PI Index: A New Quantitative Scale for Screening Insensitive High Energy Density Materials

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A great deal of effort has been given to develop better insensitive high energy density materials (IHEDMs) to be used in explosives, propellants, and pyrotechnics.[1,2] One of difficulties encountered in deriving excellent IHEDMs was that some IHEDM candidates that had great power were generally quite sensitive to deal with, while IHEDM candidates that appeared to be significantly insensitive were not so great in explosive power. A schematic two-dimensional plot between explosive power and insensitivity shown in Fig. 1 illustrated this trend well. As shown in Fig. 1, most of high energy molecules currently used lay near the lines drawn from the upper left side to down right side. Those molecules resided in the area of the lower right side had high power, but were sensitive. On the other hand, those stayed in the region of the upper left side were insensitive, but less powerful. The broken curve shown in Fig. 1 represented a current technical boundary, which new IHEDM candidates had to tackle to surpass in terms of overall nature combining with explosive power and insensitivity. If a new IHEDM candidate surpassed this curve to move toward right upper side, it should be considered as a promising candidate being an IHEDM.

In order to observe a more realistic relationship between explosive power and insensitivity, we adapted detonation velocity to represent explosive power, and put it in the X-axis.[3] We utilized impact sensitivity to depict insensitivity, and placed it in the Y-axis. Impact sensitivity of the Y-axis was illustrated by a logarithm scale of impact energy, which converted from $H_{50\%}$ value obtained with drop impact sensitivity testing apparatus.[4] Some adjustment of scales of both axes was necessary to have a drawing balanced between explosive power and insensitivity, and to provide overall feature comprising both axes. In the X axis depicting detonation velocity, the minimum and maximum were chosen as 6.5 and 10.5 km/sec, respectively. In the Y axis representing impact sensitivity, the minimum and maximum were set to be 0.25 and 125 J, respectively. The $H_{50\%}$ values corresponding to the minimum and maximum of the Y axis were 1 cm to 5 m when 2.5 kg weight of drop hammer was used.[4] Each axis was divided linearly, and scaled from zero to ten. We called these new scales of X and Y axes as P and I indices, respectively. Thus, if a certain molecule was depicted in this plot, the X and Y coordinates in this plot were P and I indices

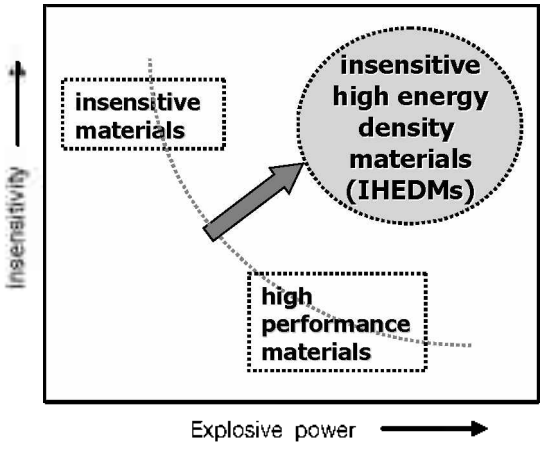

Figure 1. A schematic drawing between explosive power and insensitivity. The broken curve may represent a technical frontier in developing good IHEDMs.

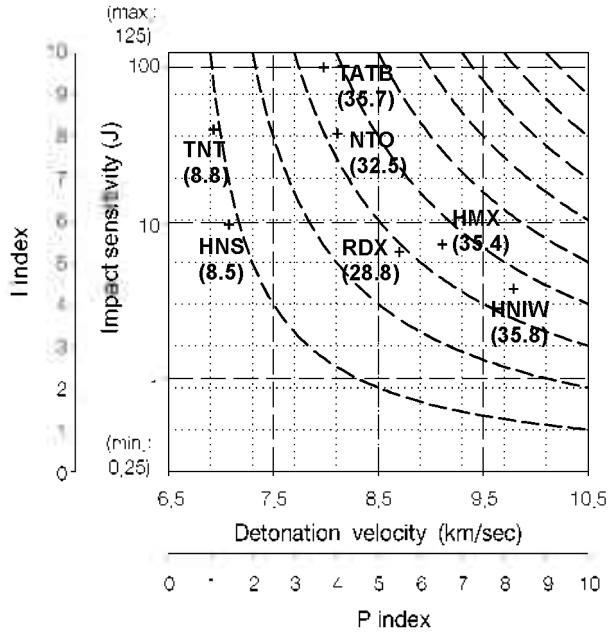

Figure 2. Two-dimensional plot for computing the PI index. In each axis, two different types of scales were shown; one in original and the other in scaled index. The PI indices of well-known explosive molecules were marked with crosshair. The values in the parentheses were the PI index for well-known explosive molecules. The chemical structures for well-known explosive molecules were shown in Fig. 3. The contour levels of PI index presented by dashed curves were from 10 in a step of 10, starting left side.

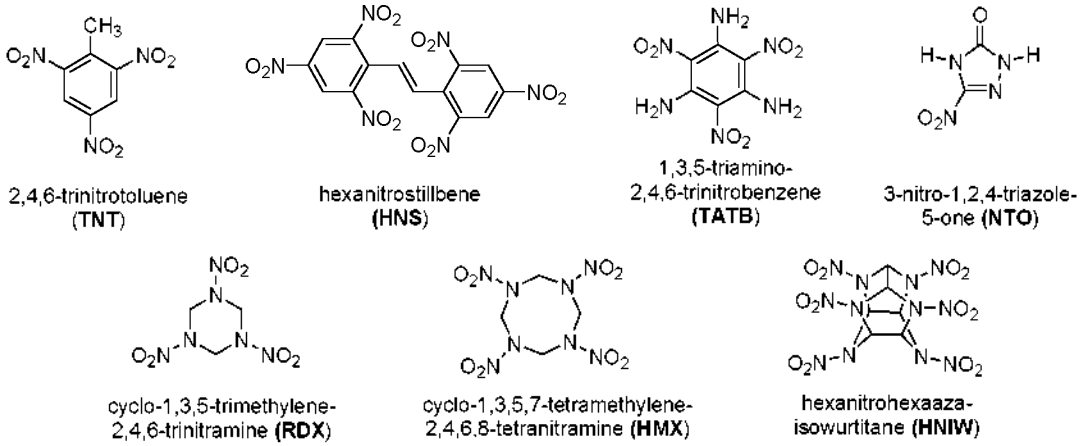

Figure 3. Chemical structures of well-known explosive molecules.

of that molecule. We proposed PI index, which was a product of P index and I index, as a quantitative scale to gauge the overall performance combining explosive power and insensitivity. The PI index was expressed as

$$\text{PI index} = (\text{P index}) \cdot (\text{I index})$$
$$= 9.26 \cdot (\text{d.v.} - 6.50) \cdot (\log(\text{i.e.}) - 0.60)$$

where d.v. is detonation velocity (unit: km/sec), and i.e. is the impact energy (unit: J) converted from $H_{50\%}$ value. The two-dimensional plot with these newly adjusted axes was shown in Fig. 2. We also made spots with explosive molecules used widely in current military applications in Fig. 2. As mentioned previously, the spots of HNIW, HMX, and RDX, all of which had high power, but were relatively sensitive, posed in the lower right corner of the plot. On the other hand, the spots of TATB and NTO, which were insensitive but less powerful, resided in the upper left side. Most of current explosive molecules and potential candidates should be included in this plot. Even if either P or I index of a certain molecule was not able to make spots in this region, the computed PI index of that molecule was able to comprehend its overall performance combining explosive power and insensitivity.

The PI indices of well-known explosive molecules were summarized in Table 1. The PI indices of TNT and HNS were 8.8 and 8.5, respectively. These two explosive molecules had a considerably poor grade as IHEDM when judged with their PI indices. The PI index of RDX was computed to be 28.8, while that of NTO was to be 32.5. Three explosive molecules, HMX, HNIW, and TATB, had the PI index values slightly better than 35. The PI indices of HMX and TATB were 35.4 and 35.7, respectively. HNIW had the PI index of 35.8, which was the highest value among these explosive molecules. These five molecules were found quite often as main ingredients in recent state-of-the-art explosive formulations. Thus, explosive molecules used in current military applications stayed near from 30 to 36, which probably represented a current technical boundary. This technical boundary was also shown as a broken line in a conceptual drawing of Fig. 1. If a

Table 1. Detonation velocities, impact sensitivities, and PI indices of well-known explosive molecules and new IHEDM candidates.

IHEDM	Detonation velocity[a]	Impact sensitivity[b]	PI index[c]
Well-known explosive molecules[d]			
TNT	6.93	40	8.8
HNS	7.08	9.8	8.5
TATB	7.98	100	35.7
NTO	8.11	37.5	32.5
RDX	8.70	6.5	28.8
HMX	9.11	7.3	35.4
HNIW	9.79	3.8	35.8
New IHEDM candidates[e]			
C01	9.49	19.9	52.6
C02	8.98	19.1	43.2
C03	9.74	4.4	37.2
C04	8.22	22.1	30.9
C05	7.56	75.7	24.4
C06	8.40	3.2	19.4

[a]Unit: km/sec [b]Unit: J [c]See the main text. [d]Values taken from experiments. etonation velocity and impact sensitivity were predicted by using ADD Method-1.

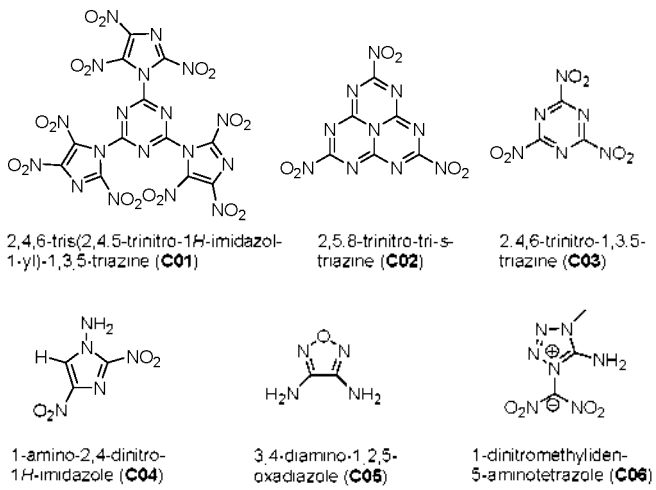

Figure 4. Chemical structures of new IHEDM candidates.

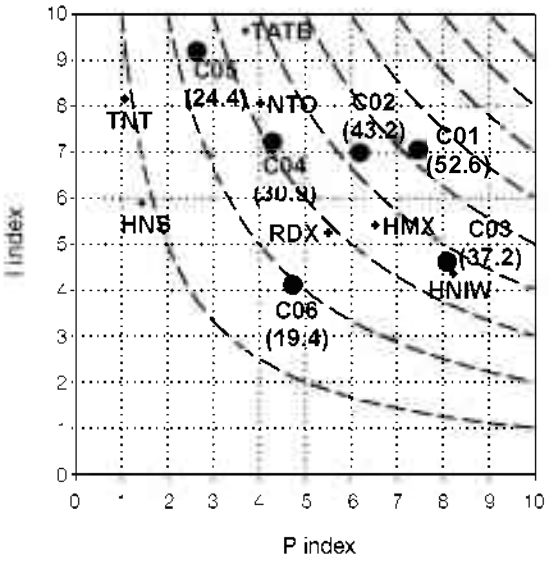

Figure 5. PI indices of new IHEDM candidates in the 2-D plot. For the levels of contour lines, see the caption of Fig. 2.

new IHEDM candidate had a PI index higher than 36, it ought to be considered to be a good one.[5] Of course, this PI index value was significantly changed due to the different setting of the minima and maxima in both axes. Different choice of the maximum and minimum of each axis prompted to have a new PI index value whose characteristics shifted toward either insensitive molecules or high power molecules. Adjusting the PI index value to be balanced between the explosive power and insensitivity was one the most important features in choosing the maxima and minima of both axes. We feel that the current setting of maxima and minima of both axes appeared to be appropriate.

We applied our newly proposed PI index to some IHEDM candidates in order to comprehend the usefulness of each candidate as IHEDM. Fig. 4 depicted chemical structures of six new IHEDM candidates. The common feature of these candidate molecules is aromatic nitrogen heterocycles with high nitrogen content. High nitrogen content by replacing carbon atoms to nitrogen atoms usually enhances the explosive power. Aromaticity generally enhances the insensitivity due to the delocalization of electrons. **C01** and **C03** are triazine derivatives, and **C02** is heptazine derivatives. Triazine and heptazine derivatives are considered as good basic skeletons to make good IHEDMs with introduction of more energetic groups.[6] To our knowledge, these candidate molecules haven't synthesized yet. **C04** is imidazole derivatives, which has been studied extensively as melt castable IHEDM to replace mediocre TNT.[7] **C05** is a derivative of furazan, and **C06** has a tetrazole moiety. Both candidates are also forecasted to be good IHEDMs.[8] All these detonation velocity and impact sensitivity of these IHEDM candidates were estimated following ADD Method-1, which was a theoretical procedure combining various computational methods including quantum mechanics, and knowledge based predictive schemes eventually to predict explosive power and impact sensitivity.[9] Detonation velocities and impact sensitivities of these candidate molecules were summarized in Table 1 along with experimental ones of well-known explosive molecules. The PI indices of these IHEDM candidates were shown in the two dimensional plot (See Fig. 5).

According to our predictive results with ADD Method-1, **C01** shows 9.49 km/sec of detonation velocity, and 19.9 J of impact sensitivity. The PI index was estimated to be 52.6, which was the best value among 6 candidates. The PI indices of **C02** and **C03** were estimated as 43.2 and 37.2, respectively. The PI indices of these candidate molecules were far better than those of well-known explosive molecules. Thus, we believe that three candidates, **C01**, **C02**, and **C03**, were indeed good candidates to be IHEDM. On the other hand, three other candidates, *i.e.* **C04**, **C05**, and **C06**, had relatively low PI index, and were forecasted not so good IHEDM candidates. However, it should be worthwhile to mention that the high PI index value may not ensure these compounds to surely be good IHEDMs. There were a number of other factors to be addressed including compatibility with other ingredients, processability with existing manufacturing processes, and long term storage stability. On the other hand, those compounds which had lower PI indices such as **C04**, **C05**, and **C06** should be dropped out early, if obtaining a good IHEDM was the main research target.

Conclusively, we proposed a novel quantitative scale, PI index, which would serve as a useful criterion for screening numerous candidates for novel IHEDM candidates. Since the PI index was the product of P and I indices, the scales of both P and I indices were carefully chosen to balance between explosive power and insensitivity. Thus, the new PI index was a useful barometer to comprehend overall performance in combining explosive power and insensitivity. In addition, since the PI index was easily formulated as simple equations, this new index was able to be implemented to logic gates in computational codes for screening IHEDMs. Combining the PI index with either P or I index may also provide a somewhat different screening concept for IHEDMs. For instance, high power explosive molecules were mainly screened by stressing P index among the candidate molecules screened with a certain lowest limit of the PI index. On the other hand, insensitive explosive molecules were also screened by imposing I index additionally. With the PI index, we were able to differentiate six different IHEDM candidates. According to our screening results, two triazine derivatives, **C01**, and **C03**, and a heptazine derivative, **C02**, were forecasted to be very good IHEDMs.

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