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Predictions of thermodynamic properties of energetic materials using COSMO-RS

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Abstract

In this work, conductor-like screening for real solvents (COSMO-RS) calculations were carried out using *COSMOtherm* program in conjunction with Gaussian03 packages. The objective was to predict thermodynamic properties for two nitrogen-rich energetic materials which are less harmful for the environment than the conventional ones, namely 3,6-di(hydrazino)-1,2,4,5-tetrazine (DHT) and 3,3'-azo-bis(6-amino-1,2,4,5-tetrazine) (DAAT) for which no experimental data are available to our best knowledge. COSMO-RS approach is a combination of quantum chemical and statistical thermodynamic basis, which allow a physically meaningful description of molecular interactions between pure molecules and solvents in solution. Recently, this approach has been used for the prediction of an enormous number of physicochemical properties especially aqueous solubility, Henry's law constant, vapor pressure and partition coefficient. The vapor pressure of pure compounds is one of the most important thermodynamic properties required for the chemical process design as well as for the fate assessment of pollutants in the environment. To validate the accuracy of COSMO-RS approach for the two molecules of interest, six reference energetic molecules have been studied, for which experimental data are available, such as cyclotetramethylene-tetranitramine (HMX), 2,4,6-trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), 1,1-diamino-2,2-dinitroethylene (FOX-7) and *n*-methyl-*p*-nitroaniline (MNA). From predicted results, a good agreement has been noted. DAAT molecule shows a lower volatility in the medium so that a low detectability compared to the DHT and other reference molecules. Both DHT and DAAT showed negative logarithmic values of Octanol-Water partition coefficients, this means that they don't have the tendency to enhance the bioaccumulation process in soils.

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1. Introduction

Nowadays, the environmental issues force to find urgent solutions to protect our planet. As chemists, it is worthwhile to take into account environmental impacts of chemical compounds prior to their synthesis in laboratories. Recently, the use of molecular modeling as a mean for predicting physicochemical properties has been of great interest for various topics in research. Among the investigated properties are the solubility [1, 2], Henry's

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law constant [3], vapor pressure [4] and octanol-water partition coefficient [5]. In fact, octanol-water partition coefficient is widely known to be an effective tool to evaluate the toxicity of many explosives [6]. Moreover, the estimation of the aqueous solubility for a substance basically predicts the mobility of the substance in presence of solvents which represent its environment. The usefulness of these properties are even more important for energetic materials because of the past problems that have caused many environmental contaminations [7]. By being aware of the risks involved by the use of energetic materials or explosives, it would be easier to prevent and control the source of contamination processes. The interest in the vapor pressure or Henry's law constant is related to the volatility of the substance in the air. Experimental values of these properties are abundant in the literature for more common small molecules. However, there is a scarcity of experimental data regarding large and new energetic molecules. The volatility or vapor pressure has a direct correlation with the detectability [8] which is an helpful property in standoff detection researches of explosives in defence and public security applications. Unfortunately, no experimental data are available for the vapor pressure of some compounds and it is difficult to be determined experimentally.

In this work, we propose predictions for physicochemical properties of two nitrogen rich compounds, namely 3,6-di(hydrazino)-1,2,4,5-tetrazine (DHT) and 3,3'-azo-bis(6-amino-1,2,4,5-tetrazine) (DAAT) using "CONductor-like Screening MOdel for Real Solvents" (COSMO-RS) method [9, 10]. This method is used to validate experimental data or when no experimental data are available. For purpose of validation of the theoretical approach, we have selected some explosives for which experimental data are available. These compounds are cyclotetramethylene-tetranitramine (HMX), 2,4,6-trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) 1,1-diamino-2,2-dinitroethylene (FOX-7) and n-methyl-p-nitroaniline (MNA). The chemical structures of these molecules are shown in Fig 1. Results of thermodynamic property predictions of these compounds were compared to literature data and discussed.

Fig. 1. Chemical structures of studied molecules

2. Methodology

2.1. COSMO-RS

Density functional theory (DFT) calculations were carried out using Gaussian 03 packages [11]. Optimized geometries of compounds were performed at 6-31+G(d,p)/B3LYP method [12-14]. Solubilities, Henry's law

constants, vapor pressures and octanol-water partition coefficients were estimated using the COSMO-RS method developed by Klamt and Eckert [15] which is incorporated in COSMOtherm code. In this approach, the σ -profile is one of the important properties provided by COSMOtherm needed for the estimation of various useful thermodynamic properties. The σ -profile $p_i(\sigma)$ is defined as the probability distribution of surface-charge density for a given molecule [9, 10, 15] and it is expressed for a molecule i by the following equation:

$$p_i(\sigma) = \frac{A_i(\sigma)}{A_i} \quad (1)$$

This probability distribution $p_i(\sigma)$ is proportional to the total surface area $A_i(\sigma)$ of all of the segments around the molecule at the charge density σ and to A_i which denotes the total cavity surface area.

COSMO-RS method has already proven, for simple systems, to be an effective and useful approach to assess thermodynamic properties [16-18]. Some works have also been done for energetic materials [19-20]. Charge distributions, and empirical data, such as the heat of fusion (ΔH_{fus}) and melting point (T_{fus}), are performed by ab initio calculations. Basically, empirical/experimental data serve as inputs in COSMOtherm code.

2.2. Heat of fusion

The entropy (ΔS_{fus}) and enthalpy (ΔH_{fus}) of fusion of compounds at a given temperature T are used as input data in COSMO-RS method for the predictions of thermodynamic properties of a mixture and the free energy of fusion, given by the following expression:

$$\Delta G_{fus} \cong (\Delta H_{fus} + T_{fus} \Delta C_{p, fus}) \left(1 - \frac{T}{T_{fus}} \right) + T_{fus} \Delta C_{p, fus} \ln \left(\frac{T}{T_{fus}} \right) \quad (2)$$

Experimental values are not often available in the literature. In case that ΔH_{fus} is not available, COSMOtherm program assumes that ΔG_{fus} is equal to zero. For ΔH_{fus} and ΔS_{fus} , the group additivity method which is an effective method developed by Chickos et al. has been used [21]. This alternative technique is used to predict thermodynamic properties. Experimental and predicted values of ΔH_{fus} and ΔS_{fus} at fusion temperature for various molecules investigated in this work are listed in Table 1. The free energy of fusion predicted by COSMOtherm at the room temperature 298.15K is also presented in Table 1. For all compounds, experimental melting point value has been used.

Table 1. Experimental and predicted fusion property values for eight energetic materials

| Molecules | T_{fus} (K) | ΔS_{fus} (J.mol ⁻¹ .K ⁻¹) | ΔH_{fus} (kJ.mol ⁻¹) | $\Delta H_{fus, litt}^b$ (kJ.mol ⁻¹) | $\Delta G_{fus}^{298.15}$ (kcal. mol ⁻¹) |
|-----------|-------------------|---|---|---|---|
| TNT | 355 ^a | 50.70 | 16.60 | - | 3.21 |
| RDX | 477 ^b | 81.97 | 39.10 | 35.78 | 1.62 |
| CL-20 | 513 ^c | 31.54 | 16.18 | 42.70 | 3.32 |
| FOX-7 | 543 ^d | 56.80 | 30.84 | - | 0.82 |
| HMX | 548 ^b | 101.86 | 55.82 | - | 6.08 |
| MNA | 425 ^e | 44.33 | 18.85 | - | 1.34 |
| DHT | 433 ^f | 60.80 | 26.33 | - | 1.96 |
| DAAT | ≈523 ^f | 83.60 | 43.72 | - | 4.50 |

^a ref [22], ^b ref [23], ^c ref [24], ^d ref [25], ^e [20], ^f [this work]

3. Results and discussion

As it was mentioned above, specific thermodynamic properties present a particular interest for energetic materials such as the vapor pressure of pure compounds, solubility of compounds in various solvents, Henry constant and Octanol-Water partition coefficient. All these properties are based on molecular surface charge densities represented in σ -profile.

3.1. σ -profile

In order to understand the behavior of molecules in solvents, σ -profile plots of all molecules included Octanol and water solvents are shown in Fig 2. From Fig 2a, we observe that reference molecules have an asymmetric distribution of charges while DHT and DAAT compounds present a symmetric distribution (Fig 2b). This observation indicates how molecules may interact in presence of specific solvents in solution. The octanol σ -profile is similar to reference molecules. However water σ -profile shows similar distribution-charge densities as those of DHT and DAAT.

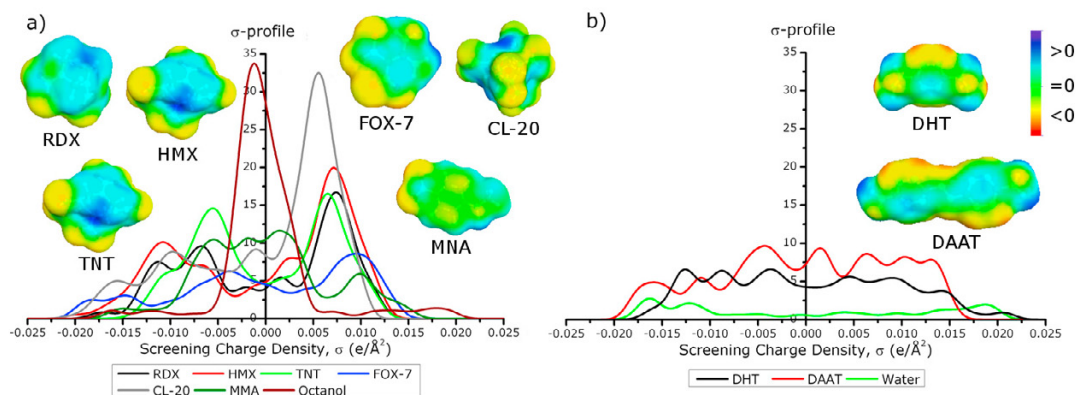


Fig. 2. Sigma profile of energetic molecules, Octanol and Water

3.2. Vapor pressure

Gas traces of explosives are generally detected in atmosphere. For defence and public security applications, volatility property predictions of explosives are useful to prevent terrorist attacks. The knowledge of the vapor pressure, and/or Henry constant is the key. Certainly, the volatility property is directly correlated to the detectability of a given substance in the air. The vapor pressure of a pure compound is calculated by assuming molecules in ideal gas phase. In fact, it is often the case when temperatures are lower than 200°C. Using the chemical potential difference of the molecule i (μ_{ig}^X) assumed as an ideal gas and the compound X (μ_X^X) is at its liquid state. The vapor pressure (P_{vap}^X) of the pure compound at the temperature T , is expressed by:

$$p_{vap}^X(T) = \exp \left\{ \frac{\mu_X^X - \mu_{ig}^X}{RT} \right\} \quad (3)$$

In Table 2, decimal logarithmic values for vapor pressure estimated by COSMOtherm program are listed. From the obtained results we generally note a satisfactory agreement with experimental data for all studied molecules. However, for low vapor pressures, the gap between experimental and predicted values is slightly higher. These deviations may be explained in terms of the assumption that molecules are considered as an ideal gas.

Table 2. Experimental and predicted decimal logarithmic values for vapor pressure at 298.15 K of eight molecules

| Molecules | $\log_{10}(P_{vap}^x)$ | $\log_{10}(P_{vap,lit}^x)^a$ |
|-----------|------------------------|------------------------------|
| RDX | -5.96 | -8.73 |
| CL-20 | -6.33 | - |
| FOX-7 | -6.67 | - |
| TNT | -3.05 | -5.40 |
| HMX | -7.31 | -12.67 |
| MNA | -4.63 | - |
| DHT | -3.70 | - |
| DAAT | -9.65 | - |

^a Ref. [26]

Regarding nitrogen-rich energetic molecules investigated in this work, DHT stands out a similar tendency, like TNT and MNA, its vapor pressure value is much higher than of other compounds. On the other hand, DAAT molecule presents a lower vapor pressure then a lower volatility. This means that DHT is easier to be detected in atmosphere than DAAT.

3.3. Henry constant

The Henry constant (k_H), is a complementary quantitative measure of explosives volatility property beside the vapor pressure. The specific characteristic of Henry constant k_H is applied to systems in thermodynamic equilibrium. This constant basically links the solubility of a solute (i) to its partial pressure above the mixture (P_i^{vap}) as shown in equation 3. More often, water-air is the system used. The objective here is to predict the detectability of several energetic molecules in water-air environment.

$$k_H = \frac{1}{p_i^{vap}(t) \cdot \gamma_i(S;T)} \quad (4)$$

where $\gamma_i(S;T)$ is the activity coefficient of a solute (S) at the temperature T . The obtained results are listed in Table 3.

We observe a higher volatility for TNT, DHT and MNA than those estimated for other energetic materials. We also note that the DAAT molecule stands out with a very low volatility in aqueous phase.

Table 3. Experimental and predicted decimal logarithmic values for Henry constant at 298.15 K of several molecules

| Molecules | $\log_{10}(k_H)$ | $\log_{10}(k_H)_{\text{lit.}}^a$ |
|-----------|------------------|----------------------------------|
| RDX | -8.96 | -10.71 |
| CL-20 | -9.38 | - |
| FOX-7 | -13.60 | - |
| TNT | -7.04 | -6.34 |
| HMX | -11.70 | -14.59 |
| MNA | -4.25 | -5.22 ^b |
| DHT | -6.70 | - |
| DAAT | -12.65 | - |

^a Ref [27], ^b [28]

3.4. Octanol-water partition coefficient

The partition coefficient (K_{OW}) is defined as the ratio of the solubility of a given solute (j) in a solvent mixture.

$$\log_{10}(K_{OW}) = \exp\left(\frac{\mu_j^{(1)} - \mu_j^{(2)}}{RT}\right) \frac{V_1}{V_2} \quad (5)$$

where V_1/V_2 is the volume ratio of solvents, and $\mu_j^{(1)}$ and $\mu_j^{(2)}$ are the chemical potentials of the solute in solvents 1 and 2.

Octanol-water is the typical mixture of solvents used for calculations of the partition coefficient. The coefficient K_{OW} determines the hydrophilic or hydrophobic feature of chemical compounds. It is widely used to especially characterize the toxicity of substances in soils. In fact, K_{OW} indicates whether or not a substance will have a tendency to accumulate in biological membranes of living organisms. In other words, it indicates if there is any prospective which would enhance the bioaccumulation process. Biological membranes are predominantly composed of lipids, thus a higher partition coefficient value is an indicator that the substance presents a high level of risk of contamination. The estimated K_{OW} for the eight explosives are presented in Table 4.

Table 4. Experimental and predicted decimal logarithmic values for Octanol-water partition coefficients at 298.15 K of several molecules

| Molecules | $\log_{10}(K_{OW})$ | $\log_{10}(K_{OW, \text{exp}})$ |
|-----------|---------------------|---------------------------------|
| RDX | 1.11 | 0.87 ^b |
| CL-20 | 3.68 | 1.92 ^b |
| FOX-7 | 0.36 | - |
| TNT | 1.83 | 1.60 ^a |
| HMX | 0.74 | 0.17 ^b |
| MNA | 1.15 | 2.10 ^c |
| DHT | -1.21 | - |
| DAAT | -2.63 | - |

^a Ref [19], ^b Ref [20], ^c Ref [28]

The predictive values showed in Table 4, are in satisfactory agreement with those found in the literature. The comparison of calculated and measured octanol-water partition coefficients indicates that both nitrogen-rich molecules, DHT and DAAT, are more hydrophilic than the rest of molecules in Table 4. This implies that, these two molecules are environmentally friendly regarding the bioaccumulation process in soils. This conclusion is in accordance with σ -profile plots shown in Fig. 2b. Indeed, from this figure, we note that DHT and DAAT show symmetric charge distributions. Hence, they have a tendency to favor solvents having the same type of charge distributions, such as water. Unlike, the other studied molecules which show asymmetric charge distributions in Fig. 2a. We note that these molecules have a preference to be surrounded by solvents presenting alike asymmetric charge distribution profile, such as octanol.

3.5. Solubility

COSMOtherm program also assesses the solubility (x_j^{sol}) property using Gibbs free energy of fusion (ΔG_{fus}) and chemical potentials of a pure compound j ($\mu_j^{(P)}$) and a compound j in an infinite dilution in the solvent i ($\mu_j^{(i)}$).

$$\log_{10}(x_j^{sol}) = \frac{[\mu_j^{(P)} - \mu_j^{(i)} - \max(0, \Delta G_{fus})]}{RT \ln(10)} \quad (6)$$

The molar fraction values are between 0 and 1. When $\mu_j^{(P)} - \mu_j^{(i)} > \Delta G_{fus}$ this leads to a molar fraction value higher than one, this situation is not possible. To get around this problem, solid-liquid equilibrium (SLE) application in COSMOtherm code was used. The SLE function gives the concentration (x_i) at which the solid (i) is in a thermodynamic equilibrium with the liquid phase in solution. In other words, SLE function determines the solute mole fraction value which is required for the saturation of a solution. This chemical equilibrium is described by the following equation:

$$\mu_j^{Solid} = \mu_j^{Liquid} + RT \ln(x_j) \quad (7)$$

where μ_j^{Solid} and μ_j^{Liquid} are the chemical potential of compound (j) in solid and liquid phase, respectively. Calculations with the SLE function are time-consuming, though the SLE seems to have the same reliability as the solubility function. The solubility values in water using equations 6 and 7 are listed in Table 5. In some cases, the solubility values provided by SLE approach are in very good agreement with experimental data in comparison with those provided by equation 6.

Table 5. Different predictive methods for water solubilities (in g/g_{solvent}) at 298.15K

| Molecules | Solubility | SLE | Experimental ^a |
|-----------|------------------------|------------------------|---------------------------|
| RDX | 1.49 x10 ⁻⁵ | 1.17 x10 ⁻⁵ | 5.64 x10 ⁻⁵ |
| CL-20 | 3.18 x10 ⁻⁵ | 6.09 x10 ⁻⁶ | 3.65 x10 ⁻⁶ |
| FOX-7 | 7.98 x10 ⁻² | 2.06 x10 ⁻³ | - |
| TNT | 2.29 x10 ⁻⁵ | 3.15 x10 ⁻⁵ | 1.15 x10 ⁻⁴ |
| HMX | 1.52 x10 ⁻⁶ | 6.58 x10 ⁻⁷ | 4.46 x10 ⁻⁶ |
| MNA | 7.04 x10 ⁻⁴ | 7.18 x10 ⁻⁴ | 8.54 x10 ⁻⁵ |
| DHT | 5.08 x10 ⁻¹ | 6.77 x10 ⁻² | - |
| DAAT | 1.41 x10 ⁻³ | 1.83 x10 ⁻³ | - |

^a Ref. [19, 28, 29]

From Table 5, we note a good reliability on COSMO-RS method regarding aqueous solvents. The obtained results show higher aqueous solubilities for DHT and DAAT than for the rest of molecules. From simulation results, we are able to select the appropriate solvent for a given chemical compound. The prediction of solubilities of compounds in various solvents is an effective tool to avoid many unnecessary tests in labs, while protecting at the same time the environment. In this work, solubilities of all molecules were also predicted in presence of some solvents such as dimethyl sulfoxide (DMSO), acetone and acetonitrile (Table 6).

Table 6. Experimental and calculated solubilities in (g/g_{solvent}) of different molecules at 298.15K

| Molecules | DMSO | | Acetone | | Acetonitrile | |
|-----------|-------------|--------------------------|------------|-------------------|--------------|-------------------|
| | Calculated | Exp. | Calculated | Exp. | Calculated | Exp. ^a |
| RDX | 1.06 | 0.41 ^a | 0.48 | 0.08 ^a | 0.33 | 0.06 |
| CL-20 | 2.92 | - | 1.92 | 1.09 ^c | 1.49 | - |
| FOX-7 | 1.95 (20°C) | 0.42 ^b (20°C) | 0.95 | - | 0.34 | - |
| TNT | 2.71 | - | 2.52 | - | 2.63 | 1.32 |
| HMX | 1.15 | 0.57 ^a | 0.28 | 0.03 ^a | 0.05 | 0.02 |
| MNA | 2.66 | | 1.11 | | 0.69 | |
| DHT | 1.10 | - | 0.68 | - | 0.06 | - |
| DAAT | 1.64 | - | 0.50 | - | 0.15 | - |

^a Ref [30], ^b Ref [31], ^c Ref [32]

From this table, we note that DHT and DAAT predicted solubility values are higher in presence of DMSO solvent than with acetonitrile. In addition, the solubility for all molecules in the three solvents is much higher than in water. We also observe (Table 6) that the predicted solubilities are overestimated compared to experimental ones. This deviation could be attributed to many factors related to variety of experimental conditions collected from different references in the literature and also to the empirical data we used as inputs in COSMOtherm simulations. These errors increase as the solubility value of the compound increases.

4. Conclusion

In summary, using COSMO-RS method we were able to assess the solubility, Henry's law constant (k_H), vapor pressure (P_{vap}) and octanol-water partition coefficient (K_{OW}). These thermodynamic properties were predicted for two nitrogen rich molecules DHT and DAAT, and six reference molecules for purpose of validation of the COSMO-RS approach. A comparison of experimental and estimated values of various properties for reference energetic molecules was presented and showed a satisfactory agreement. The Henry constant and vapor pressure predicted values indicated that DAAT has a very lower volatility than DHT molecule. In addition, DHT showed a similar physicochemical tendency to RDX. Regarding the partition coefficient, both DHT and DAAT molecules present a negative values for the term $\log_{10}(K_{OW})$. This conclusion is explained in terms of less threat for bioaccumulation processes in the environment. Aqueous solubility of both nitrogen-rich molecules is higher than the rest of studied energetic molecules (RDX, CL-20, FOX-7, TNT and HMX). Their solubility remains higher in polar aprotic solvents such as DMSO, acetone and acetonitrile. To conclude, laboratory synthesis for the investigated DHT and DAAT molecules is in progress and measurements of thermodynamic properties will be performed in purpose of comparison and validation of obtained results with COSMO-RS approach. The ultimate objective is to use this helpful tool prior to any tests in labs.

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