DOI 10.5012/bkcs.2011.32.7.2319

A Predictive Study on Molecular and Explosive Properties of 1-Aminoimidazole Derivatives

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Received April 7, 2011, Accepted May 3, 2011

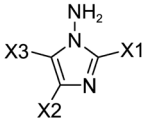
Molecular structures and chemical properties of 1-aminoimidazole derivatives have been investigated at high levels of density functional theories. Heat of formation, density, explosive performances and impact sensitivities have been estimated at the global minimum of potential energy surface. As more nitro groups are introduced, the explosive performances of 1-aminoimidazole derivatives are enhanced, while the impact sensitivity becomes more sensitive. A two-dimensional plot between explosive performance and impact sensitivity has been utilized to comprehend the technical status of new explosive candidates. Based on locations in the two-dimensional plot, 1-aminodinitroimidzole isomers appears to have a potential to be good candidates for insensitive explosives, and 1-aminotrinitroimidazole may become a powerful explosive molecule whose behavior is quite close to HMX.

Key Words : Energetic molecule, 1-Aminoimidazole, Explosive performances, Impact sensitivity, Two-dimensional plot

Introduction

Imidazole is forecasted to be a good scaffold for novel explosive molecules because aromaticity provides insensitive nature and high nitrogen content yields high power with an introduction of energetic groups.[1] According to this chemical intuition, many researchers have attempted to synthesize various nitroimidazole derivatives by introducing several nitro groups at different positions of imidazole moiety. 1,2,4,5-Tetranitroimidazole (TeNI) is probably the most powerful explosive molecule among the series of nitroimiadzole derivatives.[2] Unfortunately, based on our previous theoretical calculations, TeNI is probably not stable to exist due to the labile nature of nitro group attached to N1 atom.[3]

Aminonitroderivatives also draw attention because replacing a nitro group to an amino group enhanced insensitive nature significantly with little loss of explosive power. Although there are four positions available to introduce an amino group into an imiadzole ring, we have investigated explosive performance and sensitivity of 1-aminonitroimidazole derivatives. We have chosen 1-amino derivatives as model compounds in this study because 1-amino derivative is probably the most stable isomer due to labile nature of nitro group attached to N atom. The compounds examined in this study are depicted in Scheme 1.



1, X1=X2=X3=H
2a, X1=NO_2; X2=X3=H
2b, X2=NO_2; X1=X3=H
2c, X3=NO_2; X1=X2=H
3a, X1=X2=NO_2; X3=H
3b, X1=X3=NO_2; X2=H
3c, X2=X3=NO_2; X1=H
4, X1=X2=X3=NO_2

Scheme 1

Computational Methodology

All density functional theory (DFT) calculations were carried out using the GAUSSIAN-03 series of programs[4] on a CRAY computer. Geometries were fully optimized without restricting any symmetry. Theories utilized in this study were B3LYP/6-31G* for conformational analysis and molecular surface electrostatic potential (MESP), and BP86/6-31G** for heat of formation.[5] In predicting the heat of formation, a scheme developed by Politzer and coworkers was employed.[6] Politzer used the BP86/6-31G** level of theory and empirical atomic correction terms. According to our previous validation in various types of energetic molecules, Politzer's scheme provided reasonably good results, where an average absolute error was less than 5 kcal/mol.[7] Estimation of heat of formation in the solid phase requires to subtract sublimation energy. A regression equation developed by Charlton *et al.*[8] was used for estimating sublimation energy. Charlton *et al.* utilized three simple molecular descriptors, i.e. carbon atom number, hydrogen bond donor, and hydrogen bond acceptor. All the molecules studied in this work were assumed to be solid in room temperature because (1) the parental compound, imidazole, is solid (mp = 90 °C) and (2) the introduction of amino group in the heterocyclic rings is known to increase the melting points.[1e] To predict the density, two different methods were employed; (1) group-additivity method (GAM) and (2) molecular surface electrostatic potential (MSEP). In GAM, the most

recent parameters developed by Ammon were utilized.[9] The MSEP method used in this study was originally developed by Politzer *et al*.,[10] and was further modified by Kim *et al*.[11] Once heat of formation in the solid state and density had been predicted, explosive performances were calculated with the Cheetah program.[12] In predicting the impact sensitivity, a neural network scheme optimized by us[13] was utilized. The scheme was initially developed by Nefati *et al*.[14]

Results and Discussion

Conformational Analyses and Molecular Structures. Since all the molecular and explosive properties of an explosive molecule have to be calculated at the most stable molecular structure,[5] obtaining the global minimum in the potential energy surface is the first step in this study. The global minimum in the solid phase may not the same as the one in the gas phase because intermolecular interactions with adjacent molecules may change the molecular structure substantially. Since all the empirical parameters in predicting molecular descriptors have been developed based on the most stable molecular structure, obtaining the global minimum is still important for one to predict various molecular properties. To understand molecular structure of 1-amino-nitroimidazole derivatives, the conformational preference of the amino group attached to the imidazole ring has been investigated. A conformational analysis of **1** has been performed by rotating amino group at the B3LYP/6-31G* level. The result is shown in Figure 1. All the rotational potentials studied in this work were illustrated by using the torsional angle between the N1-C2 ring bond and one of the NH bond in the amino group. The NH bond immediately following the nonbonded electron pair in a clockwise direction was utilized to define a reference torsional angle. As shown in Figure 1, rotational potential of **1** shows a typical sp^2 type rotational barrier, where it is stable when nonbonded electron pair aligns parallel to the imidazole ring. Two stable conformers, i.e. **1-f1**, **1-f2**, where two NH bonds bisected the imidazole ring are found. The conformer **1-f2**, which is about 0.4 kcal/mol lower in energy at the B3LYP/6-31G* level, is utilized for further studies in this work.

The presence of nitro group at adjacent positions makes a substantial impact on the rotational potential of 1-amino group. Compounds **2a** and **2c** have served as model compounds in understanding the rotational potential change due to an adjacent nitro group. Figure 2 and 3 depict the rotational potential functions of **2a** and **2c**, respectively. These rotational potentials are similar each other, but differ greatly from the one of **1**. Both potentials appear to be governed by strong hydrogen bonding interactions between adjacent amino and nitro groups. At the same time, the nonbonded electron pair of the amino group had a strong repulsion with the O atom of the nitro group, and poses itself away from the nitro group.

The conformational preference of **3b** also differs from those of 1-aminoimidaole derivatives mentioned previously due to the presence of two adjacent nitro groups. The rotational potential of **3b** is shown in Figure 4. Two most stable conformations, **3b-f1** and **3b-f2**, are the mirror image of each other, and are essentially the same structure. This

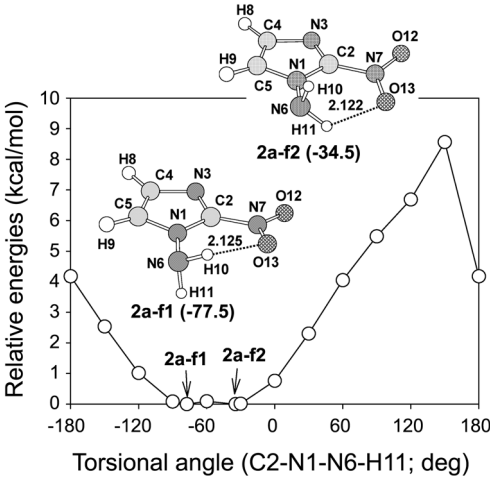


Figure 2. Rotational potential of **2a** due to the rotation of the amino group at B3LYP/6-31G*. Two conformers at the energy minima, **2a-f1** and **2a-f2**, are illustrated with the atomic numbering scheme. The values in the parentheses are C2-N1-N6-H11 torsional angle.

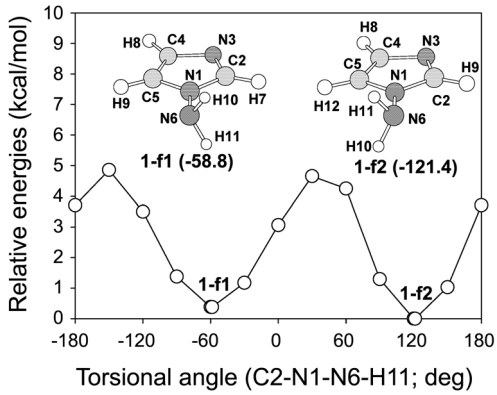


Figure 1. Rotational potential of **1** due to the rotation of the amino group at B3LYP/6-31G*. Two conformers at the energy minima, **1-f1** and **1-f2**, are illustrated with the atomic numbering scheme. The values in the parentheses are C2-N1-N6-H11 torsional angle.

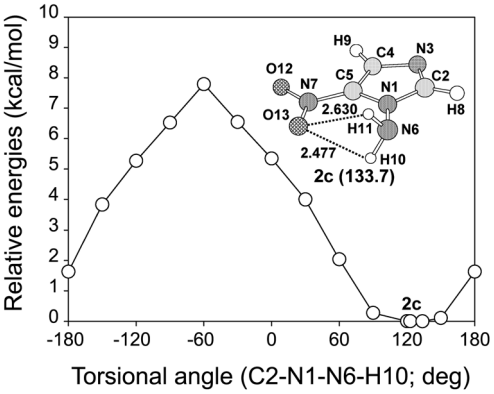


Figure 3. Rotational potential of **2c** due to the rotation of the amino group at B3LYP/6-31G*. The lowest conformer of **2c** is illustrated with the atomic numbering scheme. The value in the parenthesis is C2-N1-N6-H10 torsional angle.

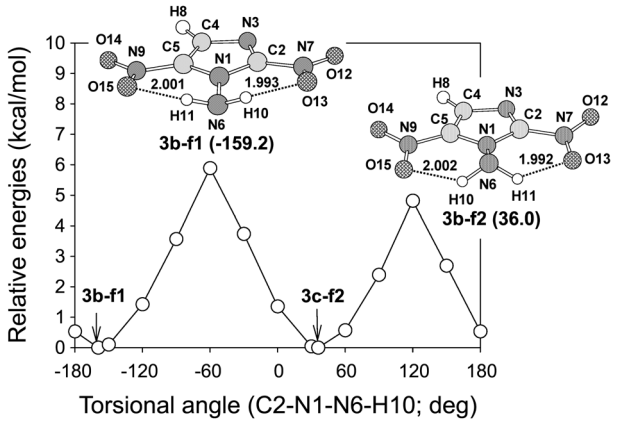


Figure 4. Rotational potential of **3b** due to the rotation of the amino group at B3LYP/6-31G*. Two conformers at the energy minima, **3b-f1** and **3b-f2**, are illustrated with the atomic numbering scheme. The values in the parentheses are C2-N1-N6-H10 torsional angle.

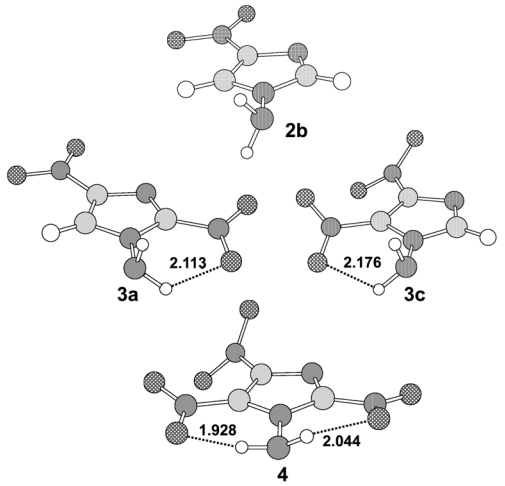


Figure 5. The most stable molecular structures of **2b**, **3a**, **3c**, and **4** in their potential energy surfaces.

structure has two strong hydrogen bonds between H atoms in amino group and O atoms in adjacent nitro groups. It is worthwhile to note that this strong hydrogen bonding is also observed in 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), which has an alternative arrangement of amino and nitro groups and is well known for its great insensitive nature.[15]

We believe that the torsional potentials of **1**, **2a**, **2c**, and **3b** explain all the conformational natures in 1-aminoimidazole derivatives well. Since the nitro group attached in C4 atom rarely alters the conformational preference of 1-amino group, the global minima of **2b**, **3a**, **3c**, and **4** are also obtained by contemplating the conformational natures of **1**, **2a**, **2c**, and **3b**. The global minima of **2b**, **3a**, **3c**, and **4** are shown in Figure 5.

Heat of Formation and Density. Calculated heat of formations of 1-aminonitroimiadzole derivatives in both the gas and solid phases along with sublimation energies are summarized in Table 1.

Heat of formation of **1** in the gas phase is predicted to be

Table 1. Predicted heats of formation[a] (both in the gas and solid phases) and sublimation energies[a] of 1-aminoimidazole derivatives

Compounds	ΔH_f° (298 K, gas phase)	Sublimation energy	ΔH_f° (298 K, solid phase)
1	59.1	21.3	37.8
2a	58.8	25.9	32.9
2b	57.9	25.9	32.0
2c	57.1	25.9	31.2
3a	62.2	30.4	31.8
3b	62.2	30.4	31.8
3c	66.8	30.4	36.4
4	75.3	35.0	40.4

[a]Units are in kcal/mol.

59.1 kcal/mol. Adding one nitro group to **1** rarely changes the heat of formation in the gas phase. Heats of formation of **2a**, **2b**, and **2c** are calculated to be 58.8, 57.9, and 57.1 kcal/mol, respectively. As the second nitro group is added, heats of formation in the gas phase are increased by approximately 5 kcal/mol. Introduction of the third nitro group raises the heat of formation in the gas phase by about 10 kcal/mol. The heat of formation of **4** in the gas phase is predicted to be 75.3 kcal/mol, which is the highest one among a series of 1-aminoimidazoles. Sublimation energy is also increased about 4-5 kcal/mol with a regular fashion, as each nitro group is added to the ring. Since both heat of formation in the gas phase and sublimation energy are increased with a similar magnitude due to the introduction of nitro groups, heats of formation in the solid phase are almost the same regardless of the number of nitro groups present in the ring. The heat of formation of **1** in the solid phase is predicted to be 37.8 kcal/mol. The heats of formations of mononitro and dinitro derivatives of 1-aminoimidazole are calculated to be in a range between 31.2 and 36.4 kcal/mol. These values are slightly lower than that of **1**. The heat of formation of **4** is 40.4 kcal/mol, which is not so far from that of **1**.

Density is known to be one of the most important input data in predicting explosive performances accurately.[16] Our preliminary study has showed that the error larger than 0.07-0.08 g/cc in predicting the density might furnish a poor performance in predicting explosive performances. Although the best way in obtaining crystal density values is the prediction of crystal structures in three-dimensional space, obtaining accurate crystal structures probably needs more efforts in scientific community.[17] We have performed a validation test in using the MSEP method to predict densities of explosive molecules,[18] and have found that the MSEP method appears to be slightly superior to GAMs, but requires much more computational efforts. We also have to mention one shortcoming of current GAM, the inability to differentiate the densities of structural isomers. The density values predicted by both GAM and MSEP are summarized in Table 2.

The density of **1** is predicted to be 1.285 and 1.343 g/cc by GAM and MSEP, respectively. According to both methods, density is increased by 0.2-0.3 g/cc as the first nitro group is

Table 2. Densities[a] predicted by GAM and MSEP

Compounds	GAM	MSEP
1	1.285	1.343
2a	1.576	1.590
2b	1.576	1.652
2c	1.576	1.537
3a	1.767	1.795
3b	1.767	1.768
3c	1.767	1.791
4	1.903	1.926

[a]Unit in g/cc.

introduced. GAM estimates densities of mononitro derivatives to be 1.576 g/cc, while MESP predicts to be 1.537-1.652 g/cc. Densities of dinitro derivatives are calculated to be 1.767 g/cc by GAM, and 1.768-1.795 g/cc by MSEP, respectively. Density of **4** is predicted to be 1.903 g/cc by GAM and 1.926 g/cc by MSEP, respectively. Densities predicted by MSEP are usually a little higher than those by GAM with Ammon's parameters, with an exception in **2c**, where GAM predicted density is 0.039 g/cc higher than MSEP predicted density. Average difference between two sets of predicted densities is 0.033 g/cc, with the largest difference of 0.076 g/cc in **2b**. The agreement becomes better as more nitro groups are introduced. We feel confident in predicted densities of 1-aminoimidazole derivatives since two completely different schemes concur.

When the predicted densities of 1-aminoimidazole derivatives are compared with those of conventional explosive molecules, 1-aminoimidazoles with more than two nitro groups appear to be a good candidate for high explosive molecules. The predicted density values of dinitro derivatives are slightly inferior to that of RDX (1.806 g/cc; *refcode* CTMTNA in Cambridge Structural Database (CSD)).[19] The predicted density of **4**, trinitro compound, is as high as that of HMX (1.903 g/cc; *refcode* OCHTET04 in CSD).

Explosive Performances. We employ computed C-J pressure and detonation velocity to gauge the explosive power of given explosive molecules. In calculating explosive performances in the Cheetah program, we assume that the explosive molecule has been packed to 97% of theoretical maximum density value. Since explosive performance is greatly dependent upon the density values, we calculate two different sets of C-J pressures and detonation velocities of 1-aminoimidazoles based on different sets of densities used, and summarize these results in Table 3.

The difference in predicted densities is reflected to predicted explosive performances as well. With an exception in **2c**, where MSEP density is lower than GAM density, all the explosive performances predicted with GAM densities are higher than those with MSEP densities. The average differences are 1.07 GPa in C-J pressure and 103 m/sec in detonation velocity. These differences are small, and do not make us confuse in understanding the explosive nature of 1-aminoimidazole derivatives. Candidate **1** without any nitro group is forecasted to have explosive performance, which is

Table 3. Predicted C-J pressure (GPa) and detonation velocities (m/sec) of 1-aminonitroimidazole derivatives

Compounds	Based on GAM density		Bases on MSEP density	
	C-J pressure	Detonation velocity	C-J pressure	Detonation velocity
1	11.37	6790	12.97	6908
2a	17.59	6880	17.98	6928
2b	17.52	6870	19.73	7133
2c	17.46	6862	16.43	6728
3a	28.22	8215	29.29	8310
3b	28.22	8216	28.26	8219
3c	28.60	8251	29.48	8329
4	37.39	9251	38.37	9335

relatively low to be used in military explosives. Adding one nitro group to **1** increases explosive performance slightly. On the other hand, adding two nitro groups to **1** causes a substantial increase in explosive performances. Detonation velocities of **3a** to **3c** are predicted to be 8200-8300 m/sec, and C-J pressures of **3a** to **3c** are predicted to be 28-29 GPa. These explosive performances are comparable or slightly better than some of insensitive explosive molecules in military application. However, they are still lower than those of high power explosive molecules. Of course, the most powerful explosive molecule in this series is **4** with three nitro groups. The predicted explosive performances of **4** are about 9300 m/sec in detonation velocity, and 38 GPa in C-J pressure. These performances are quite close to those of HMX, which is one of highly powerful explosive molecules in current military application. We can also notice that the predicted explosive performances of different isomers in a series of **2** and **3** are almost the same. According to our theoretical prediction, 1-aminoimidazole derivatives with two or three nitro groups appear to be an attractive candidate for new energetic fillers in warheads and ammunitions.

Impact Sensitivity. In contrast to explosive performance, safety nature of explosive molecules is known to be very difficult to predict in a reasonable fashion. Impact sensitivity is probably one of the most important features to characterize the safety nature of explosive molecules because many accidents in working places have a relation with inadvertent impacts to explosives. The results are shown in Table 4. The impact sensitivities in a series of 1-aminoimidazole derivatives become more sensitive as more nitro groups are introduced. Parental and mononitrated 1-aminoimidzoles are quite insensitive. The impact sensitivities represented as $H_{50\%}$ are 325.5 cm, and 244.1 cm, respectively. The impact sensitivity appears to get increased suddenly when the second nitro group is introduced into the imidazole ring. $H_{50\%}$ value of dinitrated isomers, **3a** to **3c**, is 88.3 cm, which is still considered as insensitive among military explosive molecules used as secondary explosives. Full nitrated 1-aminoimidazole, **4**, is predicted to be quite sensitive. Its impact sensitivity is close to those of RDX and HMX. As GAM, our current neural network scheme also has a shortcoming that it cannot differentiate impact sensitivities of

Table 4. Impact sensitivities ($H_{50\%,cm}$)[a] of 1-aminonitroimidazole derivatives predicted with a neural network scheme

Compounds	Impact sensitivity
1	325.5
2a	244.1
2b	244.1
2c	244.1
3a	88.3
3b	88.3
3c	88.3
4	28.6

[a]Unit in cm. The weight of drop hammer used was 2.5 kg.

structural isomers.

Two-Dimensional Plot between Performance and Sensitivity. It is very difficult for one to judge the usefulness of new explosive molecules by considering either explosive performance or sensitivity nature alone. We believe that the usefulness of new explosive candidates should be judged by a combination of explosive performance and sensitivity nature, although it may depend heavily upon the need of the users. We have devised a novel two-dimensional plot between explosive performance and impact sensitivity. Explosive performance, which is represented by either C-J pressure or detonation velocity, is displayed in the X axis, and impact sensitivity as a logarithm scale is presented in the Y axis. In this two-dimensional plot, we make spots of explosive molecules often used in current military technologies like RDX, HMX, TNT, and others. According to the spots of CL-20, HMX, and RDX, all of which have high power, but are relatively sensitive, they reside in the lower right corner of the plot. On the other hand, the spots of TATB and NTO, which are insensitive, but are less powerful, they form a region in the upper side of the plot. Thus, we are able to draw a curve through insensitive explosives to the ones with high power by connecting these explosive molecules. This curve may represent a current technical boundary, which new explosive molecule candidate should tackle to surpass in terms of explosive performance and sensitivity. The good candidate molecules should reside close to this curve, or even surpass this curve toward right upper side, the region of insensitive high explosive molecules. If a new candidate molecule poses in the left side of the curve, particularly in the left lower corner, it is not a good candidate, and should be screened out in an earlier stage. Besides explosive performance and sensitivity, we know that there are other numerous chemical and explosive features considered in finding a good explosive molecule. Thus, only good positioning in this two-dimensional plot may not ensure that the new candidate is a good one. However, it is certain that the new candidate molecule should be removed early, if it is predicted to be in a poor position in this two-dimensional plot.

Figure 6 displays the status of 1-aminoimidazole derivatives. In two plots presented by either C-J pressure or detonation velocity, both plots are almost identical. Mononitration of **1** rarely moves the spots from original position.

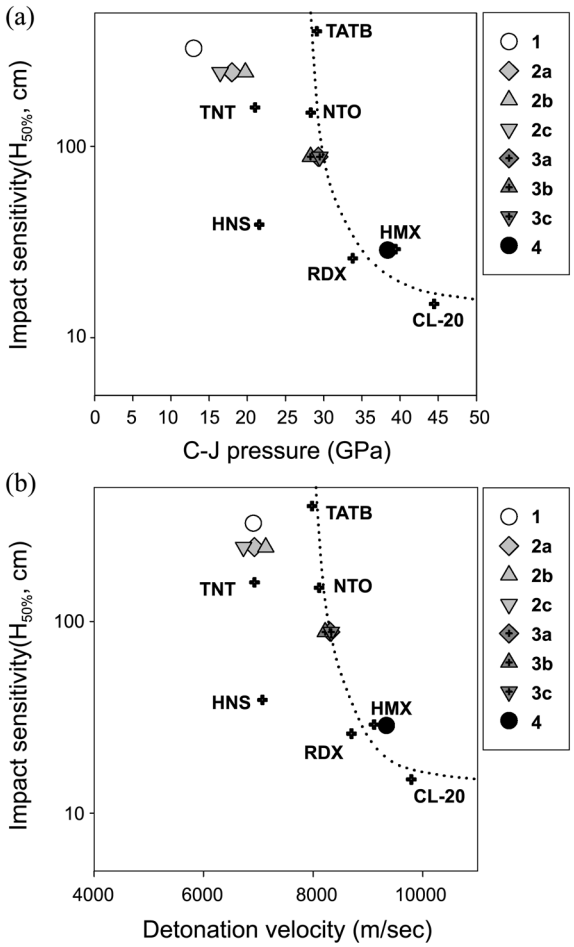


Figure 6. Two-dimensional plots between explosive performance and impact sensitivity. Explosive performance is represented by either C-J pressure (a) or detonation velocity (b).

However, dinitration of **1** shifts the spots substantially in the plot, and makes to reside on the curve in between NTO and RDX. Dinitrated isomers appear to be slightly more sensitive than NTO, but may be almost the same explosive performance with NTO. Thus, considering by the position in the two-dimensional plot, dinitrated isomers, **3a** to **3c**, may find their identity as 'insensitive explosive molecules' with similar explosive properties of NTO. The trinitratated product, **4**, appears to slightly surpass the curve toward the right side. This may tell us that **4** has excellent explosive properties when successfully synthesized. Its explosive properties are predicted to be quite close to those of HMX.

Conclusion

We have predicted various molecular and explosive properties of seven 1-aminoimidazole derivatives. Conformational preference of the 1-amino group attached to imidazole ring changed dramatically due to the presence of adjacent nitro groups. Strong hydrogen bonding between adjacent amino and nitro groups governs the conformational preference and the most stable molecular structure of 1-aminoimidazole derivatives. All the chemical and explosive properties have

been obtained at the global minimum in the conformational potential surface. Densities have been estimated by using two different methods; GAM and MSEP. Heats of formation in the solid state have been predicted by following the Politzer's scheme utilized BP86/6-31G** calculations. Explosive performances, i.e. C-J pressure and detonation velocity, have been calculated at the Cheetah program with the predicted densities and heats of formation. Impact sensitivities have been predicted by using artificial neural network scheme, which is knowledge based method. We have devised a two-dimensional plot between explosive performance and impact sensitivity to judge the usefulness of new candidate molecule in terms of explosive performance and sensitivity. Based on the positions in this two-dimensional plot, explosive properties of the dinitro products, **3a** to **3c**, appears to be in a similar position with NTO, a typical insensitive explosive molecule. Trinitro product, **4**, appears to have explosive properties close to HMX, a well-known highly powerful explosive molecule.

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