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A systematic theoretical investigation of the relationship between heats of detonation and NBO charges and ^{15}N NMR chemical shifts of nitro groups in nitramines and nitro paraffins

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ABSTRACT

A new quantitative method for predicting and calculating the heat of detonation for a series of nitro paraffins and nitramines employing the natural bond orbital (NBO) charge analysis and ^{15}N NMR chemical shifts of the nitro group is established. All calculations, including optimizations, charge analysis and $^{15}N_{Nitro}$ NMR chemical shifts, were performed using density functional (DFT) methods with 6-311+G(d,p) basis set. The results show a linear correlation between the nitro group charges and C/N-nitro bond lengths. The latter reflect the strength of the corresponding bond and thus the stability of the nitro compounds. A strong correlation was observed between the heat of detonation with the charge and ^{15}N NMR chemical shift on the nitro group in nitramines and nitro paraffins. Nitro compounds with a higher heat of detonation have less negative nitro group charges, (Q_{Nitro}) and a lower value for the $^{15}N_{Nitro}$ chemical shift in analogous compounds. From the quantitative models, the heat of detonation increase when the Q_{Nitro} values (positive coefficient) are larger and decrease when the $^{15}N_{Nitro}$ NMR chemical shift (negative coefficient) is higher. The present work provides consistent models (mean square error prediction values below 0.14 MJ kg^{-1}) in a systematic way for quick estimation of heats of detonation – with or without experimental data – for a wide range of energetic materials. This practical approach is particularly useful as a tool for the design of high-energy density materials.

1. Introduction

Characteristics of high-energy density materials (HEDMs), such as performance, sensitivity, and stability, are determined by molecular level phenomena. These properties have implications for safety and handling as well as the practical use of these materials. A deep understanding of the factors affecting the heat of detonation of energetic compounds plays an important role in design of energetic systems with the appropriate requirements of future military and civil applications. Nitro compounds are typical HEDMs and are widely used as explosives because of their superior explosive performance over conventional energetic materials. Several relationships have been found that relate explosive characteristics with measured and predicted molecular properties. The relationship between the thermal [1], impact [2,3] and electric spark [4] sensitivities and the molecular structure of nitro compounds has been a subject of considerable attention. These studies have concluded that the C–NO_2, N–NO_2 and O–NO_2 bond breaking is the key step in the detonation process in nitro explosives. In addition, one of the most important thermodynamic parameters that determine the explosive performance in HEDMs is their heat of detonation (HD). Heat of detonation may be used as a proxy for the energy available to do mechanical work and serves as an estimate for the potential damage to the surroundings [5]. The heat of detonation may be determined either experimentally [7] or theoretically [6]. The calculated value is the difference between the energies of formation of the explosive components and the energies of formation of the explosion products. However, both experimental and theoretical estimates of HD tend to differ from the actual explosion value. This is primarily because the chemical reaction is influenced by the conditions of the wave front (e.g., by the loading density of the explosive) [8].

The relationship between the heat of detonation and the electronic structure of nitro compounds can be established by charge analysis and the ^{15}N NMR chemical shifts of the nitro group. In this context, this functional group corresponds to the reaction center of the molecule and should be correlated with explosive characteristics of individual energetic materials. The particular differences in the chemical environment of the nitro groups provide a useful approach to understanding, evaluating and ultimately predicting the

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heat of detonation in a set of HEDMs. In the present study, the nitro group charges (Q_{Nitro}) are calculated by the sum of atomic charges of all three atoms on nitro group and were obtained using the natural bond orbital (NBO) analysis [9]. Recently, the nitro group charge method (NGCM) was established and applied to predict the properties of some explosives, including molecular stability and impact sensitivity [10]. Zeman [11] investigated the relationship between detonation characteristics and ^{15}N NMR chemical shifts of nitro and aza nitrogen atoms in nitramines. On the other hand, the calculated $^{15}N_{Nitro}$ NMR chemical shift for nitramines were obtained using a protocol established in our recent work [12] within the continuous sets of gauge transformations (CSGT) method [13]. *Ab initio* calculations of the NMR chemical shifts for different nuclei have proven to be useful tools in interpreting experimental data in several applications [14–16].

The tested explosive compounds were 14 nitro paraffins related to derivatives of nitromethane and propane and 22 nitramines, including cyclic and linear compounds, as shown in Tables 1–3. This study is part of a systematic and comprehensive effort to predict and calculate the heat of detonation and the purpose of this work was twofold. First, we wished to investigate the relationship between the heat of detonation and the electronic properties as a function of nitro charge and $^{15}N_{nitro}$ NMR chemical shifts in energetic compounds. Second, we wanted to establish a model to calculated and predict the heat of detonation based on the ^{15}N NMR chemical shifts and the charge of nitrogen in the nitro group. One important aspect of the present work is that it provides an easy method for quick estimation of heats of detonation with or without experimental data for a systematic set (nitramines and nitro paraffins) of energetic materials including those not yet synthesized or in development.

2. Computation details

We used the GAUSSIAN 09 [17] software package for all theoretical calculations. Molecular geometries were optimized using the B3LYP [18,19] functional and 6-311+(d,p) basis set, which can give good geometry optimizations at a relatively low computational expense. Absolute energies and C–NO_2 and N–NO_2 bond lengths of nitro paraffins and nitramines are shown in Tables 1–3. The nitro group charges (Q_{Nitro}) were calculated according to the NBO scheme as implemented in Gaussian 09 [20]. The $^{15}N_{Nitro}$ NMR calculations for all tested compounds were performed using the CSGT method and are reported in Tables 1–3. NMR shifts were computed using B3LYP/6-311+G (2d,p), and the values for the ^{15}N isotropic chemical shifts were referenced to the corresponding values for nitromethane, calculated at the same level of theory. The effect of solvent on the theoretical NMR parameters was included using the default IEF-PCM model [21] provided by Gaussian 09. Dimethylsulfoxide (DMSO), which has a dielectric constant (e) of 46.7, was used as solvent. The experimental $^{15}N_{Nitro}$ NMR chemical shifts in solution and their corresponding experimental data for some nitramines were obtained from the literature [22,23], including theoretical values for substances not yet synthesized [24]. The heats of detonation (HD), used in the present paper, were obtained from Zeman's work [25]. These values were calculated for monocrystals by means of semi-empirical relationship devised by Pepekin et al. [26] and correspond to the experimentally determined heats of detonation in the calorimetric bomb [7,26].

3. Results and discussion

3.1. Relationship between nitro charges (Q_{Nitro}), $R_{C\text{-}Nitro}/R_{N\text{-}Nitro}$ bond lengths and stability

The molecular stability of the compounds was evaluated and compared with the $R_{C\text{-}Nitro}/R_{N\text{-}Nitro}$ bond lengths and nitro group charges (Q_{Nitro}) for nitro paraffins and nitramines. Nitro compounds are very strong electron acceptors and this ability can be represented by the net charges of the nitro group. However, atomic charge is a defined quantity, not a physical observable. Higher negative charge on the nitro group implies lower electron attraction and therefore more stability of the nitro compound. In nitro-containing covalent compounds, the $R_{C\text{-}Nitro}$ and $R_{N\text{-}Nitro}$ bond is generally the weakest in the molecule, and its breakdown is the initial step in the process of molecular detonation or decomposition. The optimized C-Nitro bond lengths and the nitro charges with its corresponding total energies for a set of nitro paraffins are listed in Table 1. The $R_{C\text{-}Nitro}$ fall in the range from 1.5029 to 1.5565 Å and there is good linear relationship ($R^2 = 0.9675$) with the nitro charges values calculated with NBO scheme, as shown in Fig. 1. These results reveal as the $R_{C\text{-}Nitro}$ bond length increases as the

Table 1
Absolute energies, code designations, $R_{C\text{-}Nitro}$ bond distances, nitro charges, heats of detonation and $^{15}N_{Nitro}$ NMR calculated chemical shifts for nitro paraffins.

#	Chemical name	Code designation	Energy[a] (hartrees)	Distance $R_{C\text{-}Nitro}$ (Å)	NBO[b] charge Q_{Nitro}	Heat of detonation[c] (MJ kg^{-1})	Calculated[e] $^{15}N_{Nitro}$ (ppm)
1	Nitromethane	NM	−245	1.5029	−0.2860	4.522	0.00
2	Dinitromethane	DNM	−450	1.5133	−0.1920	6.814	−27.59
3	Trinitromethane	TNM	−654	1.5260	−0.1440	6.942[d]	−37.06
4	Tetranitromethane	TeNM	−859	1.5499	−0.1040	2.259	−47.09
5	Nitroethane	Net	−284	1.5134	−0.2690	1.686	18.49
6	1,1-Dinitroethane	1,1-DNEt	−489	1.5320	−0.2030	6.323 [d]	−44.60
7	1,1,1-Trinitroethane	1,1,1-TNEt	−693	1.5502	−0.1610	6.599	−25.80
8	1,2-Dinitroethane	1,2-DNEt	−489	1.5150	−0.2330	3.745 [d]	−3.18
9	1-Nitropropane	1-NPr	−324	1.5103	−0.2680	2.711 [d]	5.70
10	1,1-Dinitropropane	1,1-DNPr	−528	1.5427	−0.2075	4.517	−9.93
11	2,2-Dinitropropane	2,2-DNPr	−528	1.5565	−0.2175	4.435	−0.30
12	1,1,1-Trinitropropane	1,1,1-TNPr	−733	1.5427	−0.1633	5.419	−22.40
13	1,1,1,3-Tetranitropropane	1,1,1,3-TeNPr	−937	1.5512	(1) −0.152	6.250	−29.03
				1.5235	(3) −0.222		-5.94
14	2-Methyl-1,1,1,3-tetranitropropane	2-MeTeNPr	−977	1.5535	(1) −0.153	5.458	−30.35
				1.5241	(3) −0.225		-11.94

[a] Calculated with B3LYP/6-311+(d,p).

[b] Natural bond orbital analysis.

[c] Ref. [25].

[d] Predicted by Eq. (3).

[e] calculated with CSGT-B3LYP/6-311+(2d,p).