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A Trigonometric Approach to a Limiting Law on Detonation Velocity

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Abstract: Detonation velocity is an important characteristics of explosive compounds. Presently, to get some insight about the detonation velocity, a novel trigonometric model has been suggested first in 2-dimensional form and then extended to 3-dimension. In the 2D-form the detonation velocity is considered to be a function of the total energy and a newly defined "angle of detonation", Q, of an explosive molecule. The angle of detonation velocity is also shown to be a nonlinear function of the total energy. In the 3D-form another angle, Φ, affects the detonation velocity. Some regressed equations are obtained. It has been shown that Q, thus the detonation velocity asymptotically approaches to a constant value as the total energy increases in absolute value which has some direct relationship with the molecular weight of an explosive compound. It has been shown that tan Φ values correlate with density of explosives.

Introduction

Detonation velocity at which the detonation shock wave proceeds through an explosive charge is one of the important detonation characteristics [1]. The detonation velocity can be calculated by some elaborate computer codes having different level of sophistication [1-5], which enable one, especially in the design of novel explosives materials having good impact and friction sensitivities as well as high thermal stability, enhanced detonation properties etc. Also some empirical methods are to be cited which help along this line [6-10]. They are comparatively simple and faster methods than the computer codes mentioned. Numerous articles have been piled up in the literature concerning the detonation theory and/or kinetics of various explosives [11-20].

The works of Kamlet and coworkers [21-24], also Rothstein and Peterson [10] have to be mentioned related to detonation characteristics of explosives.

An empirical relation has been obtained between the detonation velocities and ^{15}N NMR chemical shift of nitrogen atoms in nitro groups of certain nitramine type explosives [25,26].

In some of detonation velocity calculations various quantum chemical methods of various levels of sophistication have been used [27-30], especially for the density calculations required in the Kamlet-Jacobs method of detonation velocity estimation which is based on the following equation.

$$D= 1.01 \; (NM^{½} \, Q^{1/2})^{1/2}(1+130\rho)$$

where ρ: density of a compound, N: moles of gaseous detonation products, M: average molecular weight of gaseous products , Q: chemical energy of detonation [21-24].

So far the detonation velocity has been interrelated to density, heat of formation, elemental composition, electric spark sensitivity and chemical energy of detonation. Density of an explosive molecule is considered to be one of the main factors affecting the detonation velocity [31]. Hence, of the greatest practical interest is crystalline density improvement either structurally or rheologically.

On the other hand, connections between the molecular structures of organic compounds and their physicochemical properties are interesting field of chemistry. The structure-property or structure- activity studies involve sets of compounds for which the property of interest are analyzed by representing their molecular structures with calculated molecular numerical descriptors and then developing certain regression models which relate the descriptors to the property/activity [32]. Topological indices of various types are used in such studies [32-38]. The topological indices are certain numbers associated with constitutional formulas by mathematical operations on the graphs representing structures [32,33].

Some properties of molecules root from the gross topology of the structures which includes the number of bonds (edges of the molecular graph), the number of atoms (vertices of the molecular graph), etc. Whereas, certain properties of molecules are interrelated to their fine topology [34-36]. These descriptors are obtained by means of elaborate mathematical/quantum chemical approaches. In some cases angles play the role of topological descriptors [36-38]. The angle of detonation velocity defined presently is such a descriptor of topological type. It is a function of a topological component; the total energy. By the help of descriptors of fine topology, some hidden functional relationships between structures and properties/ activities of molecules become evident [34-36].

In two recently developed methods, based on quantum chemical calculations, detonation velocity has been shown to be a linear function of E/M ratio, where E and M are the total energy and molecular weight of the explosive material, respectively [39,40].

There exist various theories of detonation in the literature such as the shock-wave and detonation-wave theories [41]. However, the concept is still hot theoretically. In the present study, a novel trigonometric model (related to molecular topology) has been suggested for the detonation velocity of the explosives and it has been exploited to unveil certain hidden properties and to get some insight of the concept.

Theory

Let an explosive compound has the detonation velocity of D and total energy of E. Furthermore arrange the units of D and E properly such that $D/E \leq 1$. Then, define an angle Q (angle of detonation velocity) such that

$$Q = \arccos(D/E) \qquad (1)$$

Consequently,

$$D = E\cos Q \qquad (2)$$

According to this model, the detonation velocity is the projection of the total energy on the D-axis (see Figure 1). Then the following equations hold.

$$\frac{\partial D}{\partial Q} = -E \sin Q \qquad (3)$$

$$\frac{\partial^2 D}{\partial Q^2} = -E \cos Q \qquad (4)$$

From eqs. 2 and 4 one gets

$$\frac{\partial^2 D}{\partial Q^2} = -D \qquad (5)$$

Squaring both sides of eqs. 2 and 3 and summing up side by side, eq. 6 is obtained.

$$D^2 + \left(\frac{\partial D}{\partial Q}\right)^2 \equiv E^2 \qquad (6)$$

This differential equation (eq. 6) is an equation of a circle on the plane of $(D, \partial D/\partial Q)$ axes and having radius of E.

According to the present 2-dimensional model, different explosives are characterized with certain cocentric circles having different radii, each of which is E of a specific explosive (see Figure 1). From the figure it is evident that D is directly proportional with the radius ($r = |E|$) but decreases as Q increases (however see below parts for further details about Q).

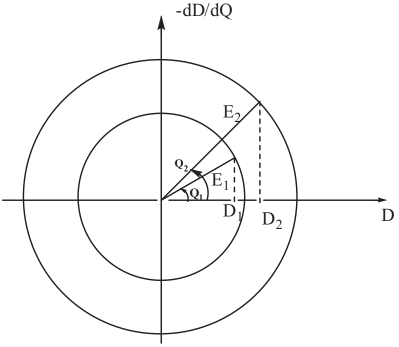

Figure 1. Geometrical meaning of eq. 2 and identity 6.

Method

In the present study, the initial geometry optimizations have been achieved by using MM2 method (molecular mechanics), followed by the semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [42,43] at the restricted level [44,45] . Then, the STO, RHF and Density Functional Theory (DFT) [46,47] type quantum chemical calculations have been consecutively performed for the geometry optimizations (finally at the level of UB3LYP/6-31G(d)) to obtain energetically the most favorable structures of the species presently considered. The exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [47,48]. The functional correlation term of B3LYP consists of Vosko, Wilk, Nusair (VWN3) local correlation [49] and Lee, Yang, Parr (LYP) correlation functional [50].

For each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding geometry optimizations). Note that the normal mode analysis for each structure yielded no imaginary frequencies for the $3N$-6 vibrational degrees of freedom, where N for the vibrational analysis is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths were thoroughly searched in order to find out whether any bond cleavage occurred during the geometry optimization process. The geometry optimizations and the vibrational analysis computations were performed by using the Spartan 06 package program [51].

Results and discussion

According to the present model, detonation velocity is dictated by the total energy and the angle of detonation velocity simultaneously. Figures 2 and 3 show the detonation velocity versus total energy and the detonation velocity angle (Q) versus detonation velocity plots, respectively. The figures display that the dependence of dependent variable (detonation velocity) to each independent variable seems to be rather chaotic although some explosives fall on the same line or curve.

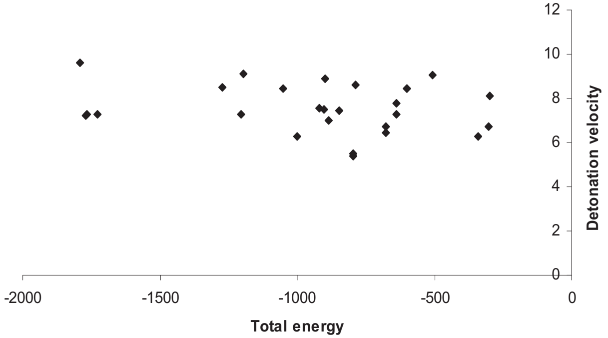

Figure 2. The detonation velocity (km/s) versus total energy (au) plot.

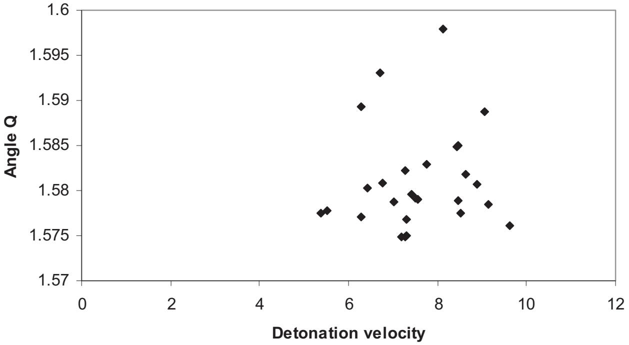

Figure 3. The detonation velocity angle (Q) (radian) versus detonation velocity (km/s) plot.

1. The dependence of angle of detonation velocity on E

Although the dependence of detonation velocity separately on E or Q is not expressible simply, the regression analysis of the data presented in Table 1 reveals that the relation Q = f(E) can be approximated as an arm of a hyperbola (see Figure 4) which is in the form of

$$Q = \frac{A}{E} + B \qquad (7)$$

having A: -7.1222157, B: 1.57128335, with R^2 (the coefficient of determination [54,55]) : 0.92 , the correlation coefficient: 0.95, DF (degrees of freedom): 25, χ^2:25.

The slope is

$$\frac{dQ}{dE} = -\frac{7.122}{E^2} \qquad (8)$$

On the other hand, the differential of D (see eq. 2 for D) is given by eq. 9.

$$dD = \cos Q dE - E \sin Q dQ \qquad (9)$$

which can be converted to

$$dD = \cos Q \left[dE - E \tan Q dQ \right] \qquad (10)$$

Since Q is in the second quadrant (see Table 1), $-E \tan Q \geq 1$, which means the effect of small changes in Q is more influential on dD than the small changes of E. Q (or cos Q) is related to fine topology of the explosives. Although, Q is the critical component of D (small changes in Q or cos Q causes considerable variation in D) it is rather insensitive to topological changes. Q varies in a small range (see Table 1).

The graph indicates that explosives having low (in absolute value) E values are characterized with relatively big values of Q (like DIGEN, MNA and DMNA) compared to ones possessing high E values (HNIW, HNS and DPM). Note that DIGEN, MNA and DMNA are low molecular weight acyclic nitramines whereas HNIW has a cage nitramine structure, HNS and DPM are aromatic nitro compounds and they all have high molecular weight. Inspection of Table 1 indicates that generally small nitramines have greater Q than the other explosives have but as the molecular weight of nitramines increase, their Q values become comparable to nonnitramine type explosives. In Figure 4 those explosives having big and small

Table 1. Some data for the explosives considered presently.

Name	MW(g)	Corrected total energy (au)	D (km/s) [52,53]	Q (rad)
DMNA	90	-339.5607	6.29	1.5893
EDNA	150	-599.3723	8.42	1.5848
MNA	76	-300.2773	6.7	1.5931
OCPX	164	-638.6573	7.28	1.5821
DMEDNA	178	-677.9375	6.42	1.5802
TNB	213	-845.6280	7.42	1.5795
1,8-DNN	218	-794.7184	5.38	1.5775
1,5-DNN	218	-794.7266	5.52	1.5777

TENN	308	-1203.6771	7.3	1.5768
TNT	227	-884.9094	7.02	1.5787
PAM	228	-900.9806	7.5	1.5791
TNN	263	-999.2030	6.27	1.5770
PA	229	-920.8343	7.57	1.5790
DPM	438	-1729.3358	7.29	1.5750
DPE	452	-1768.6195	7.2	1.5748
DIGEN	74	-299.0642	8.12	1.5979
HNS	450	-1767.4194	7.27	1.5749
Tetragen	148	-598.1450	8.46	1.5849
TNAZ	192	-786.6000	8.62	1.5817
Table 1 continued.				
CPX	162	-637.4639	7.76	1.5829
DNDC	176	-676.7560	6.75	1.5807
RDX	222	-897.2650	8.89	1.5807
TEX	274	-1052.5950	8.47	1.5788
HNIW	438	-1790.9610	9.62	1.5761
HMX	296	-1196.3540	9.13	1.5784
TNAD	296	-1273.7220	8.52	1.5774
MDN	121	-504.7299	9.05	1.5887

Q values are located at the extreme right and left side of the curve, respectively. As seen in the figure, a large group of explosives are located at the middle region of the curve. Since the slope (eq. 8) is inversely related to E^2, as E increases variation of Q becomes less and less. The practical consequence of this is that for explosives of high molecular weight, D does not change much. For instance DPM (MW: 438 g) and HNS (MW: 450) have D of 7.29 and 7.27 km/s, respectively. HNIW has detonation velocity of 9.62 km/s and this high value can be attributable to its cage structure resulting in high density. Note that generally explosives with high molecular weight have high E values (in absolute value). So as E increases the slope approaches to zero from the negative side. This means that as the structures of explosives get bigger and bigger, their angle Q values approach to a constant value, 1.57128 (radian), namely 90 degrees. Inserting this limiting value of Q into eq. 2, (D=E cos Q), reveals that for those systems D approaches to zero. Hence, for those explosives having Q values comparable and close to the limiting value, D is dictated mainly by their E values.

Figure 5 shows the dependence of Q on molecular weight (M). It is evident from the figure that generally Q decreases as M gets bigger and bigger. Note that Q is a function of E as well. So the points off-the line in Figure 4 and Figure 5 below are the ones affected greatly by the other independent variable (M and E, respectively). A regression analysis yields,

$$Q = \frac{1.8277}{M} + 1.5711 \qquad (11)$$

With R^2=0.95. A similar dependence also exists between Q and M^2.

$$Q = \frac{113.3126}{M^2} + 1.5767 \qquad (12)$$

Which has R^2: 0.89 .

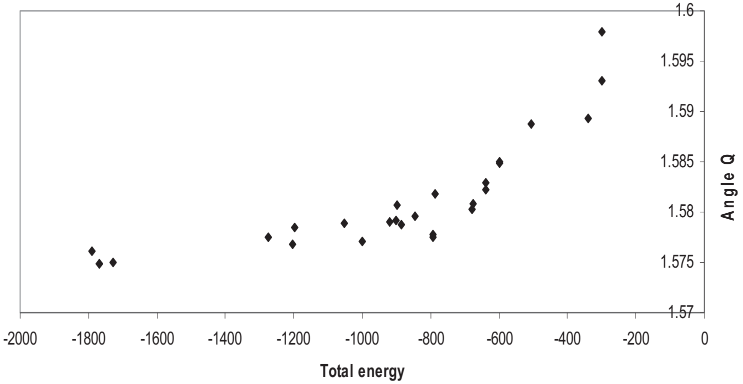

Figure 4. Variation of angle of detonation (radian) as a function of the total energy (au).

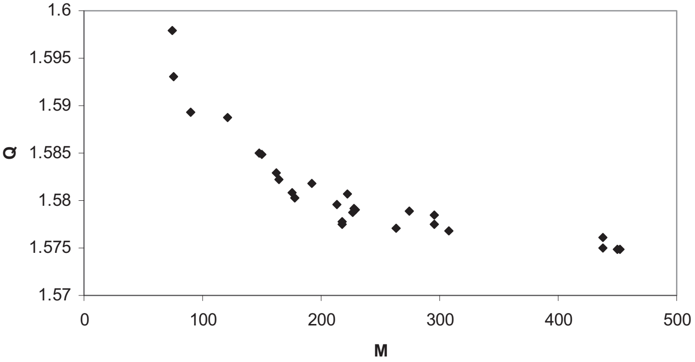

Figure 5. Variation of angle of detonation (radian) as a function of the molecular weight (g).

On the other hand, Q=f(M,E) function has the form of

$$Q = 1.5725 - \frac{5.4462}{E} + \frac{27.8920}{M^2} \qquad (13)$$

which is characterized with R^2: 0.92.

So as E becomes more and more negative or M gets bigger and bigger, Q decreases. Note that as Q gets smaller, cos Q thus D decreases. This conclusion is the limiting law which can be stated as; D decreases with increasing molecular weight, because E also increases in absolute value as M increases.

On the other hand, since Q=f(E) function (eq. 7) is obtained by regression analysis, being on the safe side, it is better to say D approaches to a constant value (rather than the mathematically predicted value of zero) as E gets bigger and bigger. In this article the detonation velocity is expressed as the function of the total energy (E) and the angle of detonation velocity (Q) . Although, D=E cos Q relation is nonlinear and indeed Q is a function of E and M (Figures 4 and 5), as it has been shown, the domain of Q is very narrow (1,5748-1,5931 rad). This limiting law is an important result to be considered while designing structures of novel explosive molecules not existing yet.

2. Adaptation of the model to 3-dimensional space.

Now consider Figure 6. The base circumference of the upside down cone of the figure stands for one of the circles of Figure 1. Namely, the radius of the base is equal to absolute value of E.

As proved in previous sections, Q spans into the second quadrant. Additionally, another angle Φ is defined as

$$\tan\Phi = \frac{|E|}{M} \qquad (14)$$

where E is the total energy (in au) so far considered and M is the molecular weight (MW) of a particular explosive in grams. Then,

$$|E| = M\tan\Phi \qquad (15)$$

Combining eqs. 2 and 15 one gets,

$$D = |M\tan\Phi\cos Q| \qquad (16)$$

Note that angles Φ and Q are independent from each other even though both are functions (besides others) of a common structure dependent variable E. Table 2 shows the E/M ratios of the explosives presently considered. As seen there, the values are quite close to each other. The smallest and the greatest ones in absolute value are 3.64 and 4.16 au/g, respectively. The corresponding Φ values are then 1.30 rad (74.63 degrees) and 1.33 rad (76.48 degrees). Like Q, angle Φ varies in a rather small range for the compounds considered. The D versus E/M relation, is expressible as

$$D = -7.83261(E/M) - 23.67035 \qquad (17)$$

having R^2: 0.85 (correlation coefficient: 0.92) [40]. Note that E/M ratio is a negative but D is a positive quantity. So to get a compromise the ratio absolutely has to be greater than ca.3.

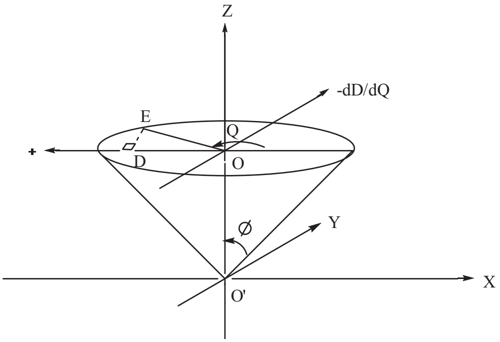

Figure 6. The geometry involved in 3D- form of the model.

Figure 7 shows the most general forms of the model for two different (a) and two isomeric explosives (b), respectively. Generally different explosives are characterized with different Φ and Q values because their molecular weights and total energies are different. For isomeric explosives their molecular weights are equal, so the cones in Figure 7b have the same height, which also should be the valid case for various conformers or (as a conjecture) different crystalline forms of an explosive.

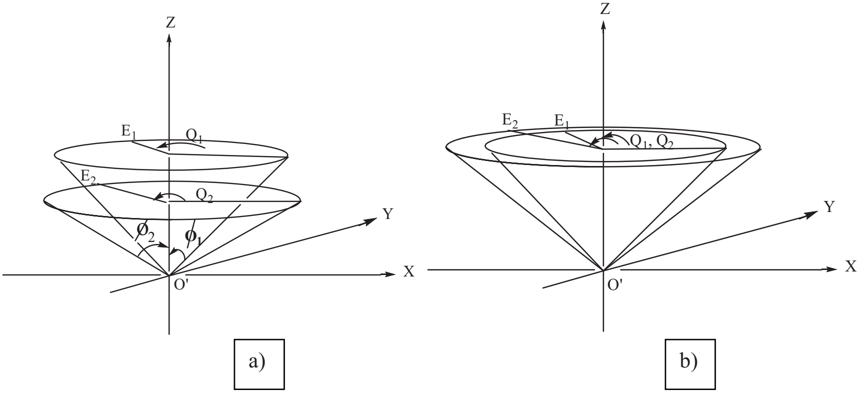

Figure 7. The most general form of the model, a) two different explosives, b) two isomeric explosives.

3. A curious relation between the density and tan Φ of an explosive

Density is an important characteristics of explosives. By changing the loading density (which is the ratio between the weight of an explosive cartridge and its volume [41]) performance of an ammunition can be changed. The loading density is of course related to the theoretical maximum density (TMD) of the charging explosive [56].

Raising the density by pressing or casting improves brisance and detonation velocity [41]. Low density explosives in contrast produce a milder thrust effect. Loading density is a very important parameter, both in propellant powders and brisant explosives. On the other hand, molecular density is as important as loading density. Density has been termed “the primary physical parameter in detonation performance [57]. An increase in the solid-state density is hence desirable in terms of the amount of material that can be packed into a volume limited warhead or propulsion configuration. Due to that, a great deal of effort accumulates on novel energetic materials having high density.

The group or volume additivity methods are the simplest, earliest and most widely used ones for the density prediction purpose. Basically, these methods base on summing up volume contributions of atoms or functional groups to get the molar volume. However, these methods have the drawback that they cannot readily account for either the isomerization and conformational changes of molecules or crystal packing efficiency. Namely, the same density value is produced for various isomers or conformations of a particular compound. Also, the crystal density variations due to crystal polymorphism is neglected.

In the literature there exist some surprisingly accurate methods of estimating the theoretical maximum density (TMD). For instance, Eremenko found that TMD could be estimated within the range of 2-3% error by a simple linear relationship (eq. 18) between the density and the hydrogen content of substituted organic molecules [58].

$$\rho(\mathrm{TMD}) = a_i - k_i H \qquad (18)$$

where ρ(TMD) is the theoretical maximum density, a_i and k_i are certain constants, H is the percent by weight hydrogen in the explosive molecule. However, the method depends on H being greater than zero and less than around 6% ($0 < H < 6\%$) [56]. Moreover, a_i and k_i vary from one group of explosives (such as liquid aliphatics) to other (e. g., solid, noncyclic aliphatic compounds having one nitro group), thus its applicability is highly limited. Keshavarz suggested an empirical method for the prediction of densities of various types of explosives based on their elemental compositions [59].

Table 2 shows the $|E/M|$ ratios and densities of some explosives. Whereas Figure 8 is the plot of density (d) vs. $|E/M|$ values which equals to tan Φ (eq. 14). This relationship so far has been unnoticed in the literature. As seen from Figure 8, density increases with the above mentioned ratio that is it increases with tan Φ .

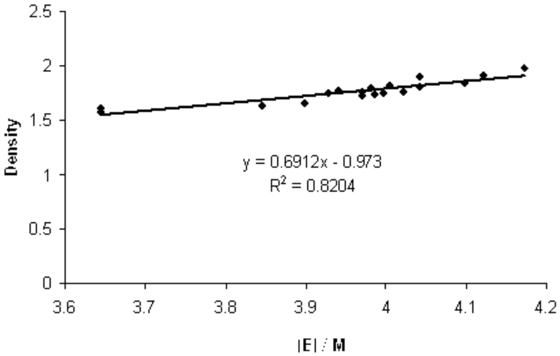

Figure 8. The relation between density (g/cm^3) and absolute value of E/M (au/g) ratio.

The regression line is given as

$$d = 0.691\left|\frac{E}{M}\right| - 0.973 \qquad (19)$$

having R^2 value of 0.82 (correlation coefficient: 0.92). According to eq. 19, for d (density) being a positive quantity $\left|\frac{E}{M}\right|$ ratio has to be greater than ca. 1.40. In Table 2, the explosive having the lowest density is DMEDNA possessing density value of 1.49 g/cm^3.

Table 2. MW, E/M and density values of some explosives.

Name	MW (g)	E/M (au/g)	Density g/cm^3 [30, 60, 61]
EDNA	150	-3.99582	1.71
OCPX	164	-3.89425	1.56
DMEDNA	178	-3.80864	1.49
TNB	213	-3.97008	1.76
1,8-DNN	218	-3.6455	1.57
1,5-DNN	218	-3.64553	1.61
TNT	227	-3.89828	1.65

PAM	228	-3.95167	1.76
PA	229	-4.02111	1.76
DIGEN	74	-4.04141	1.53
HNS	450	-3.9276	1.79
Tetragen	148	-4.04152	1.73
TNAZ	192	-4.09688	1.84
DNDC	176	-3.8452	1.63
RDX	222	-4.04173	1.81
TEX	274	-3.84159	1.99
HNIW	438	-4.08895	2.04
HMX	296	-4.04174	1.91
TNAD	296	-4.30311	1.79

Conclusion

The present trigonometric model enables one to understand some obscure facts involved behind the velocity of detonation. The most important of them is the ”limiting law of detonation velocity” which states that for a series of explosives, after a certain optimum value of the total energy (E), detonation velocity decreases asymptotically to a constant value. This statement, as a mathematical conjecture, should also hold for the size of an explosive (because E is an implicit function of molecular weight) and indeed the case. Therefore, instead of increasing the size of the explosive molecule by adding more explosophoric groups to a base structure, it is better to design more energetic base structures keeping the molecular weight small but having high maximum density. The survey of the literature implies that this line of research has been intuitively (or by trial and error) followed by some groups in the absence of any theoretical analysis as deep as the present one.

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List of abbreviations for the explosives considered.

Abbreviation	Name
CPX	1,3-Dinitroimidazolidine
DMNA	2-Nitro-2-azapropane
1,5-DNN	1,5-Dinitronaphthalene
1,8-DNN	1,8-Dinitronaphthalene
DIGEN	1-Nitro-1-azaethylene
DMEDNA	2,5-Dinitro-2,5-diazahexane
DNDC	1,4-Dinitropiperazine
DPE	1,3,5-Trinitro-2-[2-(2,4,6-trinitrophenyl)ethyl]benzene
DPM	1,3,5-Trinitro-2-(2,4,6-trinitrobenzyl)benzene
EDNA	1,4-Dinitro-1,4-diazabutane
HMX	1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (octogen)
HNIW	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
HNS	1,3,5-Trinitro-2-[(*E*)-2-(2,4,6-trinitrophenyl)vinyl]benzene
MDN	1,1-Dinitro-1-azaethane
MNA	1-Nitro-1-azaethane
OCPX	2,4-Dinitro-2,4-diazapentane
PA	2,4,6-Trinitrophenol
PAM	2,4,6-Trinitroaniline
RDX	1,3,5-Trinitro-1,3,5-triazinane (Hexogen)
TENN	1,4,5,8-Tetranitronaphthalene
TETROGEN	1,3-Dinitro-1,3-diazetidine
TEX	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane
TNAD	*trans*-1,4,5,8-Tetranitrodecahydro-pyrazino[2,3-*b*] pyrazine
TNAZ	1,3,3-Trinitroazetidine
TNB	1,3,5-Trinitrobenzene
TNN	1,4,5-Trinitronaphthalene
TNT	2,4,6-Trinitrotoluene