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Research Article

Significance of Theoretical Decomposition Enthalpies for Predicting Thermal Hazards

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Much effort is currently put into the development of models for predicting decomposition enthalpies measured using differential scanning calorimetry (DSC). As an alternative to the purely empirical schemes reported so far, this work relies on theoretical values obtained on the basis of simple assumptions. For nitroaromatic compounds (NACs) studied in sealed sample cells, our approach proves clearly superior to previous ones. In contrast, it correlates poorly with data measured in pin-hole sample cells. Progress might be obtained through a combination of the present approach with the usual Quantitative Structure-Property Relationships (QSPR) methodologies. This work emphasizes the significance of the theoretical decomposition enthalpy as a fundamental descriptor for the prediction of DSC values. In fact, the theoretical value provides a valuable criterion to characterize thermal hazards, as a complement to experimental decomposition temperatures.

1. Introduction

In view of the increasingly large number of compounds to be considered in process design or in the context of recent regulatory frameworks, there is currently much interest in the numerical estimation of thermal hazards prior to any experiment [1]. Such hazards are classified and predicted on the basis of several criteria [2], including exothermic onset temperatures (T_0) and decomposition enthalpies derived from differential scanning calorimetry (DSC) experiments [3–5]. The latter property, hereafter denoted by $\Delta_d H(\mathrm{DSC})$ and defined as positive, is a preliminary to any assessment of thermal risks. It is a relatively simple property which may be loosely defined as the opposite of the enthalpy change associated with the decomposition of the compound studied into products. Assuming that this process yields the most stable products consistent with the stoichiometry of the system, we obtain an ideal value $\Delta_d H^0$ that can be identified with the energy content of the material.

The difference between $\Delta_d H^0$ and $\Delta_d H(\mathrm{DSC})$ is determined by highly complex processes, including multiple reaction pathways, secondary reactions possibly involving the surroundings of the sample, and heat and mass transport processes within the cell. A first-principles approach to this difference is therefore out of reach, considering the computational cost inherent to ab initio molecular dynamics and the fact that reactive potentials, which could provide a more efficient alternative, are still in their infancy [6]. Therefore, some empiricism is unavoidable when it comes to predicting DSC data, and Quantitative Structure-Property Relationships (QSPR) methodologies appear as a natural approach to estimate $\Delta_d H^0 - \Delta_d H(\mathrm{DSC})$ in this context.

Although they do rely on such techniques, presently published models apply them directly to the evaluation of $\Delta_d H(\mathrm{DSC})$ in terms of standard descriptors [7–15]. As a result, they do not take advantage of the availability of simple rules to estimate decomposition products and corresponding $\Delta_d H^0$ values [16]. While QSPR approaches prove extremely useful in the lack of quantitative theories, especially for complex properties in the fields of pharmaceutical chemistry, toxicology, or risk assessment, they are some reasons to believe that their direct application to $\Delta_d H(\mathrm{DSC})$ is unlikely to provide the most reliable predictive tools.

First, QSPR descriptors are calculated on the unreacted compound, while $\Delta_d H(\mathrm{DSC})$ also depends on the decomposition products and possibly on some features of the reaction

pathways. Secondly, $\Delta_d H$(DSC) obviously depends on the formation enthalpy $\Delta_f H^0$ of the compound studied. Since a reliable evaluation of this property for arbitrary compounds requires quantum chemical computations, QSPR models are unlikely to provide accurate $\Delta_d H$(DSC) values for a wide range of compounds.

Finally, an even more significant obstacle to the application of QSPR techniques to estimate $\Delta_d H$(DSC) is the lack of consistent data. The routine application of DSC to thermal hazard evaluation yields decomposition enthalpies with experimental uncertainties around 10% [4]. However, a more significant variability is observed in practice due to the details of the experimental setup, including the temperature scanning rate, the materials of the device, or the kind of sample cell. For instance, on going from a sealed [3] to a pinhole [4] sample cell, the measured decomposition enthalpies decrease from 345 to 123 kJ/mol for 2-nitrophenol, from 284 to 130 kJ/mol for 1-methyl-3-nitrobenzene, and from 339 to 161 kJ/mol for nitrobenzene. The relative scarsity of homogeneous $\Delta_d H$(DSC) data sets makes the parametrization and validation of QSPR models very difficult and prevents the introduction of many empirical parameters that might be necessary for reliable predictions of $\Delta_d H$(DSC) along such lines.

In fact, a growing body of work demonstrates the interest of more physically grounded and/or less empirical strategies to estimate the physical properties of organic substances [17–25], including complex properties characterizing reactive hazards such as flash point temperatures [23], flammability limit temperatures [24], or mechanical sensitivities of explosives [25]. Taking advantage of theoretical $\Delta_d H^0$ values, the present work investigates a semiempirical approach to the evaluation of $\Delta_d H$(DSC) for nitroaromatic compounds (NACs), as an alternative to the straightforward application of QSPR techniques. More specifically, two predictive equations are put forward. The first one simply assumes that $\Delta_d H$(DSC) can be reasonably approximated as a constant fraction f of the energy content $\Delta_d H^0$, while the second one attempts to describe how this fraction depends on the reactivity of the compound.

2. Theory

In a first step, the present approach involves only simple thermodynamic considerations. In a second step, density functional theory (DFT) concepts are invoked in an attempt to introduce kinetic factors. Because $\Delta_d H$(DSC) primarily reflects the heat released as the sample decomposes, the energy content $\Delta_d H^0$ of the substance should provide a major contribution to measured DSC values. The difference between both quantities may be further decomposed into three correction terms accounting, respectively:

(1) for the fact that the equilibrium products relevant to the thermodynamic conditions in the sample cell may differ from the most stable ones in standard conditions (δ_{eq});

(2) for the fact that kinetics may affect the actual composition of the products (δ_{kin});

(3) for energy losses associated with heat and matter transport processes (δ_{DSC}):

$$\Delta_d H^0 - \Delta_d H\,(\text{DSC}) = \delta_{\text{eq}} + \delta_{\text{kin}} + \delta_{\text{DSC}}. \tag{1}$$

While $\Delta_d H^0$ may be estimated on the basis of standard approximations, there is no simple way to calculate the three terms on the r.h.s. of this equation. Therefore, we follow a simpler approach, assuming in a first step that each correction represents a given fraction of $\Delta_d H^0$. As a result,

$$\Delta_d H\,(\text{DSC}) = f\Delta_d H^0, \tag{2}$$

where f is a constant that does not depend on the compound under consideration. An advantage of this approach is that it automatically ensures the condition $\Delta_d H(\text{DSC}) < \Delta_d H^0$.

Going one step further, we are faced with the challenge to estimate how f depends on the compound under study. Among many factors that are likely to affect the value of this ratio, reactivity might be the one whose role is easiest to describe at least qualitatively. Indeed, a complete decomposition requires that the products be slowly cooled down to the ambient temperature. Such complete decomposition is especially unlikely for materials that remain chemically unaffected up to high temperatures. As temperature increases, the system can explore a larger fraction of the potential energy surface (PES) and is thus more likely to get stuck in metastable configurations during cooling. Therefore, the amount of energy eventually released in decomposition processes depends on the energy barriers $E^{\neq}$.

In the lack of detailed knowledge of reaction pathways, we have to be satisfied with the features of the initial and final states to evaluate the role of $E^{\neq}$. On the products side, the Bell-Evans-Polanyi principle [26] suggests that $E^{\neq}$ is likely to get lower as $\Delta_d H^0$ increases. This principle is frequently invoked to correlate reaction properties with a difference between reactants and products, especially in the field of high energy compounds [27]. Nevertheless, it is not sufficient to quantitatively estimate energy barriers, as reflected by the lack of correlation between decomposition enthalpies and decomposition temperatures [4].

Some improvement might be obtained by taking advantage of reactant features. In particular, bond dissociation energies (BDEs) appear to be ideal descriptors in view of evaluating $E^{\neq}$ [28]. However, they may be tedious to compute, requiring the optimization of complex open-shell species if large molecules are considered. An attractive alternative is provided by reactivity descriptors at the basis of conceptual DFT [29], namely, electronegativity (χ) and chemical hardness (η). In fact, an early attempt to predict DSC measurements from empirical relationships already assumed that those quantities play a primary role [8].

In the present work, the reactivity descriptors are introduced with the help of dimensionality considerations. The simplest dimensionless quantity that may be defined on the basis of χ and η is their ratio χ/η, where η is implicitly multiplied by the electron charge $e = 1$ in atomic units.

Therefore, assuming that f depends on χ and η, it should then be expandable as a power series:

$$f = f_0 + a\left(\frac{\chi}{\eta}\right) + b\left(\frac{\chi}{\eta}\right)^2 + \cdots. \quad (3)$$

Since the principle of maximum hardness implies that η is a measure of the stability of the system [29], f is expected to decrease as η increases, with the limit of large η values corresponding to an increasing resistance of the molecule to changes in its electronic structure, hence to energy release. This implies that $a > 0$ since the linear term is predominant for large values of η. On the other hand, setting $f_0 = 0$ is required if we want the energy released to decrease to zero in the hypothetical limit of an infinitely stable system with $\eta \to \infty$. This suggests a possibly improved alternative to (2):

$$\Delta_d H\,(\mathrm{DSC}) = a\left(\frac{\chi}{\eta}\right)\Delta_d H^0. \quad (4)$$

In what follows, both (2) and (4) are considered to predict $\Delta_d H$(DSC). Given many factors that may affect measured values, depending on the detailed experimental setup, associated with the approximate character of conceptual DFT inherent to the fact that it attempts to describe reactivity in term of features of the unreacted compound, it is not a priori obvious to decide which equation will prove most reliable.

An attractive feature of present models is the fact that they depend on a single input variable x, where $x = \Delta_d H^0$ if a constant fraction f of the energy content is assumed to contribute to measured DSC data as in (2), or $x = (\chi/\eta)\Delta_d H^0$ if this fraction is assumed to depend linearly on χ/η as in (4). As a consequence, their performances may be straightforwardly estimated, for instance, graphically from the plot of $\Delta_d H$(DSC) versus x, or by considering the determination coefficient R^2 between both quantities. This is especially gratifying in view of the scarcity of homogeneous data, which make it awkward to define statistically significant external test sets for multiparameters models.

3. Computational Details

In this work, the decomposition products are obtained on the basis of a simple generalization to halogenated compounds of the well-known H_2O-CO_2 arbitrary initially introduced to estimate the heats of detonation of C–H–N–O explosives [30]. More specifically, decomposition products are obtained according to the following priority order: HF > CF_4 > H_2O > CO_2 > CCl_4 > CO > HCl. If necessary, the remaining elements are converted into graphite, H_2, N_2, S_8, O_2, F_2, and Cl_2. In practice, the last three products are never obtained for the present data set because of the relative scarcity of O, F, and Cl atoms in present NACs.

The energy content $\Delta_d H^0$ is then obtained as the difference between the formation enthalpy $\Delta_f H^0$ of the substance under study and corresponding values $\Delta_f H^0(k)$ for the decomposition products k. The latter are taken from the NIST Webbook database [31]. Because experimental values of $\Delta_f H^0$ are missing for most NACs under study, theoretical values computed using the semiempirical RM1 Hamiltonian are used. This method is chosen for its relatively good performance and computational efficiency [32].

For (4), values of χ and η are obtained within the finite difference approach by simple difference and as an average of the ionization potential (IP) and electronegativity (EA):

$$\chi = \frac{\mathrm{IP} + \mathrm{EA}}{2}, \qquad \eta = \mathrm{IP} - \mathrm{EA}. \quad (5)$$

IP and EA are derived from the energies ϵ_{HOMO} and ϵ_{LUMO} of the highest occupied and lowest unoccupied molecular orbitals, obtained simply as a by-product of the RM1 computations. More specifically, IP = $-\epsilon_{\mathrm{HOMO}}$ and EA = $-\epsilon_{\mathrm{LUMO}}$ [29]. All RM1 calculations are carried out using the MOPAC7 program [33].

Typical errors associated with RM1 formation enthalpies are about 20 kJ/mol [32] while experimental uncertainties may cause much larger errors (>100 kJ/mol). Therefore, no significant improvement is expected from the use of more accurate procedures. Larger theoretical uncertainties might possibly arise from the use of the RM1 orbitals to obtain the reactivity descriptors. Therefore, we have also investigated in unpublished work the use of enthalpies and orbital energies derived from PBE0/6-31+G(d,p)//AM1 calculations combined with simple atom equivalent schemes [34]. It turned out that this higher theoretical level does not provide any significant improvement with respect to RM1-based procedures. Because RM1 calculations are much easier to carry out routinely in an industrial context, only the results obtained on this basis are presented in the sequel.

Similarly, we investigated the effect of taking into account the contribution of intermolecular interactions to $\Delta_d H^0$ despite the introduction of sublimation enthalpies calculated on the basis of simple models [35, 36]. Again, this does not significantly affect the results, as expected from the relatively small magnitude of sublimation enthalpies. Moreover, this approach is not rigorous as the compounds studied typically melt before undergoing a decomposition. Therefore, it is better to ignore the intermolecular contribution to $\Delta_d H^0$ until a more satisfactory approach is developed.

On the other hand, as an alternative to the above-mentioned decomposition rules assuming a complete oxidation of hydrogen and carbon into CO_2 whenever possible, the use of the Kistiakowsky-Wilson rules (applying the modified version for compounds with CO_2 oxygen balance < −40%) was also considered [16]. These rules favor the formation of CO over CO_2. This change has a more significant impact on the individual results than going from RM1 to PBE0 electronic structures or introducing sublimation enthalpies. Nevertheless, the overall performance of the models is not significantly affected. Therefore, only the results based on the generalized H_2O-CO_2 arbitrary are presented in this work. In the lack of significantly better rules, this is the most attractive option, implying that the effect of any incomplete oxidation is implicitly taken into account through the values of the empirical parameters.

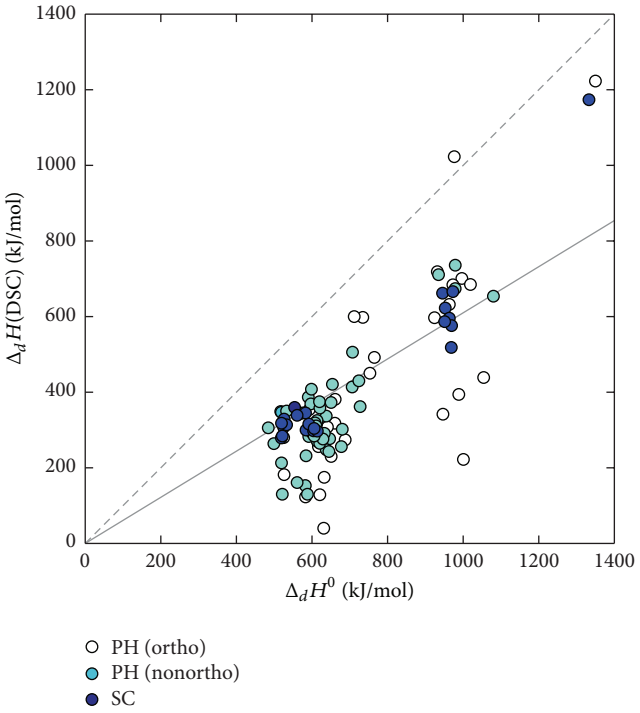


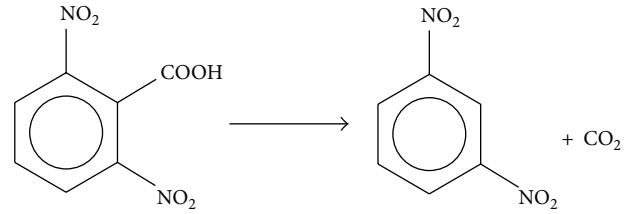
Figure 1: Experimental decomposition enthalpies $\Delta_d H$(DSC) plotted against theoretical maximal values $\Delta_d H^0$. For clarity, the regression line $y = 0.61x$ and the line $y = x$ are indicated as well.

4. Data Sets

Recent studies aimed at predicting decomposition enthalpies of NACs as measured by DSC focus on two data sets. The first one is a set of 22 enthalpies measured using a standard aluminium sealed sample cell (SC data) [3]. The second one is a set of 77 enthalpies measured in aluminium sample cells with a pin-hole on the lid (PH data) [4]. Technical details regarding these sample cells may be found in references cited in these earlier publications [3, 4]. Most modeling studies focus on the SC data set [8–12]. Only very recent ones take advantage of the PH data set [13, 15]. Both SC and PH data sets are considered in the present work. They provide 99 experimental decomposition enthalpies for 84 compounds, because some molecules have been studied using both kinds of sample cells and are thus present in the two sets.

5. Results

5.1. Observed versus Theoretical Enthalpies. Figure 1 compares experimental $\Delta_d H$(DSC) data with theoretical values $\Delta_d H^0$. Because the kind of sample cell is likely to influence the measured enthalpies, SC and PH data are shown using different colors. Furthermore, for the analysis of the 77 PH values at hand, the 35 compounds with substituents in ortho position with respect to nitro groups (ortho compounds) are treated separately, assuming that the associated $\Delta_d H$(DSC) values might prove more difficult to rationalize than corresponding data for the remaining 42 compounds deprived of ortho substituents (nonortho compounds). This assumption is motivated by the possible role of interactions between nitro groups and corresponding ortho substituents. This partition of the data set between nonortho/ortho compounds was introduced in a previous study [13].



Scheme 1

Because $\Delta_d H^0$ characterizes the total energy content of the compound studied, it should be larger than $\Delta_d H$(DSC). Figure 1 shows that this is actually the case for all compounds except for 2-chloro-3,5-dinitrobenzoic acid which lies slightly above the line $y = x$. This anomaly may be attributed to uncertainties regarding the experimental $\Delta_d H$(DSC) value from the PH data set and/or the computational procedure to derive $\Delta_d H^0$.

A correlation between theory and experiment is observed in Figure 1, as reflected by the corresponding determination coefficient $R^2 = 0.68$ which is significantly nonzero. However, the distinction of the different subsets clearly shows that the correlation is especially good for SC data, with $R^2 = 0.90$.

For PH data, the correlation is less good, although it remains significant with $R^2 = 0.62$. The distinction between nonortho and ortho compounds is especially fruitful here. Indeed, it is clear from Figure 1 that the latter (shown as white symbols) fit especially poorly into the correlation. On the other hand, among the 22 SC values, 10 are for ortho compounds. Therefore, it appears that reactions between nitro groups and neighboring substituents are likely to affect significantly $\Delta_d H$(DSC) for measurements in pin-hole sample cells, while no such effect is noted for experiments in sealed cells.

In fact, PH values appear to be prone to significant uncertainties, as already mentioned for 2-chloro-3,5-dinitrobenzoic acid. As illustrated by the data reported in the introduction to this paper to illustrate the role of the sample cell, PH enthalpies tend to be smaller than SC values, which might be explained by more significant energy losses through evaporation or sublimation of the sample in the former case.

The outliers noted in Figure 1 may be rationalized on a case-by-case basis. For instance, the most significant deviation between $\Delta_d H$(DSC) and $\Delta_d H^0$ is observed for 2,6-dinitrobenzoic acid, for which pin-hole measurements yield $\Delta_d H$(DSC) = 222 kJ/mol, to be compared with $\Delta_d H^0$ = 1001 kJ/mol. By analogy with the synthesis of trinitrobenzene from 2,4,6-dinitrobenzoic acid, this compound is expected to undergo a decarboxylation upon heating, leading to the formation of 1,3-dinitrobenzene and the release of carbon dioxide (see Scheme 1).

Thermochemical data from the NIST Webbook [31] as well as RM1 calculations indicate that this reaction is

almost athermic. It is thus likely to get unnoticed in DSC experiments. The first reactive exotherm is then associated with the decomposition of 1,3-dinitrobenzene, for which a significantly higher value $\Delta_d H(\mathrm{DSC}) = 587\,\mathrm{kJ/mol}$ was measured in a sealed sample cell. Such artefacts/complexities are clearly not properly taken into account by current predictive methods. Until new models taking advantage of the knowledge of organic chemists are developed, it will probably not be possible to reliably predict measured $\Delta_d H(\mathrm{DSC})$ data for arbitrary organic compounds.

It was noted previously that $\Delta_d H(\mathrm{DSC})$ data measured in sealed sample cells for NACs primarily depend on the number $n(\mathrm{NO_2})$ of nitro groups on the molecule [8]. Figure 1 shows that this is systematically the case for $\Delta_d H^0$ as well, hence the three clusters clearly observed on this plot, corresponding to $n(\mathrm{NO_2})$ values ranging from 1 to 3. However, this prominent role of $n(\mathrm{NO_2})$ is blurred when considering PH data, as clear from the vertical scattering of the corresponding points, which is especially significant for ortho compounds. Therefore, rationalizing present DSC data should be easiest for SC data and most difficult for ortho compounds characterized in pin-hole sample cells.

For SC data, Figure 1 suggests that rough $\Delta_d H(\mathrm{DSC})$ estimates can be obtained by defining three standard values associated, respectively, with mononitro, dinitro, and trinitro compounds. However, the success of such an approach would clearly be highly dependent on the other substituents in the molecule. For instance, it would yield spurious predictions for compounds with other energetic moieties, such as –N=O, –O–N=O, $-\mathrm{NF_2}$, or $\mathrm{N_3}$ groups. Therefore, assuming that $\Delta_d H(\mathrm{DSC}) \propto \Delta_d H^0$ as done in (2) is a more attractive approach. However, it is clear from the regression line in Figure 1 that this straightforward scaling relationship does not satisfactorily account for the high decomposition enthalpy obtained for the only trinitrocompound in the SC data set, namely, picric acid. For this molecule, the ratio $\Delta_d H(\mathrm{DSC})/\Delta_d H^0$ is close to 0.9, while it is close to 0.6 for mononitro and trinitro compounds.

5.2. Accounting for the Role of Reactivity. This observation actually motivated the considerations leading to (4) in Section 2. Indeed, the relatively large fraction of the energy content released by picric acid may be correlated with the fact it decomposes at a relatively low temperature of 220°C, the lowest among all compounds studied in sealed cells [3]. As discussed in Section 2, low temperatures favor decomposition according to the lowest energy pathways and therefore more significant releases of energy. Prior to investigating the performances of (4), it is thus interesting to plot f according to χ/η as done in Figure 2. Of course, the relatively poor correlations observed on this figure arise because it focuses on the challenging part of $\Delta_d H(\mathrm{DSC})$.

As anticipated, picric acid exhibits specially high value of this ratio. Therefore, (4) should better account for the decomposition enthalpy of this compound compared to (2). The correlation coefficients reported in Figure 2 are systematically positive, hence supporting the considerations leading to (4). To some extent, the higher value obtained for

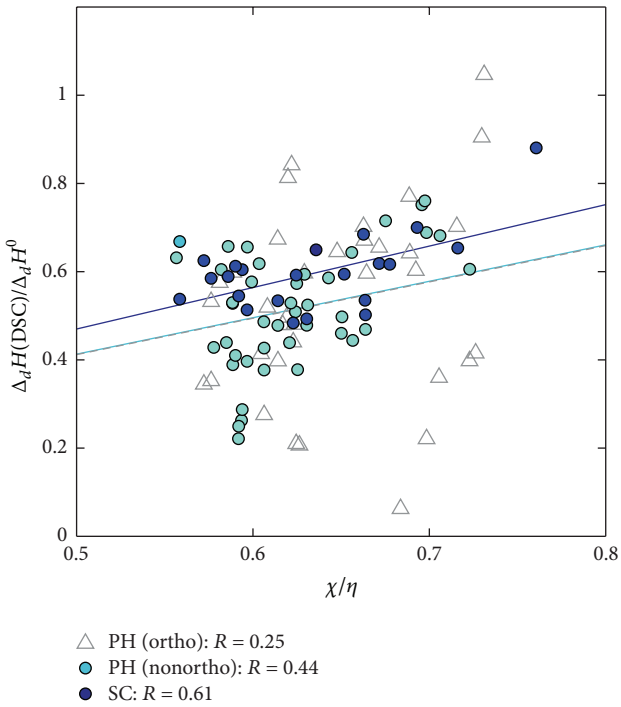


Figure 2: Correlations between f and χ/η. The regression line for SC data is shown in dark blue. Note that, for PH data, the corresponding lines for nonortho and ortho compounds are the sames (light blue/grey lines). The rightmost symbol stands for the SC value for picric acid.

SC data may be attributed to the success of the approach to account for the fact that specially high fraction of $\Delta_d H^0$ contributes to the decomposition enthalpy observed for picric acid. In contrast, the low values of the correlation coefficients calculated for PH data come as no surprise in view of the large experimental uncertainties. Specially poor correlation observed for ortho compounds is consistent with the assumption of previous authors that interactions between nitro groups and ortho substituents make decomposition enthalpies harder to rationalize [13].

Insight into the predictive value of present equations is provided by the correlation between $\Delta_d H(\mathrm{DSC})$ and $(\chi/\eta)\Delta_d H^0$ illustrated in Figure 3. Again, it is interesting to distinguish experimental values according to the corresponding sample cells. Furthermore, after discarding PH data for ortho compounds, as done previously [13], a striking correlation $R^2 = 0.86$ is observed for the 64 remaining enthalpies measured in either kind of sample cells. This achievement is all the more remarkable as a single descriptor is used. For comparison, the corresponding determination coefficient between these 64 values and $\Delta_d H^0$ is $R^2 = 0.80$.

5.3. Predicting DSC Decomposition Enthalpies. These coefficients reflect the predictive value of present approaches. In order to carry out a rigorous comparison with previous QSPR methods, (2) and (4) have been fitted and validated against previously introduced training and test sets. However,

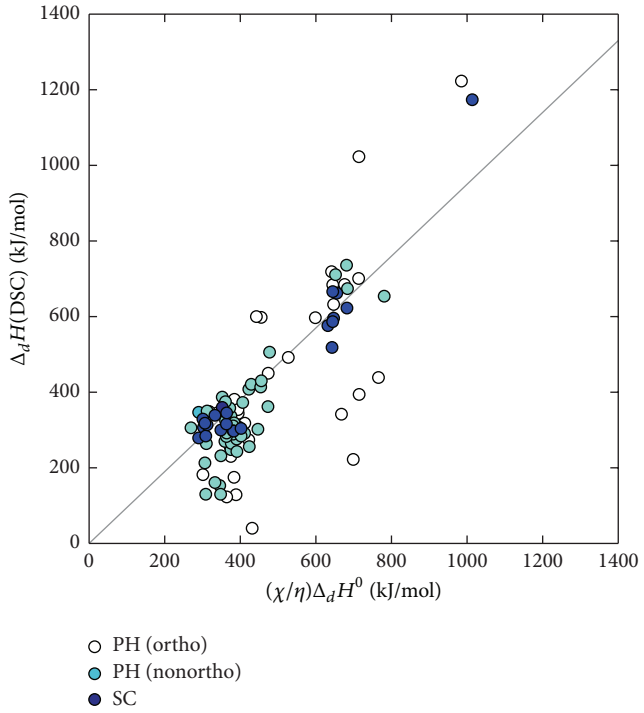


Figure 3: Observed DSC decomposition enthalpies as a function of the descriptor employed in (4).

because present equations involve only a single adjustable parameter, they can be fitted against a much smaller training set, thus allowing for a more extensive validation of their predictive value. For this purpose, we have fitted both models against a training set of only 5 compounds and used the 94 remaining compounds as an external test set. This partition and corresponding results are detailed in the appendix.

The relative performances of the various methods are summarized in Table 1. R^2 stands for the determination coefficient between fitted and observed data. Although they are mostly irrelevant for present approaches based on a single linear parameter, corresponding coefficients derived from leave-one-out cross validations (Q^2) and application of the models to external test sets (R_x^2) are reported as well for the sake of comparison with QSPR methods. These coefficients should only be used to assess the relative performance of various models though a comparison of values obtained *for the same data set*. In fact, their individual values are deprived of significance in view of the fact that the distribution of $\Delta_d H$(DSC) values in any set considered is far from Gaussian. Therefore, average absolute errors of the models are also reported in Table 1 for both the training set (AAE_{tr}) and the test (validation) set (AAE_v). The number of variables of each model (n) and the number of data included, respectively, in the training (N_{tr}) and test (N_v) sets are also provided in this table.

In principle, the predictive value of the models is best characterized by R_x^2 and AAE_v. However, this is not necessarily the case in practice owing to the small size of most test sets considered, with only 8–11 data values for the most specialized models [13]. This is reflected by the fact that R_x^2 and AAE_v values sometimes provide more optimistic expectations than statistical parameters derived from the training set. In such cases, the least optimistic criteria are clearly to be considered.

Because SC data appear easier to rationalize, present equations are first fitted against the SC data set considered in previous papers [8–10, 12]. The small size of this set (22 enthalpies) does not allow a rigorous assessment of the predictive value of QSPR methods. However, according to Q^2 coefficients, (4) taking reactivity into account appears better than (2). The only QSPR models with Q^2 values higher than the present ones were obtained in [10] as the outcome of an extensive screening of descriptors combinations. However, (2) and (4) provide average relative errors of, respectively, 13% and 10% on this data set. Keeping in mind that such deviations are comparable to experimental uncertainties, the very high determination coefficients reported in [10] probably reflect overfitting issues. Furthermore, the corresponding models proved deprived of predictive value for present PH data, for which a value of R_x^2 as low as 0.24 was reported [13].

For PH data, present equations are first fitted independently for nonortho and ortho compounds, as done in [13]. For nonortho compounds, the best correlation between measured and predicted values ($R_x^2 = 0.92$) is obtained using (4). According to the data reported in Table 1, especially average errors AAE_{tr} and AAE_v for the training and test sets, this equation and the QSPR method of [13] exhibit similar performances. In contrast, both approaches fail to provide valuable predictions for ortho compounds. As a result, they perform poorly when applied to the prediction of PH data for arbitrary compounds.

In order to better characterize the value of present equations, they are eventually fitted against a small training set of five SC values defined in Table 2. The performances of the two resulting models are summarized in the last six rows of Table 1. Despite poorer fits against the 5 compounds in the training set, (4) yields systematically better predictions than (2), which suggests that reactivity indexes are indeed useful to obtain improved predictions. This is confirmed by the fits of the two equations against the whole set of 22 SC data. Finally, it may be noted that the reliability of both models steadily decreases ongoing from SC data to PH data for nonortho compounds to PH data for ortho compounds.

Present results demonstrate that the present approach makes it straightforward to derive predictive tools performing similarly or even better than the best QSPR methods at hand, provided PH data for ortho compounds are excluded from the data set. Whenever these difficult cases are considered, present equations fail to provide meaningful predictions, while the most successful QSPR studies appear to succeed in obtaining fairly reasonable results, especially for the seven-parameters model put forward very recently in [15].

These findings are understandable. Differences between SC and PH data can only be explained by complex processes, including heat and mass transfers within the cell, energy losses through sublimation, and evaporation, which are deliberately ignored by the present approach. In view

Table 1: Comparison of presently available predictive methods. The second column indicates which kind of measurements (SC and/or PH) are used to assess the predictive value of the method. In the third column, y/n indicates whether (y) or not (n) PH data for ortho compounds are included in the test set. In the last column, c stands for the empirical parameter of present models; that is, it is equal to either f when (2) is used or $a(\chi/\eta)$ when using (4). AAE_{tr} and AAE_v values are in kJ/mol.

Model reference	Cell	PH/ortho	N_{tr}	N_v	n	R^2	Q^2	R_x^2	AAE_{tr}	AAE_v	c
Models for SC data											
Reference [9]	SC	n	22	—	6	0.91	0.84	—	—	—	
Reference [8]				—	3	0.85	0.73	—	65	—	
Reference [10]				—	3	0.98	0.97	—	22	—	
Reference [10]				—	4	0.98	0.97	—	20	—	
Reference [12]	SC	n	22	—	3	0.93	0.86	—	—	—	
Equation (2)				—	1	0.90	0.86	—	57	—	0.64
Equation (4)				—	1	0.93	0.91	—	43	—	0.97
Models for PH data and nonortho compounds											
Reference [13]	PH	n	31	11	4	0.91	0.86	0.84	68	56	
Equation (2)					1	0.67	0.63	0.90	72	75	0.54
Equation (4)					1	0.69	0.66	0.92	65	65	0.85
Models for PH data and ortho compounds											
Reference [13]	PH	y	27	8	4	0.94	0.91	0.42	55	112	
Equation (2)					1	0.68	0.61	0.30	140	130	0.61
Equation (4)					1	0.66	0.60	0.24	126	138	0.93
Generic models for PH data											
Reference [13]	PH	y	58	19	4	0.84	0.81	0.43	65	96	
Equation (2)					1	0.69	0.65	0.44	105	100	0.58
Equation (4)					1	0.68	0.65	0.41	95	94	0.89
Reference [14]	PH	y	55	22	7	0.77	0.64	0.70	66	92	
Reference [14]					4	0.76	0.66	0.67	66	—	
Reference [14]					7	0.74	0.68[a]	0.75	67	86	
Reference [15]					7	0.86	0.79	0.84	53	82	
Reference [15]					4	0.76	0.70	0.79	65	88	
Equation (2)					1	0.59	0.55	0.70	92	129	0.54
Equation (4)					1	0.58	0.54	0.68	88	114	0.84
Generic models for all compounds/sample cells, fitted using SC data											
Equation (2)	SC	n	5	17	1	0.94	0.88	0.90	40	54	0.61
Equation (4)					1	0.91	0.85	0.94	40	43	0.95
Equation (2)	SC + PH	n	5	59	1	0.94	0.88	0.81	40	74	0.61
Equation (4)					1	0.91	0.85	0.84	40	64	0.95
Equation (2)	SC + PH	y	5	94	1	0.94	0.88	0.68	40	98	0.61
Equation (4)					1	0.91	0.85	0.68	40	88	0.95

[a]7-fold cross validation.

of the correlation reported in Figure 1, such effects mostly affect PH data, especially for ortho compounds. Because reactivity, as described here with the help of χ and η, is only one factor among many others that may contribute to the difference between $\Delta_d H$(DSC) and $\Delta_d H^0$, it is not surprising that present models perform better for SC data.

On the other hand, in view of the ability of QSPR techniques to learn from the data at hand and to account implicitly for complex and poorly known processes through an automatic selection of suitable descriptors, it comes as no surprise that they are especially competitive with the present semiempirical approach in the most difficult cases of PH data for ortho compounds.

6. Discussion

The present work opens new perspectives with regard to $\Delta_d H$(DSC) prediction in the context of thermal hazards assessment. Indeed, it can be noted that, at least for SC data, present descriptors $\Delta_d H^0$ and possibly $(\chi/\eta)\Delta_d H^0$ exhibit striking correlations with experiment. With determination coefficients of, respectively, 0.90 and 0.93, these two descriptors correlate better with measured $\Delta_d H$(DSC) data than any individual descriptor previously considered for QSPR analyses of this particular data set [8, 9]. This suggests that future QSPR approaches should include them in the pool of descriptors. Alternatively, it is tempting to resort to the QSPR machinery to estimate the ratio (or the difference) between $\Delta_d H^0$ and $\Delta_d H$(DSC), hence focusing the power of such techniques on the most challenging aspects of DSC decomposition enthalpies.

The present semiempirical approach is therefore complementary to mainstream QSPR techniques. It provides general equations involving complex quantities that should lend themselves to QSPR prediction. The originality of present models with respect to previous ones appears clearly in Table 1. Because they involve a single adjustable parameter, they can be fitted against small training sets and assessed using extended test sets. They are extremely robust and provide reliable predictions whenever a good fit of the training set is obtained. However, they cannot capture the complex processes that may affect decomposition enthalpies derived from DSC experiments.

Notwithstanding the originality of present approaches due to their less empirical character compared to previous ones, another distinctive feature of the present work is the fact that SC and PH data are considered simultaneously. Initially, the development of distinct models for these two kinds of measurements was motivated by the fairly large differences observed between SC and PH data obtained for the same compound, as those mentioned in the introduction. However, one may wonder whether such differences, up to about 220 kJ/mol, are actually significant. For practical reasons, it may be necessary in some cases to use either SC or PH sample cell, depending on the behavior of the compound under study. For instance, SC cells may be required for highly volatile compounds [4]. As a consequence, it is not possible to define a standard sample cell that would be used for all thermal characterization studies. In the context of hazard evaluation, we must therefore be satisfied with comparison involving SC as well as PH data.

Among present compounds, 15 have been experimentally characterized using both SC and PH sample cells. Figure 4 compares the two kinds of measurements. They clearly exhibit a significant correlation ($R^2 = 0.73$) because the two dinitro compounds considered exhibit significantly higher decomposition enthalpies than mononitro compounds, regardless of the sample cell used. However, focusing on mononitro compounds, the correlation between both sets of measurements happens to be negative. Whereas the decomposition enthalpy of 4-nitroaniline is 224 kJ/mol larger than for 2-nitrophenol according to PH data, it is 66 kJ/mol lower according to SC data. Therefore, it is difficult to conclude regarding the relative severity of thermal hazards associated with these two compounds. In other words, enthalpy differences < 250 kJ/mol appear to be insignificant.

In fact, even larger differences between SC and PH data were observed by Ando et al. [4]. They are explained by these authors in terms of evaporation of volatile species though pin-hole or the presence of residual air in sealed sample cells that might initiate an oxidation. In view of such results, $\Delta_d H^0$ might prove a valuable alternative to DSC data in view of characterizing the severity of hazards associated with runaway reactions.

7. Conclusions

This work confirms that $\Delta_d H^0$ is a major contribution to $\Delta_d H$(DSC) and should be explicitly taken into account in order to estimate this experimental property. It points to a number of approaches that should yield improved results compared to current applications of the QSPR methodology to $\Delta_d H$(DSC), including the development of semiempirical models along present lines or the application of QSPR to quantities related to the difference between $\Delta_d H^0$ and $\Delta_d H$(DSC).

On the other hand, the present work establishes that decomposition enthalpies measured using pin-hole sample cells are especially difficult to rationalize as they represent widely varying fractions of $\Delta_d H^0$. This result provides a clear justification for the opposition of some researchers, mentioned in [4], to the use of pin-hole cells. In view of the fact that $\Delta_d H^0$ correlates better with data measured in sealed cells than values measured in pin-hole cells, present results suggest that $\Delta_d H^0$ provide an equally reliable thermal hazard indicator compared to DSC enthalpies. In practice, this does not question the usefulness of DSC analyses which remain necessary to determine decomposition temperatures and monitor the thermal events that may occur to a given material under heating.

Finally, the fact that a small but systematic improvement is obtained on introducing reactivity indices supports the underlying assumption that species whose decomposition occurs at relatively low temperatures tend to release a more significant fraction of their energy. In addition, the analysis of the measurements carried out in pin-hole cells supports the view that they are especially difficult to rationalize for compounds with substituents in ortho positions with respect to nitro groups, presumably as a result of reactions between these neighboring substituents.

Appendix

Detailed Outcome of Present Models

See Tables 2, 3, and 4.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

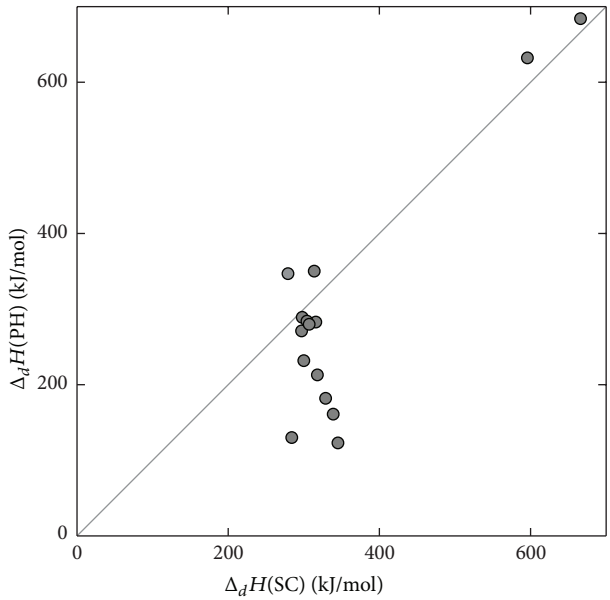


Figure 4: DSC decomposition enthalpies: PH versus SC values.

Table 2: Properties of the 22 compounds studied in sealed sample cells: name, electronegativity χ, chemical hardness η, calculated solid-state formation enthalpy $\Delta_f H^0$, maximal energy content $\Delta_d H^0$, and DSC decomposition enthalpies $\Delta_d H$(DSC) for the set of data measured in sealed sample cells [3]. All enthalpies are in kJ/mol. The stars indicate the five compounds included in the training set.

Name	χ (eV)	η (eV)	$\Delta_f H^0$	$\Delta_d H^0$	Equation (2)	Equation (4)	$\Delta_d H^0$(DSC) [3]
4-Nitroaniline (∗)	4.753	8.512	35	519	317	276	279
1-Methyl-3-nitrobenzene	5.417	9.152	38	521	318	294	284
2-Nitrobenzoic acid	5.917	9.500	−286	614	375	364	297
3-Nitrobenzoic acid	5.983	9.490	−296	604	369	363	298
4-Nitrophenol	5.372	9.003	−119	584	357	332	300
p-Nitrobenzoic acid (∗)	6.067	9.140	−294	606	370	383	304
2-Nitroaniline	4.773	8.283	41	525	320	288	307
3-Nitrobenzenamine	4.763	8.129	49	533	325	297	314
3-Nitrophenol	5.378	8.758	−111	592	361	346	316
1-Methyl-4-nitrobenzene	5.465	9.262	36	519	317	292	318
1-Methyl-2-nitrobenzene (∗)	5.319	9.296	42	526	321	287	329
Nitrobenzene	5.603	9.434	77	561	342	317	339
2-Nitrophenol	5.372	8.602	−120	583	356	347	345
1-Chloro-4-nitrobenzene	5.785	9.099	46	554	338	335	360
1,2-Dinitrobenzene	6.312	9.512	91	969	591	612	518
2,6-Dinitrotoluene (∗)	6.065	9.306	47	969	592	601	576
1,3-Dinitrobenzene	6.419	9.474	74	951	581	613	587
2,4-Dinitrotoluene	6.195	9.226	41	963	588	616	596
1,4-Dinitrobenzene	6.514	9.097	75	953	581	649	623
2,4-Dinitrophenol	6.096	8.796	−128	945	577	624	662
4-Methyl-1,2-dinitrobenzene (∗)	6.113	9.225	50	973	594	614	666
Picric acid	6.711	8.824	−112	1333	814	965	1174

Table 3: The same data as in Table 2 for the 42 nonortho compounds studied in pin-hole sample cells.

Name	χ (eV)	η (eV)	$\Delta_f H^0$	$\Delta_d H^0$	Equation (2)	Equation (4)	$\Delta_d H^0$(DSC) [4]
1-Methyl-3-nitrobenzene	5.417	9.152	38	521	318	294	130
2-Amino-4-nitrophenol	4.680	7.908	−138	588	359	331	130
2-Amino-5-nitrophenol	4.820	8.121	−143	582	355	329	153
Nitrobenzene	5.603	9.434	77	561	342	317	161
1-Methyl-4-nitrobenzene	5.465	9.262	36	519	317	292	213
4-Nitrophenol	5.372	9.003	−119	584	357	332	232
1-Methoxy-3-nitrobenzene	5.270	8.692	−81	645	394	372	243
1-Methoxy-4-nitrobenzene	5.261	8.939	−88	638	389	357	248
3-Nitrobenzoic acid methyl ester	5.920	9.467	−267	678	414	403	256
2,6-Dichloro-4-nitrobenzenamine	5.178	8.332	−32	499	305	295	264
4-Nitrobenzene acetic acid	5.679	9.367	−324	620	379	358	265
1-Ethoxy-4-nitrobenzene	5.213	8.913	−111	614	375	342	270
1-(3-Nitrophenyl)-ethanone	5.873	9.462	−96	629	384	372	276
4-Nitrophenylhydrazine	4.868	8.426	163	647	395	356	277
3-Nitrophenol	5.378	8.758	−111	592	361	346	283
p-Nitrobenzoic acid	6.067	9.140	−294	606	370	383	284
3-Nitrobenzoic acid	5.983	9.490	−296	604	369	363	289
1-(4-Nitrophenyl)-ethanone	5.954	9.159	−93	633	386	392	291
4-Nitrobenzyl alcohol	5.649	9.319	−125	600	367	346	292
4-Nitrobenzoic acid methyl ester	6.007	9.149	−265	680	415	425	302
2-Methyl-4-nitroaniline	4.687	8.421	1	484	296	257	306
3-Nitrobenzamide	5.924	9.492	−115	611	373	363	311
4-Nitrobenzamide	5.903	9.355	−118	608	371	365	319
3-Nitrobenzyl alcohol	5.395	9.169	−112	614	375	344	325
1-Chloromethyl-4-nitrobenzene	5.261	8.940	−88	638	389	357	337
4-Nitroaniline	4.753	8.512	35	519	317	276	347
3-Nitrobenzenamine	4.763	8.129	49	533	325	297	350
3-Nitrobenzene acetic acid	5.604	9.352	−324	621	379	354	358
4-Nitrobenzoic acid hydrazide	5.911	9.088	2	727	444	450	362
N-(3-Nitrophenyl)-Acetamide	5.099	8.449	−129	597	364	343	369
3-Nitrobenzaldehyde	5.915	9.467	−52	650	397	387	373
2-Methoxy-5-nitrobenzenamine	4.597	7.898	−106	620	378	343	375
N-(4-Nitrophenyl)-acetamide	5.130	8.596	−135	590	360	335	387
4-Nitrobenzoyl chloride	6.383	9.040	−106	598	365	402	408
3-(3-Nitrophenyl)-2-propenoic acid	5.627	8.753	−238	706	431	432	414
4-Nitrobenzaldehyde	5.998	9.143	−49	654	399	408	421
3-Nitrobenzhydrazide	5.854	9.303	−2	724	442	434	430
3-(4-Nitrophenyl)-2-propenoic acid	5.808	8.601	−238	707	432	455	506
3,5-Dinitrobenzonitrile	6.777	9.375	225	1080	659	743	654
3,5-Dinitrobenzoic acid	6.707	9.605	−292	979	597	651	674
1-(Chloromethyl)-3,5-dinitrobenzene	6.452	9.250	11	935	571	621	711
3,5-Dinitrobenzamide	6.561	9.429	−118	979	598	648	736

Table 4: Same data as in Table 2 for the 35 ortho compounds studied in pin-hole sample cells.

Name	χ (eV)	η (eV)	$\Delta_f H^0$	$\Delta_d H^0$	Equation (2)	Equation (4)	$\Delta_d H^0$(DSC) [4]
5-Chloro-2-nitrobenzotrifluoride	6.208	9.080	−606	631	385	411	40
2-Nitrophenol	5.372	8.602	−120	583	356	347	123
4-Fluoro-2-nitrotoluene	5.547	8.856	−136	621	379	370	129
2-Nitrobenzene acetic acid	5.618	9.265	−312	632	386	365	175
1-Methyl-2-nitrobenzene	5.319	9.296	42	526	321	287	182
2,6-Dinitrobenzoic acid	6.657	9.532	−270	1001	611	665	222
2-Nitroanisole	5.135	8.911	−75	651	397	357	230
2-Nitrobenzamide	5.776	9.554	−108	617	377	355	256
2-nitrobenzoic acid	5.917	9.500	−286	614	375	364	271
2-Nitrobenzoic acid, methyl ester	5.841	9.510	−257	688	420	402	274
2-Nitroaniline	4.773	8.283	41	525	320	288	280
N-(2-Nitrophenyl)-acetamide	5.133	8.292	−128	597	365	352	297
2-Nitroacetophenone	5.798	9.399	−85	641	391	376	308
2-Nitrobenzaldehyde	5.846	9.376	−42	660	403	392	318
2-Nitrobenzenemethanol	5.646	9.284	−113	613	374	355	319
4-Chloro-1,2-dinitrobenzene	6.367	9.024	68	946	578	636	342
2-Nitrobenzenesulfenylchloride	5.355	7.735	62	570	348	375	344
3-Methyl-4-nitrophenol	5.301	9.002	−150	576	351	323	345
4-Chloro-2-nitrobenzenamine	4.972	8.098	10	517	316	302	349
4-Chloro-3-nitrobenzoic acid	6.012	9.049	−308	593	362	375	354
(2-Nitrophenyl)-hydrazine	4.722	8.126	178	661	404	366	381
2,4-Dinitrobenzoic acid	6.735	9.318	−282	988	603	680	394
1,5-Difluoro-2,4-dinitrobenzene	6.747	9.290	−279	1054	644	729	439
4-Hydroxy-3-methoxy-5-nitrobenzaldehyde	5.356	8.513	−388	753	460	451	450
2-Nitro-5-thiocyanatobenzoic acid	5.702	8.277	−112	765	467	502	492
2,4-Dinitrobenzenamine	5.501	8.493	24	924	564	570	597
2-Nitrobenzoic acid, hydrazide	5.647	9.111	9	734	448	433	598
2-Nitrocinnamic acid	5.634	9.059	−233	712	434	421	600
2,4-Dinitrotoluene	6.195	9.226	41	963	588	616	632
4-Methyl-1,2-dinitrobenzene	6.113	9.225	50	973	594	614	684
3,4-Dinitrobenzenemethanol	6.100	9.199	−100	1019	622	643	685
3,4-Dinitrobenzoic acid	6.684	9.341	−274	996	608	679	701
2,6-Dinitrobenzenamine	5.580	8.103	32	932	569	611	719
2-Chloro-3,5-dinitrobenzoic acid	6.614	9.046	−296	976	596	680	1023
2-Methyl-1,3,5-trinitrobenzene	6.807	9.328	57	1350	824	938	1223

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