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Novel correlation for predicting impact sensitivity of nitroheterocyclic energetic molecules

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Abstract

A novel correlation is introduced for predicting impact sensitivity of a variety nitroheterocyclic molecular types, such as nitropyridines, nitroimidazoles, nitropyrazoles, nitrofurazanes, nitrotriazoles and nitropyrimidines. This approach is based on elemental composition and two structural parameters of $C_aH_bN_cO_d$ nitroheterocyclic energetic compounds. The results for mentioned compounds are compared with complex neural networks computations which use compositional and topological descriptors. Root mean square (rms) of deviation of different nitroheterocyclic molecules including nitropyridines, nitroimidazoles, nitropyrazoles, nitrofurazanes, nitrotriazoles and nitropyrimidines are 58 and 71 cm for new correlation and neural networks computations methods, respectively.

Keywords: Correlation; Nitropyridines; Nitroimidazoles; Nitropyrazoles; Nitrofurazanes; Nitrotriazoles; Nitropyrimidines; Impact sensitivity; Safety

1. Introduction

The heavy reliance on experimentation and measurement of a variety of candidate energetic materials is lengthy and expensive because the development, manufacture, testing and fielding of a new energetic material is so costly in time and money. Due to sensitivity and performance problems, it is important to eliminate of any poor candidate before expending resources in its synthesis. Detonation velocity and pressure, thermal properties and sensitivity are the most concern factors in searching new explosives one. A new candidate explosive, after the initial research is ultimately widely used, may well be determined by other factors such as cost, toxicity, melting point, etc. Predictive methods of energetic systems have provided a considerable insight into the understanding of factors affecting the behavior of explosives and propellants so that some new approaches have been recently introduced for predicting detonation parameters of different classes of explosives as well as performance of propellants [1–15].

Energetic organic substances contain metastable capable of undergoing very rapid and high exothermic reactions. Sensitivity of an energetic compound is a complex matter and its understanding is in large part of a chemical problem. Some properties contribute to the materials response to the stimulus in a sensitivity test which is a consequence of the kinetics and thermodynamics of thermal decomposition of the explosive. They include (i) the ease with which a detectable reaction of any kind can be initiated in an explosive, (ii) establishment the tendency of small reaction can grow to destructive properties and (iii) the ease with a higher order detonation can also be established in an explosive.

Impact and shock sensitivity are two of the most commonly used measurements of many kinds of sensitivity which have been identified in terms of stimuli causing detonation, e.g. heat, friction, impact, shock and electrostatic charges. The measurements using shock sensitivity tests have been performed for some pure explosives [16]. The drop weight impact test is convenient and the most common method of assessing sensitivity for measuring impact sensitivity. In this test a weight of 50% probability in causing an explosion (h_{50}) was measured when hit by a hammer with a standard weight. Although the test is itself is extremely easy to implement, obtaining reliable experimental results is known to be relatively difficult. Due to difficulty associated

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with puzzles in initiation mechanism of explosion caused by mechanical impacts, it is believed that hot spots in the material contribute to initiation in the drop weight impact test. Since factors in the impact experiment that might affect the formation and growth of hot spots could strongly affect the measurements, the results are often not reproducible. However, the results are extremely sensitive to the conditions under which the tests are performed. Despite large errors present in some of experimental data, most studies have attempted to associate molecular properties with sensitivities rely on drop weight impact measurements [12,16–53].

In spite of the fact that many methods for predicting impact sensitivities have been developed, e.g. the oxygen balance of the molecules [17,18], molecular electronegativities [26,27] and quantum mechanical computation [53], a generalized simple reliable method is still needed to explosive users in industry. Since safe handling of novel energetic molecules is one of the most important issues to chemist who concern synthesis of energetic materials, development simple correlations is of significant importance. Several correlations have been recently introduced for selected class of explosives including polynitroaliphatics, polynitroaromatics and nitamines [12]. The purpose of this work is to complete our previous work [12] which presents at the first time a novel correlation for predicting impact sensitivity of a variety of nitroheterocyclic molecular types containing nitropyridines, nitroimidazoles, nitropyrazoles, nitrofurazanes, nitrotriazoles and nitropyrimidines. The paper shows success in finding a reasonable good correlation between impact sensitivity and elemental composition as well as two structural parameters. Since complex neural networks architecture with a wide range of molecular descriptors have been recently used as a predictive methodology for impact sensitivity to cover various types of energetic molecules [54], the new correlation will be compared with this method for mentioned nitroheterocyclic energetic compounds.

2. Sensitivity of nitroheterocyclic energetic compounds

Explosives, propellants and pyrotechnics are used extensively for both civilian and military applications. Heterocyclic compounds have received a great amount of interest in recent years because they generally have a higher heat of formation, density and oxygen balance than their carbocyclic analogues. They can provide new explosives and propellants with higher performance or enhanced insensitivity to thermal or shock insults as well as developing pyrotechnics with reduced smoke.

A variety of well-known nitroheterocyclic energetic compounds containing nitropyridines, nitroimidazoles, nitropyrazoles, nitrofurazanes, nitrotriazoles and nitropyrimidines have been developed and their impact sensitivities reported in literature [16]. There are no correlations reported for predicting their impact sensitivities. Large differences of impact sensitivities between some isomers of nitrohetrocycles, e.g. 1,2,3-triazoles and 1,2,4-triazoles, are important problem in obtaining desirable correlation. Large uncertainties associated with some of experimental data also hamper for explosives scientists to find good correlations between some of molecular descriptors and impact sensitivity of nitroheterocycles. However, neural networks architectures have been recently used as prediction methodology for impact sensitivity to cover various types of energetic molecules including nitroheterocycles. Cho et al. [54], for example, have used optimized neural network architecture by utilizing 17 molecular descriptors which were composed of compositional and topological descriptors in an input layer, and 2 hidden neurons in a hidden layer. They showed that subsets composed of compositional and topological descriptors provide better results than those composed of electronic descriptors including Lowest unoccupied molecular orbital from MOPAC (LUMO_MOPAC), Highest occupied molecular orbital from MOPAC (HOMO_MOPAC), Dipole moment from MOPAC (Dipole_MOPAC) and Heat of formation from MOPAC (HF_MOPAC).

It is important to understand better the relationship between molecular structures of energetic compounds and their sensitivities to specific stimuli. Sensitivity of an energetic compound is a complex matter and its understanding is large part of a chemical problem.

It is proposed here that impact sensitivity of nitrohetrocycles can most appropriately be expressed as its elemental composition and some structural parameters. The results indicated that the following general equation is suitable for various types of $C_aH_bN_cO_d$ nitroheterocycles including nitropyridines, nitroimidazoles, nitropyrazoles, nitrofurazanes, nitrotriazoles and nitropyrimidines:

$$\log h_{50} = \frac{y_1 a + y_2 b + y_3 c + y_4 d + \sum_{i=5} y_i \mathrm{SP}_i}{\mathrm{MW}} \quad (1)$$

where y_1, y_2, y_3, y_4 and y_i are adjustable parameters which are obtained by the best fit to experimental impact sensitivities data for different mentioned nitrohetrocyclic molecules, SP_i the number of specific structural parameters and MW is the molecular weight of the explosive. As seen, this correlation has structural terms which can be useful for obtaining a generalized correlation. Various structural parameters have been examined so that can give reliable predictions as compared to neural network computation of impact sensitivity. We have used a database archived by Storm et al. [16], where the experimental values of impact sensitivity for various nitroheterocyclic molecules have been collected. The database of Storm et al. was not augmented by others because experimental data of impact sensitivity varied widely depending upon instrumental types, experimental conditions and the others. To obtain adjustable parameters, we removed data of insensitive molecules whose experimental values are given as 'greater than 320 cm'. The results showed that the number of –CNC– and –CNNC– moieties in aromatic ring are important structural parameters for predicting impact sensitivity of nitroheterocycles.

Multiple linear regression method [55] was used to find adjustable parameters. Since the equation set is overdetermined [55], the left-division method for solving linear equations uses the least squares method. Thus, optimized correlation has the