,59,60
10	-623.1	-637.4	-624.0	-637.3	-132.5	-219.2	50.4	65.9	90.4	112.0	-639	59,61
11	-432.5	-444.8	-426.4	-441.4	-258.6	-332.4	31.8	83.7	44.6	110.7	-504	59,60
12	-658.8	-659.7	-658.3	-659.6	-77.1	-140.0	26.2	10.0	47.2	17.1	-633	53,58,62,63
13	-522.7	-541.3	-526.2	-542.5	-120.9	-176.9	25.2	23.3	41.2	31.2	-552	53,63
14	-535.3	-536.3	-537.0	-538.8	-168.3	-262.7	149.9	35.7	255.3	55.8	-521	53,60
15	-456.6	-472.1	-458.7	-467.6	-228.1	-309.8	33.9	64.7	47.1	79.3	-476	60,61,64
16	-466.4	-484.8	-451.5	-478.9	-232.3	-288.9	32.2	48.6	39.5	62.1		

[a] Method of atomic charges evaluation in the cation.
[b] The origin of dispersive and repulsive parameters (Table VI).
[c] Mean of values taken from references.

CONCLUDING REMARKS

X-ray analysis revealed that the cation in 9(10-methyl)-acridinimine hydriodide maintains theconstitution of the imino tautomeric form of 9-acridinamine. This proves that the tautomeric phenomenon should not be omitted in the case of this compound and its derivatives.

Theoretical calculations demonstrate that the Coulombic energy of halide salts of nitrogen organic bases, evaluated using partial atomic charges fitted to the molecular electrostatic potential on the DFT level, approximate experimental values of the lattice energy very well. This fact forms a very convenient framework on which to consider the lattice energetics of this group of compounds and sheds a new light on the nature of cohesive forces in organic ionic crystals.

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REFERENCES

1. J. Rak, J. Blazejowski and R. Zauhar, *J. Org. Chem.*, **57**, 3720 (1992).
2. A. V. Karyakin, A. M. Grigorovskii and N. G. Yaroslavskii, *Dokl. Akad. Nauk SSSR*, **67**, 679 (1949).
3. R. M. Acheson, M. L. Burstall, C. W. Jefford and B. F. Sansom, *J. Chem. Soc.*, 3742 (1954).
4. A. V. Karyakin and A. V. Shabya, *Dokl. Acad. Nauk SSSR, Ser. Khim.*, **116**, 969 (1957).
5. A. C. Capomacchia, J. Casper and S. G. Schulman, *J. Pharm. Sci.*, **63**, 1272 (1974).
6. A. C. Capomacchia and S. G. Schulman, *J. Pharm. Sci.*, **64**, 1256 (1975).
7. L. N. Short, *J. Chem. Soc.*, 4584 (1952).
8. Z. V. Pushkareva and Z. Yu. Kokoshko, *Dokl. Akad. Nauk SSSR*, **93**, 77 (1953).
9. A. K. Sukhomlina, *Zh. Obshch. Khim.*, **28**, 1038 (1958).
10. Yu. N. Sheinker and E. M. Peresteni, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **131**, 1366 (1960).
11. J. P. Kokko and J. H. Goldstein, *Spectrochim. Acta*, **19**, 1119 (1963).
12. F. N. Li, O. G. Rodin, V. V. Redchenko and V. F. Traven, *Zh. Obshch. Khim.*, **61**, 186 (1991).
13. J. Rak and J. Blazejowski, *J. Photochem. Photobiol. A: Chem.*, **67**, 287 (1992).
14. J. Lubkowski and J. Blazejowski, *J. Phys. Chem.*, **95**, 2311 (1991).
15. J. Lubkowski and J. Blazejowski, *J. Chem. Soc., Faraday Trans.*, **87**, 1333 (1991).
16. J. Lubkowski, P. Dokurno and J. Blazejowski, *Thermochim. Acta*, **176**, 183 (1991).
17. A. Albert and B. Ritchie, *J. Chem. Soc.*, 458 (1943).
18. G. M. Sheldrick, *SHELXS-86: Program for the solution of crystal structure* (University of Göttingen, Germany, 1986).
19. G. M. Sheldrick, *SHELX-76: Program for the solution of crystal structure determination* (University of Cambridge, England, 1976).

20. C. K. Johnson, *ORTEP: Repport ORNL-3794* (Oak Ridge National Laboratory, Tennessee, USA, 1965).
21. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*; S1 (1983).
22. J. Blazejowski and J. Lubkowski, *J. Therm. Anal.*, **38**, 2195 (1992).
23. P. W. Atkins, *Physical Chemistry*, 3rd ed. (W. H. Freeman, New York, 1986).
24. A. I. Kitajgorodsky, *Molecular Crystals and Molecules* (Academic Press, New York-London, 1973).
25. G. C. Maintland, M. Rigby, E. B. Smith and W. A. Wakeham, *Intermolecular Forces: Their Origin and Determination* (Clarendon Press, Oxford, 1987).
26. F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, **16**, 146 (1983).
27. W. Press, *Acta Crystallogr., Sect. A*, **29**, 257 (1973).
28. G. Raghurama and R. Narayan, *J. Phys. Chem. Solids*, **44**, 633 (1983).
29. J. Lingren and I. Olovsson, *Acta Crystallogr., Sect. B*, **24**, 549 (1968).
30. J. Lingren and I. Olovsson, *Acta Crystallogr., Sect. B*, **24**, 554 (1968).
31. R. W. G. Wyckoff, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **67**, 91 (1928).
32. G. L. Bottger and A. L. Geddes, *Spectrochim. Acta*, **21**, 1701 (1965).
33. C. Rerat, *Acta Crystallogr.*, **13**, 72 (1960).
34. C. J. Brown, *Acta Crystallogr.*, **2**, 228 (1949).
35. K. Hensen, P. Pallmann and J. W. Bats, *Z. Anorg. Allg. Chem.*, **556**, 62 (1988).
36. D. Mootz and J. Hocken, *Z. Naturforsch., Teil B*, **44**, 1239 (1989).
37. F. Jellinek, *Acta Crystallogr.*, **11**, 626 (1958).
38. A. Zalkin, *Acta Crystallogr.*, **10**, 557 (1957).
39. G. M. Sheldrick and W. S. Sheldrick, *Acta Crystallogr.*, **26**, 1334 (1970).
40. E. Wait and H. M. Powell, *J. Chem. Soc.*, 1872 (1958).
41. W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab initio Molecular Orbital Theory* (Wiley, New York, 1986).
42. J. K. Labanowski and J. W. Andzelm (eds), *Density Functional Methods in Chemistry* (Springer Verlag, New York, 1991).
43. R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).
44. C. M. Breneman and K. B. Wiberg, *J. Comput. Chem.*, **11**, 361 (1990).
45. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *GAUSSIAN 94, Revision B.2* (Gaussian, Inc., Pittsburgh PA, USA, 1995).
46. F. London, *Z. Phys. Chem.*, **B11**, 222 (1930).
47. J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).
48. R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965).
49. J. Rulewski, P. Dokurno, P. Skurski and J. Blazejowski, *Mol. Cryst. Lig. Cryst.*, this issue.
50. V. I. Poltev, *Kristallografiya*, **22**, 453 (1977).
51. C. R. A. Catlow, K. M. Diller and M. J. Norgett, *J. Phys. C: Solid State Phys.*, **10**, 1395 (1977).
52. D. E. Williams, *PCK 83: A crystal molecular packing analysis program* (Quantum Chemistry Program Exchange; Indiana University, Bloomington, USA), Program No. 481.
53. J. W. Wilson, *J. Chem. Soc., Dalton Trans.*, 890 (1976).

54. J. Blazejowski, *Thermochim. Acta*, **68**, 233 (1983).
55. J. Blazejowski and E. Kowalewska, *Thermochim. Acta*, **105**, 257 (1986).
56. J. Lubkowski and J. Blazejowski, *Thermochim. Acta*, **121**, 413 (1987).
57. J. Lubkowski and J. Blazejowski, *J. Chem. Soc., Faraday Trans. 1*, **82**, 3069 (1986).
58. H. D. B. Jenkins and D. F. C. Morris, *Mol. Phys.*, **32**, 231 (1976).
59. J. Lubkowski and J. Blazejowski, *Thermochim. Acta*, **157**, 259 (1990).
60. D. A. Johnson and J. F. Martin, *J. Chem. Soc., Dalton Trans.*, 1586 (1973).
61. B. M. Derakhshan, A. Finch, P. N. Gates and M. Stephens, *J. Chem. Soc., Dalton Trans.*, 601 (1984).
62. A. L. Goodlife, H. D. B. Jenkins, S. V. Martin and T. C. Waddington, *Mol. Phys.*, **21**, 761 (1972).
63. P. Dokurno, J. Lubkowski and J. Blazejowski, *Thermochim. Acta*, **165**, 31 (1990).
64. S. T. Nwankwo, *Thermochim. Acta*, **47**, 157 (1981).
65. M. W. Lister, S. C. Nyburg and R. B. Poyntz, *J. Chem. Soc., Faraday Trans. 1*, **70**, 685 (1974).