

Parametrization of Semiempirical Models against *ab Initio* Crystal Data: Evaluation of Lattice Energies of Nitrate Salts

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A method to estimate the lattice energies E_{latt} of nitrate salts is put forward. First, E_{latt} is approximated by its electrostatic component E_{elec} . Then, E_{elec} is correlated with Mulliken atomic charges calculated on the species that make up the crystal, using a simple equation involving two empirical parameters. The latter are fitted against point charge estimates of E_{elec} computed on available X-ray structures of nitrate crystals. The correlation thus obtained yields lattice energies within 0.5 kJ/g from point charge values. A further assessment of the method against experimental data suggests that the main source of error arises from the point charge approximation.

1. Introduction

The design of new drugs, polymers, or energetic materials takes advantage of methods to evaluate their properties before synthesis, using only the structural formula of the constitutive compounds as input. Such *a priori* predictive schemes usually rely on the parametrization of more or less empirical models against extensive experimental data.¹ Unfortunately, some properties do not lend themselves to direct experimental measurements. For instance, direct determination of the lattice energies (E_{latt}) of salts are often not possible as many such crystals dissociate into atoms rather than gaseous ions. While several estimation methods are available for inorganic salts,^{2–6} the lack of experimental data is a significant obstacle to the development of similar procedures for molecular organic salts. Accordingly, a recent method is restricted to simple salts containing spherical or highly symmetric cations (NH_4^+ , Na^+ , and K^+) and small molecular anions.⁷

The development of a more general method for organic salts is stimulated by recent investigations of ionic compounds as potential constituents of energetic materials.^{8,9} Indeed, the nitrate anion NO_3^- is a useful oxidizer sometimes employed in explosives or propellants, for instance with ammonium NH_4^+ as counterion.¹⁰ The energy content of ammonium nitrate is quite low, partly because of the significant contribution of the electrostatic contribution E_{elec} to the lattice energy. Larger cations might lead to more energetic nitrate salts of potential interest as green substitutes for ammonium perchlorate in propellant formulations. The quest for such compounds would benefit from the availability of computational methods to estimate the energy content of unsynthesized nitrate salts. Considering the limited accuracy of predicted densities and other approximations in the thermochemical modeling of propellant performances, an accuracy of 0.5 kJ/g on calculated formation enthalpies is usually considered satisfactory.^{10,11} While the

energy of isolated ions can in principle be obtained from quantum-chemical calculations, a model is needed to estimate lattice energies.

This work focuses on the Coulomb term E_{elec} that provides the dominant contribution to the lattice energy, not only for simple ionic crystals but also for more complex molecular salts.^{12,13} To make up for the lack of experimental lattice energies, theoretical values of E_{elec} are derived from calculations on available X-ray structures of nitrate crystals. A simple equation is parametrized using the reference data thus obtained. Its ability to predict lattice energies of new salts is assessed through a cross-validation procedure and tentative predictions of the formation enthalpies of salts with no available crystal structure.

2. Training Set

The X-ray structures of the organic salts used in this work were retrieved from the Cambridge Structural Database (CSD).¹⁴ Crystals containing multiply charged ions are not considered. Since they exhibit very high lattice energies that contribute negatively to the energy content of the material,⁷ they are not interesting for applications in propellants. On the other hand, only crystals made up of H, C, N, and O atoms are used. Most of them exhibit either ammonium or pyridinium as the nitrate counterion. In what follows, they will be referred to using their CSD identifier, i.e., a string of six uppercase letters. Only one inorganic crystal is included in the training set, namely the low-temperature polymorph (phase V) of ammonium nitrate $\text{NH}_4^+\text{NO}_3^-$.¹⁵ The enthalpy differences between the ammonium nitrate polymorphs lie within a few kilojoules per mole and may thus be safely neglected in the present context.¹⁶ In addition to ammonium nitrate, the training set consists of 45 organic nitrate salts, containing cations of various sizes (up to 55 atoms) and sometimes neutral species (nitric acid for OPENDN, water for BONKOE and YUFKUF). The present model has been parametrized for nitrate salts only, keeping in mind practical applications. However, in contrast to earlier methods,^{2–7} it is not restricted to salts made of small ions.

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3. Computational Details

The reference values of E_{elec} used to derive the present correlation are calculated explicitly on the 46 X-ray structures of the training set using atomic point charges.¹⁷ The latter are optimized to describe the B3LYP/6-31G* electrostatic potential of the isolated ions, using the CHELPG algorithm¹⁸ as implemented in the Jaguar program.¹⁹ The summation of the Coulomb expression for E_{elec} is carried out using the Ewald summation method and the Tinker program.²⁰

While the Coulomb energy E_{elec} depends on both the CHELPG atomic charges and the interatomic distances, only the dependence on the charges may be explicitly included in the lack of crystal data. E_{elec} should increase as the ionic charges get more localized and decrease with the ion size, as the mean distance between charged groups increases. Therefore, it should correlate with the following descriptor which exhibits similar variations:

$$\delta^2 = \frac{1}{N} \sum_i q_i^2 \quad (1)$$

where q_i is the charge of atom i and the summation runs over the N atoms in the chemical unit. In other words, the crystal contains N atoms per ion pair. To compute δ^2 , the use of the CHELPG values for q_i is quite natural as E_{elec} is derived precisely from the CHELPG atomic charges. However, such charges are known to be numerically ill-defined and thus deprived of physical meaning.²¹ Therefore, although they may be used to define electrostatic descriptors on the basis of the induced potential, a direct definition of the descriptors in terms of the CHELPG charges is questionable.

Therefore, simpler atomic charges models are also investigated. Mulliken charges provide the natural framework to describe electrostatic interactions within the SCC-DFTB model.²² In addition, for simple molecular salts, they yield values of E_{elec} in fair agreement with the values obtained using their CHELPG counterparts and with observed lattice energies.¹⁷ On the other hand, they may be obtained much more efficiently as the SCC-DFTB model relies on the tight-binding formalism. Finally, the use of formal atomic charges is also addressed in this paper, to assess the role of electron delocalization on the ionic species. Fractional values of the formal charges are used only when required by symmetry.

In the present scheme, E_{elec} is assumed to correlate with δ . The quadratic dependence of the Coulomb energy on the charges suggest the following expression (in atomic units)

$$E_{\text{elec}} = e^2/R_0 + \delta^2/R_1 \quad (2)$$

where $e = 1$ is the unit charge, R_0 and R_1 are empirical parameters. The constant e^2/R_0 does not depend on the nitrate crystal considered, and may be viewed as the contribution to E_{elec} of two opposite unit charges lying at a distance R_0 from each other. The second term in eq 2 is the contribution of two charges $\pm\delta$ separated by the effective distance R_1 .

The values of e^2/R_0 and $1/R_1$ are obtained using the singular value decomposition procedure.²³ Then, a leave-one-out cross-validation is carried out,²⁴ whereby a value of E_{elec} is predicted for every crystal using a model parametrized against the point charge energies of all other crystals in the data set. To assess the significance of the correlations obtained, the square correlation coefficient R^2 and the standard deviation σ derived from the fit are compared to the corresponding values obtained for the cross-validation, i.e., for E_{elec} values predicted rather than fitted.

TABLE 1: Crystal Structures Used To Derive the Present Model and Associated Lattice Energies (kJ/mol) Derived from Eq 2 and Calculated within the Point Charge (PC) Approximation for the Observed X-ray Structures^a

crystal	eq 2	PC
HAWYIN	519	459
ZIZJAT	502	460
KUCPED	517	474
NOZWEE	497	497
YIJHEE	514	498
FOJWAC	519	499
VEGZOW	570	505
EDOWEZ	502	507
HUQRAM	506	512
OPENDN	536	516
VAZZEB	518	519
QOGPOR	565	526
IBOLOA	563	527
NISGIF	574	529
TAGUDN	556	531
FAQCIJ	586	534
ECADIV	524	536
RAVQIO	491	537
HOFJER	555	543
CYTIDN	528	543
ECADER	558	544
SIBVUU	581	544
GULHEA	589	549
JOJRAB	580	549
BZCYTN	513	553
MIFTUQ	551	554
XAKVAG	551	556
HUZLUJ	544	557
MORPHN	534	560
IBOLUG	590	562
HUHSOS	524	564
MEGUAN	573	577
WIKGEC	588	581
LOKFIA	581	585
GLYCNI	612	596
VAXLIP	552	602
EDOHIO	532	607
JIFKIS	606	610
GLGLYN	570	611
LETGIA	611	616
BONKOE	562	632
YUFKUF	586	633
ZUHNAR	589	645
MACMNO	608	647
UREANT	637	652
NH4NO3	670	696

^a The crystals are referred to using their CSD identifier, except for NH_4NO_3 which stands for ammonium nitrate.

Finally, a preliminary application of the model obtained for E_{elec} to the evaluation of solid-state formation enthalpies is carried out, assuming as a first approximation $E_{\text{latt}} \approx E_{\text{elec}}$. The solid-state formation enthalpy is obtained by subtracting E_{latt} from the contribution $\Delta_f H^\circ(g)$ of the individual species that make up the crystal:

$$\Delta_f H^\circ = \Delta_f H^\circ(g) - E_{\text{latt}} - 2RT \quad (3)$$

R and T stand respectively for the ideal gas constant and temperature. $\Delta_f H^\circ(g)$ is derived from density functional calculations. For this purpose, the P2 atom equivalents²⁵ are added to BP/DN** energies calculated on AM1 geometries, following a procedure that yields enthalpies within 0.2 kJ/g from experiment for small ions.¹⁷

4. Point Charge Electrostatic Energies

The point charge electrostatic energies calculated for the 46 crystals of the database are reported in Table 1. Although

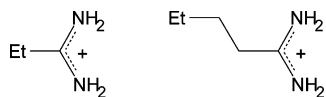


Figure 1. Cations of nitrate crystals ECADER (left) and ECADIV (right).

crystals with cations of very different sizes are considered (from 12 to 55 atoms) the values of E_{elec} , reported on a per mole basis, are quite similar. Indeed, 95% of them lie in the range 450–650 kJ/mol. This result is consistent with the lattice energies reported by Politzer and Murray, whose magnitudes are quite similar unless doubly charged ions are considered.⁷ The most significant value (696 kJ/mol) is observed for ammonium nitrate, presumably because of the relatively small size of the ions. As expected, increasing the size of the neutral substituent on a charged group decreases the electrostatic contribution to the crystal cohesion as a result of the increased charge spacing. For instance, E_{elec} decreases from 544 kJ/g to 536 kJ/g on going from ECADER to ECADIV (Figure 1). This demonstrates that it cannot be estimated on the basis of group-additivity, unless unphysical negative values are introduced for contributions associated with uncharged moieties.

In fact, assuming a constant value of 558 kJ/mol for electrostatic energies of nitrate salts yields a standard deviation of only 53 kJ/mol from the theoretical point charge values, or 0.40 kJ/g if the values are reported on a per gram basis. The most significant deviations concern the lattice energies of crystals made of relatively small ions, which tend to be underestimated by as much as 1.93 kJ/g for ammonium nitrate, and 0.7–0.8 kJ/g for some organic nitrates (UREANT and MACMNO). Thus, it is desirable to improve on this rough approximation. In what follows, the role of atomic charges is included via eq 2.

5. Correlation

Using either CHELPG or formal atomic charges, the regression yields poor correlations between E_{elec} and δ^2 , with $R^2 < 0.34$. This may be explained by the fact that formal charges neglect bond polarization and electron transfer associated with electronegativity differences between atoms. On the other hand, as explained previously, CHELPG atomic charges should be used only through the electrostatic potential. In what follows, only the results obtained using the SCC-DFTB charges are discussed. In this case, a better correlation is obtained, with $R^2 = 0.56$ and a root-mean-square deviation $\sigma = 35$ kJ/mol from point charge data. In other words, the model explains about 56% of the variance observed for E_{elec} . Keeping in mind that interatomic distances are ignored, significant improvement appears unlikely. The standard deviations of the empirical parameters e^2/E_0 and $1/R_1$ are $<0.5\%$ of their actual values. Moreover, similar values of R^2 and σ (respectively 0.52 and 36 kJ/mol) are obtained using the data predicted in the cross-validation step. On going from the previous assumption of a common value of E_{elec} (in kJ/mol) for all nitrate salts to eq 2, the root-mean-square deviation from point charge values decreases from 53 to 36 kJ/mol, or from 0.4 to 0.2 kJ/g when reported on a per gram basis. This 2-fold reduction is significant for practical applications. In fact, the present scheme yields lattice energies within 0.5 kJ/g from the point charge values, as illustrated in Figure 2.

It may be worth pointing out that using lattice energies in kJ/g throughout this study, values of R^2 as high as 0.99 (for the regression) and 0.97 (for the cross-validation) would have been obtained. This is a striking illustration of the fact that R^2 is no

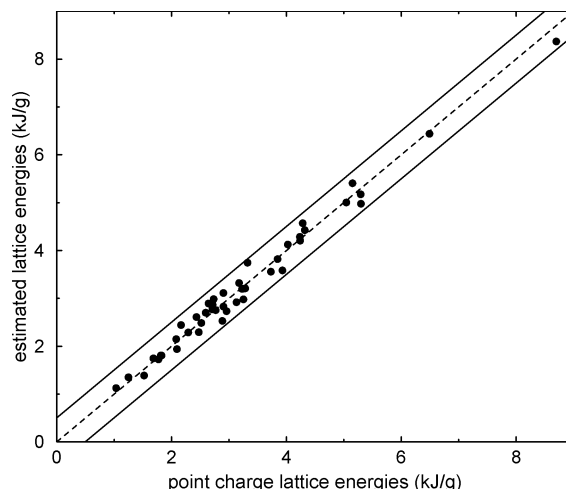


Figure 2. Plot of the electrostatic energies estimated using eq 2 and SCC-DFTB charges vs point charge values calculated explicitly using the observed crystal structures.

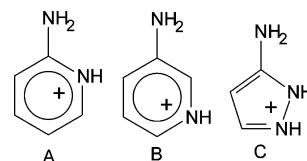


Figure 3. Chemical structures of the ring-containing cations listed in Table 2: 2-aminopyridinium (A), 3-aminopyridinium (B), and 3-aminopyrazolium (C).

sufficient criterion to assess the significance of empirical correlations, even if a cross-validation is carried out. To further demonstrate this point, the cross-validation of a four parameters model previously developed for ammonium salts⁷ yields $R^2 = 0.99$, using data reported on a per mole basis. In fact, such apparently good results are obtained because lattice energies of NH_4^+ salts depend essentially on the total charge Q of the anion. As the data set contains only ammonium crystals with $Q = -1$ or $Q = -2$, we are left with a set of two data points. Actually, removing doubly charged anions reduces the value of R^2 associated with the cross-validation from 0.99 to 0.31.

For the present model, the regression yields $R_0 = 3.31$ Å and $R_1 = 1.91$ Å. Since the point charge values of E_{elec} lie in the range 450–700 kJ/mol, the constant term $e^2/R_0 = 420$ kJ/mol provides the major contribution. The value of R_0 is consistent with the interpretation of this term as the contribution to E_{elec} of charged groups in closest proximity. Indeed, it is consistent with typical separations between charged groups in close contact, and especially with a previous observation that the $\text{N} \cdots \text{N}$ distances between nitrogen atoms of $-\text{NH}_3^+$ and NO_3^- moieties typically lie between 3.2 and 3.5 Å.¹⁷ On the other hand, the charges on the cationic charged groups and on NO_3^- are approximately $\pm e$. This interpretation provides a simple explanation for the similarity of the lattice energies of nitrate salts. Indeed, whatever the crystal, the shortest distances between the nitrate ions and the cationic charged groups remain quite similar. Increasing the size of the cation induces larger distances between ions, but does not prevent nitrate ions from remaining in close contact with cationic charged groups. In other words, the shortest interionic distances are unchanged. As a result, a major contribution to E_{elec} is roughly constant. The actual dependence of E_{elec} on the nitrate salt probably depends on the details of the ion packing in the crystal and is only qualitatively described by the second term in the rhs of eq 2 which represents the energy of two charges $\pm e$ lying 1.91 Å

apart. This term accounts for the decrease of E_{elec} with the addition of neutral groups, as illustrated by the values calculated for ECADER and ECADIV (Table 1). Moreover, the value of E_{elec} estimated for ammonium nitrate using eq 2 is underestimated by only 0.32 kJ/g. The deviation from the point charge value is thus reduced 6-fold with respect to the previous assumption of a common value for the lattice energies of nitrate salts.

For ammonium nitrate, it is also interesting to note that the experimental lattice energy (8.46 kJ/g) lies below the point charge E_{elec} value (8.70 kJ/g). This suggests that the contribution of the short-range van der Waals interactions to E_{latt} is negative (i.e., destabilizing with the present sign convention, as it contributes negatively to the crystal cohesion). More accurate estimates of E_{elec} would be valuable to confirm this point, since the difference might be irrelevant with regard to the description of E_{elec} in term of CHELPG atomic charges. A negative short-range contribution would imply a predominance of the short-range atom–atom repulsion over the van der Waals stabilizing energy. This possibility is not excluded in view of the very high compacity of the ammonium nitrate crystal, with a Kitaigorodsky packing coefficient $C_K = 0.86$ (usually, $C_K < 0.75$ for organic molecular crystals²⁶). It might be rationalized with the concept of repulsive destabilizing contacts put forward by Dunitz and Gavezzotti.²⁷ As pointed out by these authors, interatomic distances in crystals may be short enough for the atom–atom potential (defined according to a given empirical force field) to be positive. In such circumstances, short-range interactions contribute negatively to the crystal cohesion. However, while Dunitz and Gavezzotti attributed this effect to the enhancement of attractive intermolecular forces with increased numbers of atoms in the molecules, it is clear that the high compacity of ammonium nitrate does not stem from the size of the ions, but rather from the magnitude of electrostatic forces. A simple picture emerges from such considerations: in salts made of small molecular ions, the large electrostatic forces might push the ions so close to each other than the short-range energy may be destabilizing. This might explain why the present model appears to underestimate the cohesion of salts made of small ions, such as ammonium nitrate (Table 1).

6. Application

To further assess the reliability of eq 2 and illustrate its potential interest, it is used in this section to evaluate the lattice energies of additional nitrate salts for which X-ray data is lacking, on the basis of the common approximation $E_{\text{latt}} \approx E_{\text{elec}}$. A direct validation of the results is not possible since E_{latt} is not available from experiment. Therefore, an indirect validation is carried out, whereby the lattice energies derived from eq 2 are used to estimate solid-state formation enthalpies $\Delta_f H^\circ$ that may be compared to experimental values compiled in the ICT database.²⁸ The results are reported in Table 2. They are quite reasonable, considering the significant approximations involved, i.e.:

(1) the use of atom equivalents derived from gas-phase studies of neutral molecules to estimate the formation enthalpies of the isolated ions;

(2) the assumption $E_{\text{latt}} \approx E_{\text{elec}}$;

(3) the point charge approximation for E_{elec} ;

(4) the limitations of eq 2 as a predictive model for E_{elec} .

Despite all these simplifications, most estimated values of $\Delta_f H^\circ$ are within 0.5 kJ/g from experiment. The most significant deviation (+0.73 kJ/g) is consistent with the largest errors observed so far on applying the P2 procedure to ions (≈ 0.2

TABLE 2: Calculated Enthalpies of Isolated (“Gas-Phase”) Ions $\Delta_f H^\circ(\text{gas})$ and Estimated (calcd) and Measured (obsd) Formation Enthalpies of Nitrate Crystals (in kJ/g)^a

cation	$\Delta_f H^\circ(\text{gas})$	calcd	obsd
NH ₄ ⁺	+3.93	−4.49	−4.57
H ₃ C−NH ₃ ⁺	+3.09	−3.40	−3.75
HC(CH ₃) ₂ −NH ₃ ⁺	+1.70	−2.90	−3.39
O ₂ NO−CH ₂ −CH ₂ −NH ₃ ⁺	+1.35	−2.27	−2.77
2-aminopyridinium	+2.40	−1.14	−1.57
3-aminopyridinium	+2.50	−1.04	−1.58
3-aminopyrazolium	+3.51	−0.43	−1.16

^a Figure 3 shows the chemical structures of some of the cations. The contribution $\Delta_f H^\circ(\text{gas})$ of the isolated ions is obtained using the P2 procedure.²⁵ The lattice energy contribution to the crystal formation enthalpies is obtained from eq 2.

kJ/g) and eq 2 to the evaluation of E_{elec} (≈ 0.5 kJ/g). However, Table 2 indicates that $\Delta_f H^\circ$ is systematically overestimated, especially for the most extended cations. This suggests that a stabilizing contribution is missing. This might be either the van der Waals interactions or the effect of the point charge approximation, which appears to underestimate the cohesion of molecular crystals arising from Coulomb interactions.²⁹ In both cases, this contribution is expected to scale with the number of atoms. An empirical additive correction of 5.6 kJ/mol per atom yields values of $\Delta_f H^\circ$ within 0.3 kJ/g from experiment for the seven salts in the validation set. In view of its magnitude, the need for this correction cannot be explained only by the lack of van der Waals interactions, which are typically <1 kJ/mol per atom. Therefore, the systematic lack of cohesion appears to arise partly because of the point charge approximation. In view of the scarcity of experimental values for lattice energies of molecular salts, a more reliable modeling of the missing contribution to the cohesion in eq 2 should rather take advantage of formation enthalpies, for which extensive compilations are available.³⁰

7. Conclusions

The present work supports previous findings obtained for crystals of neutral molecules, namely the fact that the point charge approximation underestimates E_{elec} . On the other hand, while lattice energies of nonionic molecular crystals increase with the size of the molecules³¹ and may be estimated using group contribution approaches,³² lattice energies of molecular salts decrease with the size of the constitutive species.

Two approaches are commonly used to estimate the properties of materials before their actual synthesis: in most cases, a correlation is drawn between the property of interest and descriptors derived from the molecular structure.⁷ The other straightforward approach relies on the crystal packing technique.¹⁷ The present method combines the advantages of both approaches: it exhibits the simplicity of semiempirical models parametrized against experiment, but does not depend on experimental data beyond X-ray structures. This intermediate approach should get even more interesting as a growing number of crystal properties may be obtained from simulations.

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