

# Evaluation of solid-state formation enthalpies for energetic materials and related compounds

Didier Mathieu, Philippe Simonetti\*

Commissariat à l'Energie Atomique, Le Ripault, BP16, 37260 Monts, France

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## Abstract

Solid-state formation enthalpies of energetic materials and related compounds are estimated from the difference between the calculated gas-phase formation enthalpies and sublimation enthalpies. The rms deviation from the observed values is 0.21 kJ/g using the most accurate method. The errors mostly depend on the limitations of the methods available to calculate the gas-phase contribution. For instance, the rms deviation increases by approximately 0.15 kJ/g on going from Density Functional Theory (DFT) to semi-empirical methods for this purpose. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Density Functional Theory; PIMM; Enthalpy

## 1. Introduction

In view of practical applications, energetic materials must combine good performances with a low vulnerability. A strong emphasis on the latter might lead to new compounds whose high safety is obtained at the expense of the performance. To insure against such a case, the performances of new materials should be evaluated prior their actual synthesis. This calculation requires accurate thermochemical data as input, including solid-state formation enthalpies  $\Delta_f H^\circ(\text{sol})$ . The latter are obtained as the difference between the gas-phase values  $\Delta_f H^\circ(\text{gas})$  and sublimation enthalpies  $\Delta_{\text{sub}} H^\circ$ . Efficient quantum chemical methods provide estimates of  $\Delta_f H^\circ(\text{gas})$  typically within a few tenths of kiloJoules per gram from the experiment [1]. While for most compounds this is comparable to the magnitude of  $\Delta_{\text{sub}} H^\circ$ , sublimation enthalpies greater than 4 kJ/g have been measured for porphyrin

derivatives [2]. Thus, to avoid a significant contribution of sublimation enthalpies to the error on  $\Delta_f H^\circ(\text{sol})$ , they should be estimated at least within 0.1 kJ/g from the experimental value. With the aim of calculating reliable detonation parameters, it is desirable to obtain enthalpies with errors no greater than 0.5 kJ/g [3].

Recently, a general scheme aimed at predicting  $\Delta_f H^\circ(\text{sol})$  for organic solids has been put forward and applied to energetic compounds [4,5]. However, as it requires costly geometry optimizations and electronic structure calculations using Density Functional Theory (DFT), it cannot be applied in the early stages of the design of new materials whenever extensive screening of candidate compounds is involved. Such extensive searches for optimized molecules are carried out in the context of recent approaches based on the computer generation of synthons, starting either from the gross formula [6] or from Markush structures [7]. On the other hand, the accuracy gained from the use of DFT for  $\Delta_f H^\circ(\text{gas})$  is likely to be spoiled by the limitations of the model equation employed to evaluate  $\Delta_{\text{sub}} H^\circ$  [8].

\* Corresponding author.

E-mail address: philippe.simonetti@cea.fr (P. Simonetti).

The present paper, following ideas introduced by Politzer and coworkers [4,9], outlines the procedures aimed at reducing the computational cost of the original method, while improving its accuracy through better estimates of  $\Delta_{\text{sub}}H^\circ$ . After a description of the methods used to calculate  $\Delta_fH^\circ(\text{gas})$  and  $\Delta_{\text{sub}}H^\circ$ , they are applied to the calculation of  $\Delta_fH^\circ(\text{sol})$  for a set of compounds used in the formulation or processing of energetic materials. The results are essentially reported on a per mass basis as such values are more relevant both for the comparison of different estimation methods and in view of applications in the field of energetic materials.

## 2. Model equations

In the present study,  $\Delta_fH^\circ(\text{gas})$  and  $\Delta_{\text{sub}}H^\circ$  are evaluated independently from the molecular structure of the isolated compound. Evaluation of  $\Delta_fH^\circ(\text{gas})$  is especially straightforward. Two main approaches are used. Whenever efficiency is crucial, the PIMM force field (1991 parameterization) [10] is employed, as it turned out to provide a reasonable trade-off between accuracy and efficiency. In particular, geometries and enthalpies obtained with PIMM appear to be more reliable than the results of semi-empirical methods [1,10]. Somewhat more accurate values may be derived from the P2 procedure of Rousseau and Mathieu [11]. Because it uses DFT energies obtained from the single-point calculations on molecular structures optimized with the MMFF/Spartan force field [12], this procedure is much more efficient than the previous ones [5,9,14]. However, owing to the deficiencies of this implementation of the force field, it is not very reliable for some series of compounds, especially nitroaromatics. In both PIMM and P2 models, the formation enthalpy is obtained from the expression

$$\Delta_fH^\circ(\text{gas}) = E + \sum_k H_k \quad (1)$$

where the index  $k$  runs over the constituent atoms of the system. With the PIMM force field, the parameter  $H_k$  stands for the standard formation enthalpies of the free atoms, and the energy  $E$  is fitted so that Eq. (1) gives the formation enthalpy of the molecule [10]. In the P2 approach,  $E$  is the total DFT energy and the  $H_k$  includes not only the formation enthalpies of free

atoms, but also thermal effects, the zero-point energy of the molecule and empirical corrections to  $E$  aimed at correcting the limitations of the functional employed [11].

Having selected a method to calculate the gas-phase formation enthalpies, a scheme to evaluate sublimation enthalpies is needed, such as the equation introduced by Politzer et al. [4]. However, it turned out necessary to slightly modify this equation in view of applications to molecules of very different sizes [8]. Finally, for a large calibration set (245 compounds) no significant correlation could be found if only the original set of descriptors was retained, namely the total molecular surface area  $S$ , and the electrostatic parameters  $\sigma_{\text{tot}}$  and  $\nu$  describing the magnitude of the electrostatic potential on the molecular surface and the balance between the positive and negative regions, respectively [4]. However, a good fit was obtained using the following equation:

$$\Delta_{\text{sub}}H^\circ = \sum_k \sigma_k S_k + a\nu\sigma_{\text{tot}} + b \sqrt{\sum_{A,H} \frac{S_A S_H}{S}} \quad (2)$$

where explicit expressions have been introduced to represent the short-range Van der Waals interactions at the molecular surfaces, the electrostatic energy and the hydrogen bond contribution. The Van der Waals contribution is expressed in terms of the atomic surface areas  $S_k$  and surface tensions  $\sigma_k$ . The hydrogen bond contribution is assumed to scale as the average concentration of hydrogen bonds, written in terms of the contributions  $S_A$  and  $S_H$  to the total molecular surface  $S$ , where the indexes  $A$  and  $H$  refer to proton acceptors and labile protons, respectively. The square root in Eq. (2) reflects the fact that the interactions sites  $A$  and  $H$  are not free as they lie on the molecules [15]. For the time being, all hydrogen bonds are treated on the same footing, notwithstanding the difference in the bond energies for different hydrogen-bonded pairs  $A-H$ . The fitting of the parameters involved in Eq. (2) was carried out in two steps. First, the electrostatic parameter  $a$  and the atomic surface tensions  $\sigma_k$  were calibrated against a training set of 128 molecules unable to get involved in hydrogen bonds [15]. The rms deviation between fitted and measured sublimation enthalpy was  $\lesssim 0.05$  kJ/g, and no error  $> 0.16$  kJ/g. Then, this model without the H-bond term was applied to 64 hydrogen-bonded compounds. The differences between the measured

Table 1  
Optimal values of the parameters used in Eq. (2) according to the atomic charges describing the electrostatic potential

Parameter	PIMM charges	EEM charges
$a$	408	813
$b$	21.5	19.5
$\sigma_{\text{H}}$	0.236	0.236
$\sigma_{\text{C}}$	0.558	0.542
$\sigma_{\text{N}}$	0.500	0.346
$\sigma_{\text{O}}$	0.493	0.336
$\sigma_{\text{Cl}}$	0.440	0.407

and predicted sublimation enthalpies for those compounds were defined as the H-bond contribution and fitted to the last term of Eq. (2) through the adjustable parameter  $b$ . The rms error, however, was twice as large as for the materials deprived of H-bonds, and the largest one approximately 0.25 kJ/g. Thus, predicted sublimation enthalpies are expected to be less accurate for the H-bonded crystals. A detailed report of this estimation method for  $\Delta_{\text{sub}}H^\circ$  will be given elsewhere [15]. A nice feature of the present model may be noted by considering the sublimation enthalpy that would be obtained from molecular mechanics calculations, for compounds whose crystal structure is available. As most classical force fields describe the intermolecular interactions using Van der Waals, Coulomb and hydrogen bond potentials, the resulting expression for  $\Delta_{\text{sub}}H^\circ$  would consist of three terms, corresponding to those involved in Eq. (2). The final parameters obtained for Eq. (2) are reported in Table 1, according to the model used for the electrostatic potential (Section 3). Some parameters, namely the surfaces tensions of nitrogen and oxygen and the electrostatic coefficient  $a$ , differ significantly on going from one electrostatic potential model to the other, owing to the correlation between the values of the potential at the molecular surface and the presence of heteroatoms on the molecule. It will be checked in the following section that this underdetermination of the parameters does not affect the calculated sublimation enthalpies.

### 3. Computational methods

As one must resort to a simple model equation to estimate the sublimation enthalpies, there is no point

in using highly accurate and expensive methods to obtain the required geometries and electrostatic potentials [8]. Therefore, all the descriptors involved in Eq. (2) were calculated for the molecular geometries optimized using the PIMM force field. The Van der Waals definition is adopted for the molecular surface. Notwithstanding the practical advantages of this choice, it allows a straightforward definition of the atomic surface areas  $S_k$  that would be more involved if isodensity surfaces were used. The  $S_k$  areas were computed using the NSC routine of Eisenhaber et al. [16]. The molecular electrostatic potential (required for the calculation of the descriptors  $\nu$  and  $\sigma_{\text{tot}}$ ) is represented in terms of atomic charges. Because the geometry is optimized using the PIMM force field, the associated atomic charges have been used. However, these charges are not aimed at providing a reliable description of the molecular electrostatic potential. Therefore, approximate CHELPG potential-derived atomic charges [17] have been calculated from the electronegativity equalization principle [18]. For this purpose, the dependence of the total energy on the atomic charges  $q_k$  is expressed as

$$E = \sum_k E_k(0) + \chi_k q_k + \frac{1}{2} \eta_k q_k^2 + \sum_{k,k'} q_k q_{k'} J_{k,k'} \quad (3)$$

where the parameters  $\chi_k$  and  $\eta_k$  depend only on the atomic number of the atom  $k$ , and  $E_k(0)$  stands for the energy associated with atom  $k$  of the system when its charge  $q_k = 0$ . The latter quantity has no influence on the charge distribution. Indeed, minimization of  $E$  with respect to  $N$  charges  $q_k$ , accounting for the constraint that the  $q_k$  sum to 0 for a neutral molecule, yields  $N - 1$  equations for the charges

$$\chi_k + \eta_k q_k + \sum_{k' \neq k} J_{k,k'} q_{k'} = \chi_{k+1} + \eta_{k+1} q_{k+1} + \sum_{k' \neq k+1} J_{k+1,k'} q_{k'} \quad (4)$$

These equations, together with the charge neutrality constraint, allow to determine atomic charges  $q_k$ , hereafter denoted as EEM charges as they derive from an electronegativity equalization method. Indeed, Eq. (4) expresses the equality of the electronegativity (or chemical potential) between atoms  $k$  and  $k + 1$ . The present version of EEM is similar to that of Mortier et al. [18]. However, instead of a bare Coulomb

potential for  $J_{k,k'}$ , the Klopman interpolation [19] is used

$$J_{k,k'} = \frac{1}{\sqrt{R_{k,k'}^2 + (1/4)((1/U_k) + (1/U_{k'}))^2}} \quad (5)$$

The Hubbard parameters  $U_k$  are obtained from the differences between the experimental ionization potentials and electron affinities for isolated atoms, taken from the NIST Chemistry Webbook database [13]. Electronegativities  $\chi_k$  and hardnesses  $\eta_k$  are parameters of EEM approaches that depend on the definition selected for the target atomic charges. In the present work, they were fitted against CHELPG potential-derived charges calculated at the B3LYP/6-31G\* level of theory for a set of 167 molecules containing H, C, N, O, F and Cl atoms. The final values obtained are reported in Table 2. They should not be confused with values compiled for isolated atoms. Indeed, the latter are derived from the standard definitions of electronegativity and hardness involving the number of electrons in the system considered [22]. This number is not

Table 2

Electronegativities  $\chi$  and hardnesses  $\eta$  optimized to mimic B3LYP/6-31G\* potential-derived atomic charges (atomic units)

Atom type	$\chi$	$\eta$
H	0.2056	0.4918
C	0.2193	0.3343
N	0.2696	0.4595
O	0.6700	1.3863
F	0.2589	0.5882
Cl	0.1802	1.3544

well defined for atoms in molecules, hence the need for a parameterization against atomic charges. The values reported in Table 2 are specific to the CHELPG charges model. Further details will be reported elsewhere [15].

#### 4. Results

The methods outlined in the preceding sections have been applied to energetic materials and related

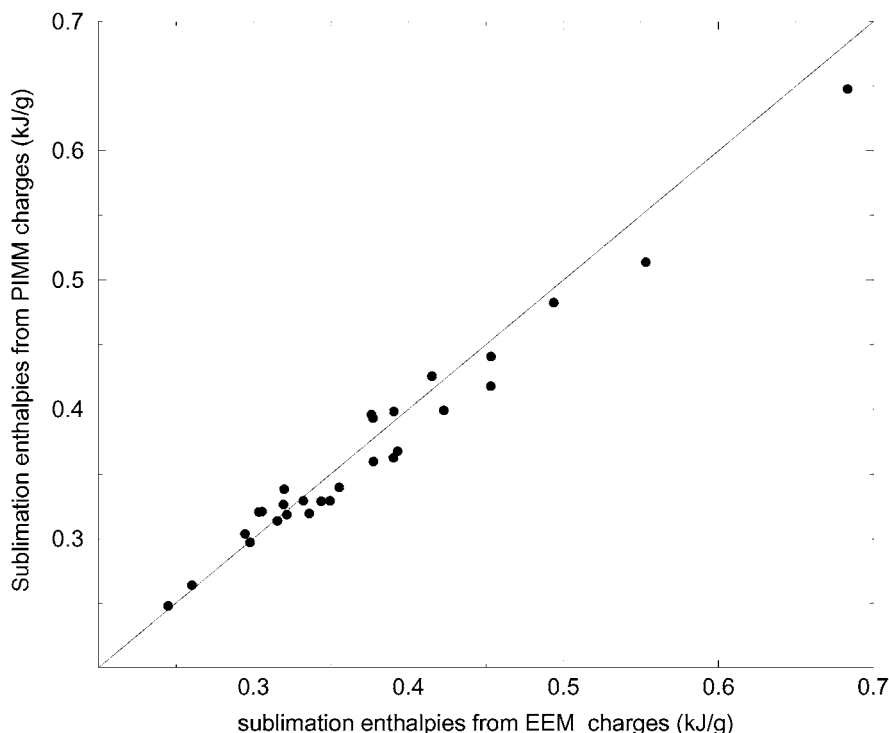


Fig. 1. Comparison of standard sublimation enthalpies  $\Delta_{\text{sub}}H^\circ$  calculated from Eq. (2) using the electrostatic potential derived either from EEM or PIMM atomic charges.

compounds whose solid-state formation enthalpies have been measured and compiled in the I.C.T. database [20]. Values of  $\Delta_f H^\circ$  (gas) or  $\Delta_{\text{sub}} H^\circ$  are available for only few of these materials. It should be realized that the solid-state enthalpies reported by I.C.T. often appear unreliable in view of the discrepancies between independent measurements. For instance, the formation enthalpies reported for 1-methyl-3,3-diphenylurea range from  $-0.47$  to  $0.02$  kJ/g. This is understandable as many measurements were carried out more than 30 years ago. The most recent values were systematically retained. Moreover, data from the

NIST Chemistry Webbook [13] were preferred whenever available. Even there, the values reported may be significantly scattered, ranging from  $-0.40$  to  $-0.29$  kJ/g for triaminotrinitrobenzene (TATB) and from  $-0.69$  to  $-0.33$  kJ/g for RDX. Finally, 34 materials were selected to assess the present estimation procedures. Some of them are well-known energetic materials, e.g. trinitrotoluene (TNT), HMX or TATB. The others are used in the fields of propellants or explosives, e.g. as plasticizers, stabilizers or processing aids. Some nitroaromatic and nitramine compounds are considered, although their formation

Table 3

Experimental solid-state formation enthalpies and differences between the calculated and observed values for the 34 compounds studied (kJ/g)

Molecule	$\Delta_f H^\circ$ (sol) <sub>obs</sub> [21]	$\Delta_{\text{PIMM}}$	$\Delta_{\text{PM3}}$	$\Delta_{\text{P2}}$
Diphenylethyne	1.75	0.17	0.23	0.17
2,2'-Azo-bis-isobutyronitrile	1.50	0.53	0.35	0.25
2,5-Dimethyl-4'-methoxyazobenzene	0.84	-0.10	-0.55	-0.32
2-Naphthyl phenylamine	0.73	0.25	0.22	0.21
Diphenylamine	0.69	0.29	0.23	0.23
Hexogene (RDX)	0.36	0.32	0.03	0.07
Octogene (HMX)	0.25	0.69	0.27	0.23
1,3,3-Trinitroazetidine (TNAZ)	0.19	0.14	-0.06	0.24
Flexzone 6H	-0.08	0.39	0.16	0.29
Trinitrobenzene	-0.17	-0.08	-0.17	0.07
Trinitrotoluene (TNT)	-0.28	-0.14	-0.15	0.00
Triaminotrinitrobenzene (TATB)	-0.29	-0.63	-0.65	-0.10
<i>N,N'</i> -dimethyl- <i>N,N'</i> -diphenyl-urea	-0.30	0.25	0.24	0.24
1,3-Diethyl-1,3-diphenylurea	-0.39	0.14	0.14	0.14
1-Methyl-3,3-diphenylurea	-0.47	0.37	0.38	0.23
<i>N,N</i> -diphenyl-urea	-0.53	0.41	0.43	0.29
Melamine	-0.60	0.41	0.74	0.17
<i>N,N</i> -diphenyl- <i>N'</i> -ethylurea	-0.63	0.44	0.41	0.26
Ethylenedinitramine	-0.79	0.77	0.68	-0.22
Diphenylurethane	-1.16	0.29	0.33	0.15
Dinitroglycoluril (DINGU)	-1.35	0.35	0.02	0.17
Diphenyl phthalate	-1.54	0.12	0.36	0.17
Butylated hydroxytoluene	-1.67	0.18	0.05	0.13
Camphor	-2.10	0.36	0.29	0.34
Ethyl- <i>N,N</i> -phenylethylcarbamate	-2.18	0.39	0.39	0.15
Dicyclohexyl phthalate	-2.82	0.32	0.35	0.19
1,1,2,2-Tetrafluoro-1,2-diphenylethane	-3.11	0.28	0.51	0.37
Resorcinol	-3.34	0.20	0.34	0.32
Pyrrole-2,4-dicarboxylic acid	-3.83	0.47	0.54	0.16
Sebacic acid dimethylester	-4.50	0.23	0.36	0.13
<i>N,N'</i> -dicarbethoxy-ethylenediamine	-4.80	0.42	0.57	-0.03
1,2,5-Hexanetriol	-5.29	-0.05	-0.07	-0.05
Etriol	-5.56	-0.03	0.23	0.39
Trimethyl citrate	-6.09	-0.17	0.43	0.08
rms Deviation		0.35	0.37	0.21
Largest negative error		-0.63	-0.65	-0.32
Largest positive error		+0.77	+0.74	+0.39

enthalpies are not reliably estimated by the P2 procedure as they stand beyond the core parameterization of the underlying MMFF force field [11]. In addition to the P2 and PIMM levels, the PM3 method is used for the sake of comparison. To evaluate the sublimation enthalpies, the  $\nu$  and  $\sigma$  descriptors were calculated using electrostatic potentials derived from PIMM and EEM atomic charges, but the values of  $\Delta_{\text{sub}}H^\circ$  turn out to be very similar in both cases, as illustrated in Fig. 1. The fact that the EEM charges, designed to mimic DFT potential-derived atomic charges, does not significantly improve the model based on PIMM charges could be a consequence of the statistical underdetermination of the CHELPG charges [21]. Indeed, this well-known drawback of the CHELPG procedure explains why the charges thus obtained cannot be well represented by more physical models of the charge distribution. However, keeping in mind the fact that the electrostatic contribution to  $\Delta_{\text{sub}}H^\circ$  is derived on purely empirical grounds, only a qualitative estimate may be expected. Thus, any charge model might be suitable as long as it properly accounts for the relative magnitude and sign of the electrostatic potential on the molecular surface. In view of the similarity between both the models for  $\Delta_{\text{sub}}H^\circ$ , only the enthalpies calculated using the EEM charges are discussed in the sequel. The latter are compiled in Table 3.

All in all, the relative accuracy of the three procedures with regard to the estimation of  $\Delta_f H^\circ(\text{sol})$  is the same as for  $\Delta_f H^\circ(\text{gas})$  [1,11], namely  $\text{PM3} \simeq \text{PIMM} < \text{P2}$ , in line with the assumption—suggested by the good fit obtained for sublimation enthalpies [15]—that the deviations between the calculated and observed solid-state formation enthalpies are mostly due to inaccuracies of calculated gas-phase values. When the P2 procedure is used to derive  $\Delta_f H^\circ(\text{gas})$ , the rms deviation between the calculated and observed  $\Delta_f H^\circ(\text{sol})$  is only 0.21 kJ/g. A better agreement can hardly be expected in view of the scattering of experimental data on one hand, and the simplifications involved in the computational schemes on the other. In fact, a systematic overestimation of the calculated enthalpies was expected for nitrogenous compounds, especially nitroaromatics, because of the poor reliability of the MMFF structures for such systems [11]. Thus, the very good agreement between P2 and observed values for TNT and TATB is surprising. With regard to TATB, its solid-state formation enthalpy is

much underestimated when PIMM or PM3 are used for  $\Delta_f H^\circ(\text{gas})$ . This suggests that  $\Delta_{\text{sub}}H^\circ$  could be significantly overestimated for this material. This very high value of  $\Delta_{\text{sub}}H^\circ$  would then make up for the expected overestimation of  $\Delta_f H^\circ(\text{gas})$  expected in view of the poor MMFF geometry [11]. The limitations of molecular mechanics explain the tendency of the P2 estimates to be overestimated for such compounds as 2,2'-azo-bis-isobutyronitrile, HMX or 1,3,3-trinitroazetidine (TNAZ), despite the underestimated value for ethylenedinitramine. Other significant overestimations at the P2 level occur for compounds with hydroxyl groups: resorcinol, etriol, or strained molecules such as camphor. Similar deviations are observed using PIMM or PM3 for  $\Delta_f H^\circ(\text{gas})$ . Estimates of solid-state enthalpies are relatively poor for molecules with intramolecular hydrogen bonds, like etriol or TATB. On one hand, the energetics of intramolecular hydrogen bonding is challenging for the simple models used in the present work, including P2 which relies on molecular mechanics structures. On the other hand, atoms involved in such intramolecular bonds might be less available to contribute to  $\Delta_{\text{sub}}H^\circ$  through intermolecular bonds. Eq. (2) does not account for this fact. More generally, it is somewhat less accurate whenever strong H-bonds are present. Melamine provides an illustration as a value of  $\Delta_{\text{sub}}H^\circ = 0.95$  kJ/g has been measured for this compound [13], approximately 0.25 kJ/g higher than the estimate from Eq. (2), one of the most severe discrepancy noted so far [15]. The latter contributes significantly to the deviations reported in Table 3 for this particular compound.

Finally, the overall accuracy obtained for  $\Delta_f H^\circ(\text{sol})$  is comparable to that obtained for  $\Delta_f H^\circ(\text{gas})$ . Indeed, the rms deviations obtained from the experiment in present work are 0.35 and 0.21 kJ/g, respectively at the PIMM and P2 levels, while corresponding values of 0.30 and 0.18 kJ/g<sup>1</sup> have been reported for the gas-

<sup>1</sup>The rms error on a per mole basis was only 15 kJ/mol in the former study versus 50 kJ/mol for the compounds considered in this work. The fact that the rms errors (kJ/g) are similar in both the cases ( $\approx 0.2$  kJ/g) shows that the much larger errors (kJ/mol) obtained in the present work arise not only because of the present focus on energetic compounds, but also because larger molecules are studied. This clearly illustrates the need to consider values reported on a per mass basis for a relevant comparison between the methods. Furthermore, the use of kilojoules per gram units allows a more stringent test of prediction schemes, since a trivial cause for correlation is thus removed.

phase enthalpies, albeit on a different set of molecules [11]. Using the P2 procedure, the present study compares well with earlier more expensive approaches [4,5], presumably because of the separate treatment introduced for the nitro groups [11] and the more reliable equation for  $\Delta_{\text{sub}}H^\circ$  [8,15]. However, focussing on energetic materials, the P2 approach is expected to be less accurate than the alternative methods not depending on analytical force fields [5,9].

## 5. Conclusions

Solid-state formation enthalpies have been estimated for 34 organic compounds related to the field of energetic materials. Since the sublimation enthalpy can be relatively well described by a simple expression, the main difficulty lies in the efficient evaluation of the gas-phase formation enthalpy. Nevertheless, the procedures presented here provide cost-effective approaches to  $\Delta_f H^\circ(\text{sol})$ , suitable to help in the design of new energetic materials. Further progress will require an increased reliability of gas-phase estimates. The latter might be achieved through the introduction of group increments to be used with the PIMM force field. Such an approach has been adopted to derive formation enthalpies from the MM3 force field [23]. However, for a significant number of compounds, a better agreement with experiment can hardly be expected in view of the lack of reliable measurements.

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