Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Encoding hexanitrobenzene (HNB) and 1,3,5-triamino-2,4,6-trinitrobenenze (TATB) as two distinctive energetic nitrobenzene compounds by machine learning

Rong Wang, † Jian Liu, † Xudong He, † Weiyu Xie, *† and Chaoyang Zhang*†,‡

† *Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), P. O. Box 919-311, Mianyang, Sichuan 621900, China.*

‡ *Beijing Computational Science Research Center, Beijing 100048, China.*

Supplementary information

Table of contents

S1: HOF calculations for a solid.

(A) HOF calculations of gaseous molecules

As for the isodesmic reaction, one example of the isodesmic reaction for TATB (compound A) is illustrated in Figure S1. The heat of reaction ΔH_{298} at 298 K was calculated on the level of B3LYP method/6-31g(d) with following eq 1:

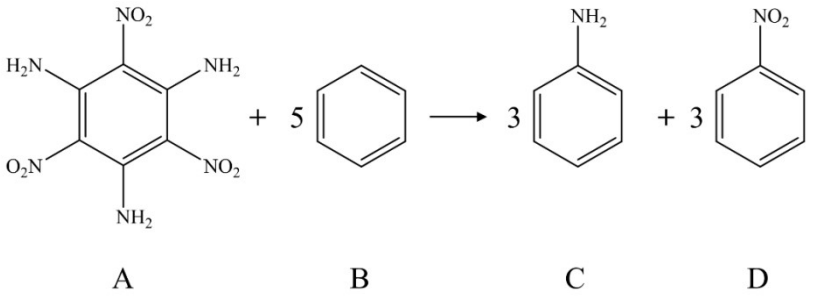


Figure S1. Isodesmic reaction designed for calculating HOF of TATB.

$$\Delta H_{298} = \Delta H_{f,\ P} - \Delta H_{f,\ R} \qquad (1)$$

where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ represent the HOFs of reactants and products at 298 K, respectively. For compounds in the isodesmic reactions with available data, they were directly adopted, as shown in Table S1.

Table S1. The HOFs of references compounds from CRC handbook. The unit of ΔH^{g}_{fExp} is kJ/mol.

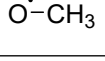
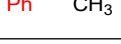
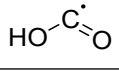
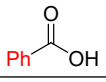
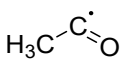
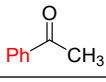
Name	Molecular structural formula	ΔH^{g}_{fExp}
Benzene	PhH	82.9
Nitrobenzene	$PhNO_2$	68.5
Phenol	PhOH	-96.4
Tolune	$PhCH_3$	50.5
Benzoic acid	PhCOOH	-294.0
Anisole	$PhOCH_3$	-67.9
Aniline	$PhNH_2$	87.5
Acetophenone	$PhCOCH_3$	-86.7
Benzaldehyde	PhCHO	-36.7
Benzonitrile	PhCN	215.7
Benzamide	$PhCONH_2$	-100.9
Ethoxybenzene	$PhOCH_2CH_3$	-101.6
Ethylbenzene	$PhCH_2CH_3$	29.9

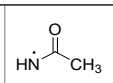
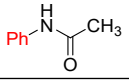
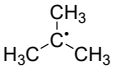
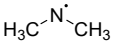
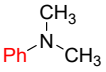
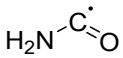
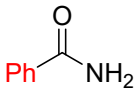
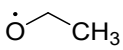
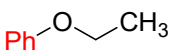
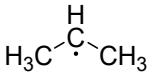
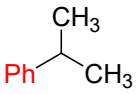
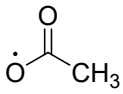
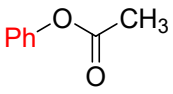
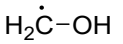
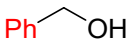
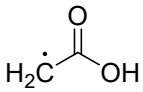
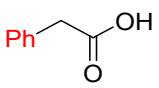
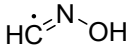
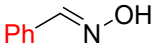
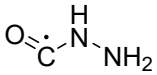
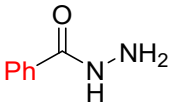
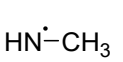
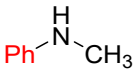
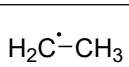
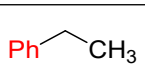
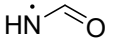
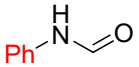
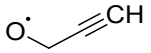
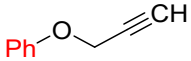
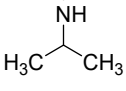
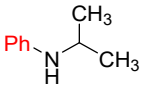
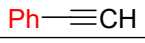
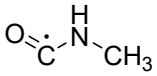
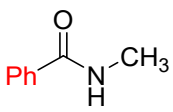
For the compounds in the isodesmic reactions without available experimental HOFs, the atomization scheme was employed with calculations on the G3 level to predict their HOFs, as shown in Table S2. By means of the atomization scheme, the standard HOF of a molecule ($^{\Delta H^{g}_{f}}$) can be calculated by eq 2.

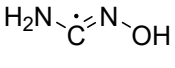
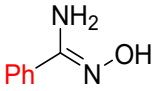
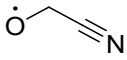
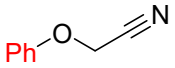
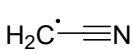
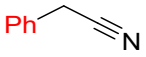
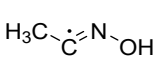
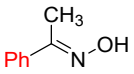
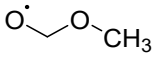
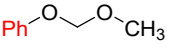
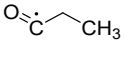
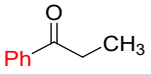
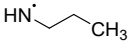
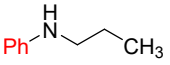
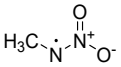
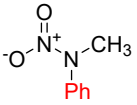
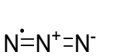
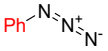
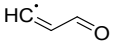
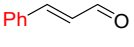
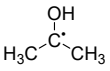
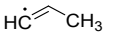
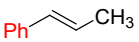
$$\Delta H_f^g = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta E_{ZPE} + \Delta E_T + \Delta nRT \quad (2)$$

where $^{\Delta E_0}$ means the change in total energy between the products and reactants at 0 K; $^{\Delta E_{ZPE}}$ is the value of difference between the zero-point energies of the products and reactants at 0 K; $^{\Delta E_T}$ is the thermal correction from 0 to 298 K. The $^{\Delta(PV)}$ value means the ^{PV} work term and equals $^{\Delta nRT}$ for the reactions of an ideal gas. For the isodesmic reaction in this work, $^{\Delta n = 0}$, so $^{\Delta(PV) = 0}$. From Table S2, we can confirmed that the largest error is only 6.9 kJ/mol, showing the high reliability of the G3 method.

Table S2. $^{\Delta H^{g}_{f}}$ of mono-substituted benzene molecules used for designing isodesmic reactions. $^{\Delta H^{g}_{fExp}}$ and $^{\Delta H^{s}_{fG3}}$ denote the $^{\Delta H^{g}_{f}}$ derived from experimental measurements and G3 calculations in kJ/mol, respectively.

Functional group			Benzene based compound				
Name	**Structure**	**Symbol**	**Name**	**Structure**	**ΔH^{s}_{fExp}**	**ΔH^{s}_{fG3}**	**Error**
hydro	H·	-H	benzene	Ph–H	82.9	87.3	4.4
nitro		-NO_2	nitrobenzene		68.5	63.4	-5.1
hydroxy	·OH	-OH	phenol	Ph–OH	−96.4	−89.5	6.9
methoxy		-OCH_3	anisole		−67.9	−69.3	-1.4
methyl	·CH_3	-CH_3	toluene	Ph–CH_3	50.5	54.2	3.7
carboxy		-COOH	benzoic acid		−294.0	−294.3	-0.3
amino	·NH_2	-NH_2	aniline	Ph–NH_2	87.5	92.2	4.7
cyano	C≡N	-CN	benzonitrile	Ph—≡N	215.7	218.6	2.9
acetyl		-$COCH_3$	acetophenone		−86.7	−81.5	5.2
formyl	HC=O	-CHO	benzaldehyde		−36.7	−34.9	1.8

acetylamino		-$NHCOCH_3$	*N*-phenylacetamide			−105.0	
tert-butyl		-$C(CH_3)_3$	tert-butylbenzene		−23.0	−22.8	0.2
dimethylamino		-$N(CH_3)_2$	*N*,*N*-dimethylaniline			102.3	
carbamoyl		-$CONH_2$	benzamide		−100.9	−94.5	6.4
ethanoxy		-OCH_2CH_3	ethoxybenzene		−101.6	−99.8	1.8
isopropyl		**-$CH(CH_3)_2$**	**cumene**			**4.9**	
acetoxy		-$OOCCH_3$	phenyl acetate			−275.0	
hydroxymethyl		-CH_2OH	phenylmethanol			−88.5	
carboxymethyl		-CH_2COOH	phenylacetic acid			−297.3	
(hydroxyimino)methyl		-CHNOH	benzaldehyde oxime			134.5	
hydrazinecarbonyl		-$CONHNH_2$	benzohydrazide			21.0	
methylamino		-$NHCH_3$	*N*-methylaniline			97.9	
ethyl		-CH_2CH_3	ethylbenzene		29.9	32.3	2.4
formamino		-NHCHO	*N*-phenylformamide			−55.7	
prop-2-yn-1-oxy		-OCH_2CCH	(prop-2-yn-1-yloxy)benzene			191.6	
isopropylamino		-$NHCH(CH_3)_2$	*N*-isopropylaniline			35.6	
ethynyl		-CCH	ethynylbenzene			322.5	
methylcarbamoyl		-$CONHCH_3$	*N*-methylbenzamide			−96.1	

N′-hydroxycarbamimidoyl		-CNH_2NOH	*N*′-hydroxybenzimidamide			114.0	
cyanomethanoxy		-OCH_2CN	phenoxyacetonitrile			90.4	
cyanomethyl		-CH_2CN	phenylacetonitrile			201.3	
1-(hydroxyimino)ethyl		-CCH_3NOH	1-phenylethan-1-one oxime			77.3	
methoxymethoxy		-**OCH_2OCH_3**	**(methoxymethoxy) benzene**			**−225.7**	
propionyl		-$COCH_2CH_3$	propiophenone			−103.7	
propylamino		-$NHCH_2CH_2CH_3$	*N*-propylaniline			48.2	
methyl(nitro)amino		-NCH_3NO_2	*N*-methyl-*N*-phenylnitramide			132.8	
azido		-NNN	azidobenzene			419.9	
3-oxoprop-1-en-1-yl		-CHCHCHO	cinnamaldehyde			27.9	
2-hydroxypropan-2-yl		-$COH(CH_3)_2$	2-phenylpropan-2-ol			−170.9	
prop-1-en-1-yl		-$CHCHCH_3$	prop-1-en-1-ylbenzene			120.8	

(B) HOF calculations for a solid

As most energetic compounds are in the solid state, the calculation of detonation properties requires solid-phase heat of formation ($^{\Delta H^{s}_{f}}$). According to Hess's law of constant heat summation, the solid-phase heat of formation can be acquired from the gas-phase heat of formation ($^{\Delta H^{g}_{f}}$) and heat of sublimation ($^{\Delta H_{sub}}$):

$$\Delta H_f^s = \Delta H_f^g - \Delta H_{sub}$$

As for the heat of sublimation, Politzer et al.[3] reported that it correlates with the molecular surface

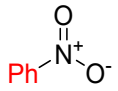
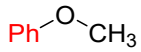
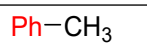
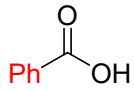
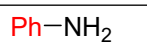
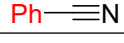
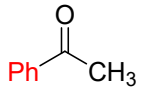
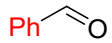
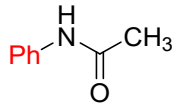
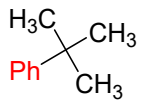
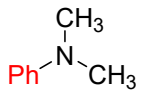
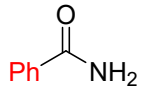
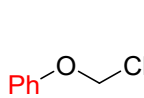
area and the electrostatic interaction $\nu\sigma_{tot}^2$ index for energetic compounds. The empirical expression of this approach is as follows:

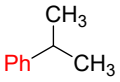
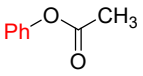
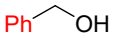
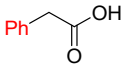
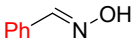
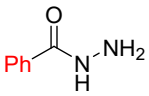
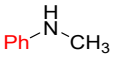
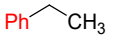
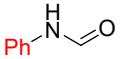
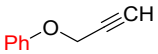
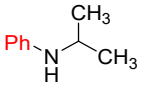
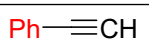
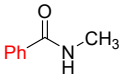
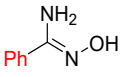
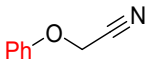
$$\Delta H_{sub} = aA^2 + b\left(\nu\sigma_{tot}^2\right)^{0.5} + c$$

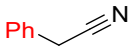
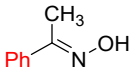
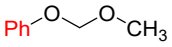
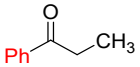
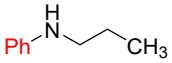
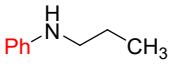
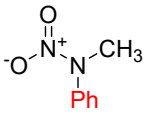
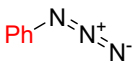
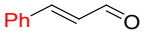
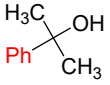
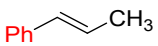
where A represents the surface area of the 0.001 electrons bohr^{-3} isosurface of the electronic density of the molecule, ν describes the degree of balance between positive potential and negative potential on the isosurface, and σ_{tot}^2 means a measure of the variability of the electrostatic potential on the molecular surface. The coefficients a, b, and c have been obtained by Rice et al. for the energetic materials: a = 2.670 × 10^{-4} kcal mol^{-1} Å^{-4}, b = 1650 kcal mol^{-1}, and c = 2.966 kcal mol^{-1}.[4] The descriptors A, ν and σ_{tot}^2 were calculated using the Multiwfn program.[5]

S2: BDE calculations.

Table S3. The calculated BDE (in kJ/mol) of forty mono-substituted benzene molecules. BDE_{G3} and BDE_{b3lyp} denote BDE calculated by B3LYP/6-31g(d)+D3 and G3 methods, respectively.

Name	Structure	BDE reaction	BDE_{G3}	BDE_{b3lyp}	Error
benzene		Ph → Ph• + •H	472.6	458.9	−2.9%
nitrobenzene		$PhNO_2$ → Ph• + $•NO_2$	316.0	300.0	−5.1%
phenol		PhOH → Ph• + •OH	467.8	455.7	−2.6%
anisole		$PhOCH_3$ → Ph• + $•OCH_3$	435.1	406.2	−6.6%
		$PhOCH_3$ → PhO• + $•CH_3$	266.0	253.6	−4.7%
toluene		$PhCH_3$ → Ph• + $•CH_3$	430.4	418.9	−2.7%
benzoic acid		PhCOOH → Ph• + •COOH	463.7	445.7	−3.9%
aniline		$PhNH_2$ → Ph• + $•NH_2$	436.2	419.8	−3.8%
benzonitrile		PhCN → Ph• + •CN	572.3	564.2	−1.4%
acetophenone		**$PhCOCH_3$ → Ph• + $•COCH_3$**	**416.5**	**401.3**	**−3.6%**
		$PhCOCH_3$ → PhCO• + $•CH_3$	346.0	341.2	−1.4%
benzaldehyde		PhCHO → Ph• + •CHO	419.8	409.6	−2.4%
N-phenylacetamide		$PhNHCOCH_3$ → Ph• + $•NHCOCH_3$	469.7	442.6	−5.8%
		$PhNHCOCH_3$ → PhNH• + $•COCH_3$	351.2	352.0	−2.0%
		$PhNHCOCH_3$ → $PhNHCO•$ + $•CH_3$	359.0	336.3	−4.2%
tert-butylbenzene		$PhC(CH_3)_3$ → Ph• + $•C(CH_3)_3$	422.0	380.1	−9.9%
N,*N*-dimethylaniline		$PhN(CH_3)_2$ → Ph• + $•N(CH_3)_2$	404.4	372.4	−7.9%
benzamide		$PhCONH_2$ → Ph• + $•CONH_2$	427.6	407.6	−4.7%
		$PhCONH_2$ → PhCO• + $•NH_2$	403.0	392.9	−2.5%
ethoxybenzene		$PhOCH_2CH_3$ → Ph• + $•OCH_2CH_3$	432.6	402.0	−7.1%
		$PhOCH_2CH_3$ → PhO• + $•CH_2CH_3$	276.7	255.5	−7.6%

cumene		$PhCH(CH_3)_2 \rightarrow Ph\bullet + \bullet CH(CH_3)_2$	429.8	398.7	−7.2%
phenyl acetate		$PhOOCCH_3 \rightarrow Ph\bullet + \bullet OOCCH_3$	447.0	396.9	−11.2%
phenylmethanol		$PhCH_2OH \rightarrow Ph\bullet + \bullet CH_2OH$	417.3	402.9	−3.5%
phenylacetic acid		$PhCH_2COOH \rightarrow Ph\bullet + \bullet CH_2COOH$	428.1	405.8	−5.2%
		$PhCH_2COOH \rightarrow PhCH_2\bullet + \bullet COOH$	333.2	310.4	−6.8%
benzaldehyde oxime		$PhCHNOH \rightarrow Ph\bullet + \bullet CHNOH$	491.8	461.8	−6.1%
		$PhCHNOH \rightarrow PhCHN\bullet + \bullet OH$	246.4	222.7	−9.6%
benzohydrazide		$PhCONHNH_2 \rightarrow Ph\bullet + \bullet CONHNH_2$	435.1	413.2	−5.0%
		$PhCONHNH_2 \rightarrow PhCONH\bullet + \bullet NH_2$	310.0	294.5	−5.0%
N-methylaniline		**$PhNHCH_3 \rightarrow Ph\bullet + \bullet NHCH_3$**	**426.6**	**401.9**	**−5.8%**
		$PhNHCH_3 \rightarrow PhNH\bullet + \bullet CH_3$	296.4	285.3	−3.8%
ethylbenzene		$PhCH_2CH_3 \rightarrow Ph\bullet + \bullet CH_2CH_3$	431.6	405.6	−6.0%
N-phenylformamide		$PhNHCHO \rightarrow Ph\bullet + \bullet NHCHO$	475.4	449.2	−5.5%
(prop-2-yn-1-yloxy)benzene		$PhOCH_2CCH \rightarrow Ph\bullet + \bullet OCH_2CCH$	434.9	403.5	−7.2%
		$PhOCH_2CCH \rightarrow PhO\bullet + \bullet CH_2CCH$	215.7	184.4	−14.5%
N-isopropylaniline		$PhNHCH(CH_3)_2 \rightarrow Ph\bullet + \bullet NHCH(CH_3)_2$	431.8	405.5	−6.1%
		$PhNHCH(CH_3)_2 \rightarrow PhNH\bullet + \bullet CH(CH_3)_2$	309.5	280.4	−9.4%
ethynylbenzene		$PhCCH \rightarrow Ph\bullet + \bullet CCH$	591.8	581.6	−1.7%
N-methylbenzamide		$PhCONHCH_3 \rightarrow Ph\bullet + \bullet CONHCH_3$	432.4	410.1	−5.2%
		$PhCONHCH_3 \rightarrow PhCO\bullet + \bullet NHCH_3$	401.5	382.1	−4.8%
N′-hydroxybenzimidamide		$PhCNH_2NOH \rightarrow Ph\bullet + \bullet CNH_2NOH$	470.6	444.8	−5.5%
phenoxyacetonitrile		$PhOCH_2CN \rightarrow Ph\bullet + \bullet OCH_2CN$	436.5	405.1	−7.2%

1-phenylethan-1-one oxime		$PhCH_2CN \rightarrow Ph\bullet + \bullet CH_2CN$	402.2	371.6	−7.6%
1-phenylethan-1-one oxime		$PhCCH_3NOH \rightarrow Ph\bullet + \bullet CCH_3NOH$	475.1	445.7	−6.2%
(methoxymethoxy)benzene		$PhOCH_2OCH_3 \rightarrow Ph\bullet + \bullet OCH_2OCH_3$	425.2	389.9	−8.3%
		$PhOCH_2OCH_3 \rightarrow PhOCH_2\bullet + \bullet OCH_3$	365.5	339.5	−7.1%
		$PhOCH_2OCH_3 \rightarrow PhOCH_2O\bullet + \bullet CH_3$	343.2	324.9	−5.3%
propiophenone		$PhCOCH_2CH_3 \rightarrow Ph\bullet + \bullet COCH_2CH_3$	418.5	401.8	−4.0%
		$PhCOCH_2CH_3 \rightarrow PhCO\bullet + \bullet CH_2CH_3$	348.1	335.1	−3.7%
N-propylaniline		$PhNHCH_2CH_2CH_3 \rightarrow Ph\bullet + \bullet NHCH_2CH_2CH_3$	431.8	404.8	−6.3%
N-propylaniline		**$PhNHCH_2CH_2CH_3 \rightarrow PhNH\bullet + \bullet CH_2CH_2CH_3$**	**309.8**	**288.4**	**−6.9%**
N-methyl-*N*-phenylnitramide		$PhNCH_3NO_2 \rightarrow Ph\bullet + \bullet NCH_3NO_2$	416.9	391.4	−6.1%
		$PhNCH_3NO_2 \rightarrow PhNCH_3\bullet + \bullet NO_2$	153.7	134.9	−12.2%
		$PhNCH_3NO_2 \rightarrow PhNNO_2\bullet + \bullet CH_3$	294.1	285.3	−3.0%
azidobenzene		$PhNNN \rightarrow Ph\bullet + \bullet NNN(\bullet N_3)$	379.1	356.2	−6.0%
		$PhNNN \rightarrow PhN\bullet + \bullet N_2$	−0.7	5.2	−797.8%
cinnamaldehyde		$PhCHCHCHO \rightarrow Ph\bullet + \bullet CHCHCHO$	503.9	489.8	−2.8%
2-phenylpropan-2-ol		$PhCOH(CH_3)_2 \rightarrow Ph\bullet + \bullet COH(CH_3)_2$	419.6	386.6	−7.8%
prop-1-en-1-ylbenzene		$PhCHCHCH_3 \rightarrow Ph\bullet + \bullet CHCHCH_3$	493.6	480.9	−2.6%

S3: v_D calculations.

1. Kamlet–Jacobs equations[2]:

$$p = 1.558\rho_0^2\varphi$$

$$v_D = 1.01\varphi^{\frac{1}{2}}(1 + 1.30\rho_0)$$

$$\varphi = 0.489N\overline{M}^{\frac{1}{2}}Q^{\frac{1}{2}}$$

where p is the C-J denotation pressure, in unit of GPa; v_D is the denotation velocity, in unit of km/s; ρ_0 is the density of EMs, in unit of g/cm^3; N is the amount of generated gaseous products per gram EMs, in unit of mol/g; $\overline{M}$ is the mean molar mass of gaseous products, in unit of g/mol; Q is the denotation heat of EMs, in unit of J/g.

For EMs of c.f. $C_aH_bO_cN_d$:

(1) When $c \geq 2a + \frac{b}{2}$, the reaction equation is:

$$C_aH_bO_cN_d \rightarrow \frac{1}{2}dN_2 + \frac{1}{2}bH_2O + aCO_2 + \frac{1}{2}\left(c - \frac{1}{2}b - 2a\right)O_2$$

The mean molar mass of the EM is:

$$M = 12a + b + 16c + 14d$$

N, $\overline{M}$ and Q are:

$$N = \frac{1}{4M}(b + 2c + 2d)$$

$$\overline{M} = \frac{28d + 18b + 88a + 16(2c - b - 4a)}{d + b + 2a + \left(c - \frac{1}{2}b - 2a\right)} = \frac{24a + 2b + 32c + 28d}{\frac{1}{2}b + c + d} = \frac{4M}{b + 2c + 2d}$$

$$Q = \frac{28.9b + 94.1a - 0.239\Delta H_f^0}{M} \times 4.184 \times 10^3$$

where ΔH_f^0 is the standard formation enthalpy of the EM; $\Delta H_f^0[N_2(g)] = 0$, $\Delta H_f^0[H_2O(g)] = 57.8\ kcal/mol$, $\Delta H_f^0[CO_2(g)] = 94.1\ kcal/mol$, $\Delta H_f^0[O_2(g)] = 0\ kcal/mol$, $\Delta H_f^0[C(s)] = 0\ kcal/mol$.

(2) When $2a+\frac{b}{2}>c\geq\frac{b}{2}$, the reaction equation is:

$$C_aH_bO_cN_d \rightarrow \frac{1}{2}dN_2+\frac{1}{2}bH_2O+\frac{1}{2}\left(c-\frac{1}{2}b\right)CO_2+\left[a-\frac{1}{2}\left(c-\frac{1}{2}b\right)\right]C$$

N, $\overline{M}$ and Q are:

$$N=\frac{1}{4M}(b+2c+2d)$$

$$\overline{M}=\frac{56d+88c-8b}{b+2c+2d}$$

$$Q=\frac{28.9b+94.1\left(\frac{c}{2}-\frac{b}{4}\right)-0.239\Delta H_f^0}{M}\times 4.184\times 10^3$$

(3) When $\frac{b}{2}>c$, the reaction equation is:

$$C_aH_bO_cN_d \rightarrow \frac{1}{2}dN_2+cH_2O+\frac{1}{2}(b-2c)H_2+aC$$

N, $\overline{M}$ and Q are:

$$N=\frac{1}{2M}(b+d)$$

$$\overline{M}=\frac{2b+32c+28d}{b+d}$$

$$Q=\frac{57.8c-0.239\Delta H_f^0}{M}\times 4.184\times 10^3$$

S4: Oxygen balance (OB%) definition

For EMs in c.f. $C_aH_bO_cN_d$:

$$OB\%=\frac{c-\frac{1}{2}b-2a}{c}\times 100\%$$

S5: ML results of BDE

Table S4. Test scores of the ML models of BDE. The results of the best models are highlighted in bold.

		Ridge	Lasso	SVR	RFR	GBR	MLP	Ensemble	GRU
$BDE_{C\text{-}NO_2}$	RMSE	11.60	11.42	10.96	11.89	11.37	**10.60**	10.77	11.09
(kJ·mol^{-1})	MAE	8.73	8.62	8.11	9.00	8.55	**8.02**	8.05	8.01

	R^2	0.730	0.738	0.759	0.716	0.741	**0.775**	0.767	0.753
$BDE_{N\text{-}NO2}$ ($kJ \cdot mol^{-1}$)	RMSE	13.64	**13.4**	13.91	13.68	13.71	13.97	13.51	13.71
	MAE	10.72	**10.61**	10.89	10.81	10.81	10.92	10.64	10.85
	R^2	0.258	**0.276**	0.229	0.254	0.251	0.223	0.272	0.251

S6: Top molecules by ρ_{ML} and v_{DML}.

Table S5. Top 30 Molecules by ρ_{ML}. ρ_{ML} and v_{DML} are in g cm^{-3} and m s^{-1}, respectively.

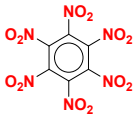
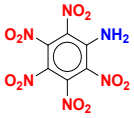
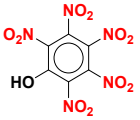
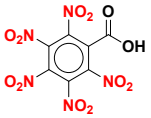
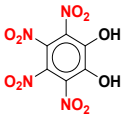
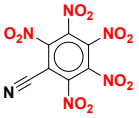
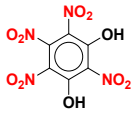
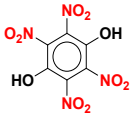
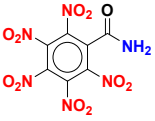
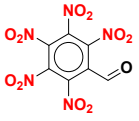
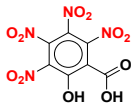
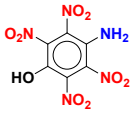
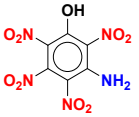
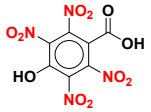
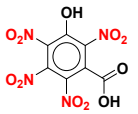
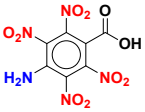
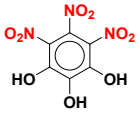
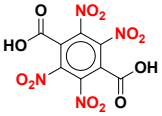
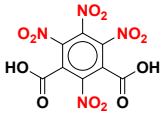
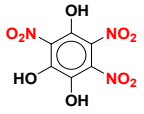
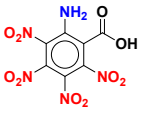
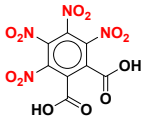
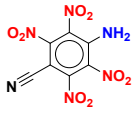
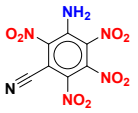
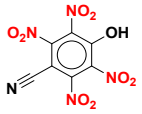
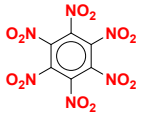
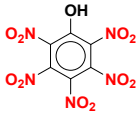
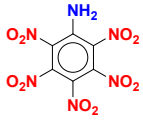
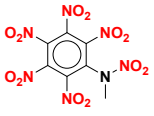
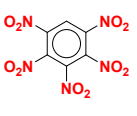
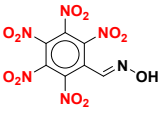
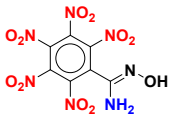
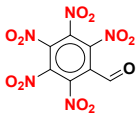
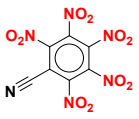
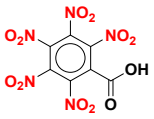
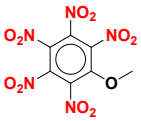
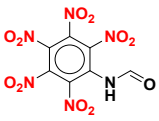
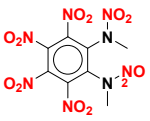
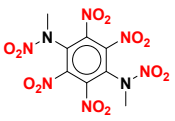
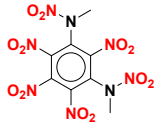
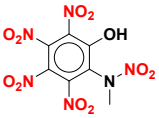
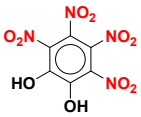
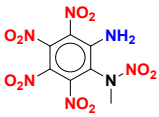
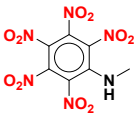
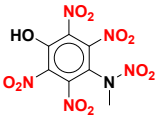
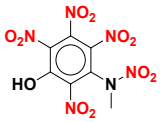
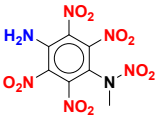
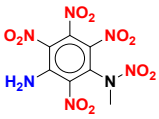
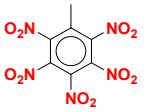
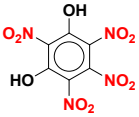
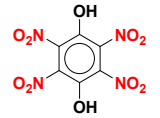
Structure						
ρ	1.942	1.925	1.923	1.916	1.910	1.904
v_D	9266	8897	8910	8664	8539	8701
Structure						
ρ	1.903	1.903	1.899	1.899	1.899	1.897
v_D	8468	8468	8611	8415	8415	8704
Structure						
ρ	1.896	1.896	1.896	1.896	1.896	1.895
v_D	8246	8427	8427	8229	8229	8207
Structure						
ρ	1.895	1.894	1.893	1.893	1.892	1.887
v_D	8207	8072	8037	8037	8048	7989
Structure						
ρ	1.886	1.886	1.885	1.884	1.884	1.883
v_D	8210	8034	8456	8264	8264	8278

Table S6. Top 30 Molecules by v_{DML}. ρ_{ML} and v_{DML} are in g cm^{-3} and m s^{-1}, respectively.

Structure						
v_D	9266	8910	8897	8889	8790	8723
ρ	1.942	1.923	1.925	1.883	1.874	1.876
Structure						
v_D	8716	8704	8701	8664	8657	8615
ρ	1.878	1.897	1.904	1.916	1.880	1.867

Structure						
v_D	8611	8600	8592	8586	8571	8571
ρ	1.899	1.853	1.876	1.837	1.834	1.834
Structure						
v_D	8543	8539	8530	8527	8525	8525
ρ	1.860	1.910	1.858	1.849	1.859	1.859
Structure						
v_D	8524	8524	8511	8468	8468	8456
ρ	1.864	1.864	1.845	1.903	1.903	1.885

S7: Performance of ML in predicting BDE of C-NO_2 and N-NO_2.

Table S7. Comparison of machine-learnt BDE (BDE_ML) and quantum chemistry calculated BDE (BDE_QC) of 12 molecules with v_D>7000 m/s.

	v_D_ML (m s^{-1})	BDE_ML (kJ mol^{-1})	BDE_QC (kJ mol^{-1})	Abs_BDE (kJ mol^{-1})	BDE_%
1	7609	260	257	3	1.2
2	7052	264	275	-11	-4.1
3	7704	267	271	-4	-1.6
4	7395	279	273	7	2.4
5	7154	285	285	0	-0.1
6	7119	288	297	-9	-3.2
7	7028	289	272	17	6.3
8	7523	291	286	6	2.0
9	7271	296	289	7	2.5
10	7685	296	300	-3	-1.1
11	7207	301	307	-6	-2.1
12	7825	304	301	3	1.1

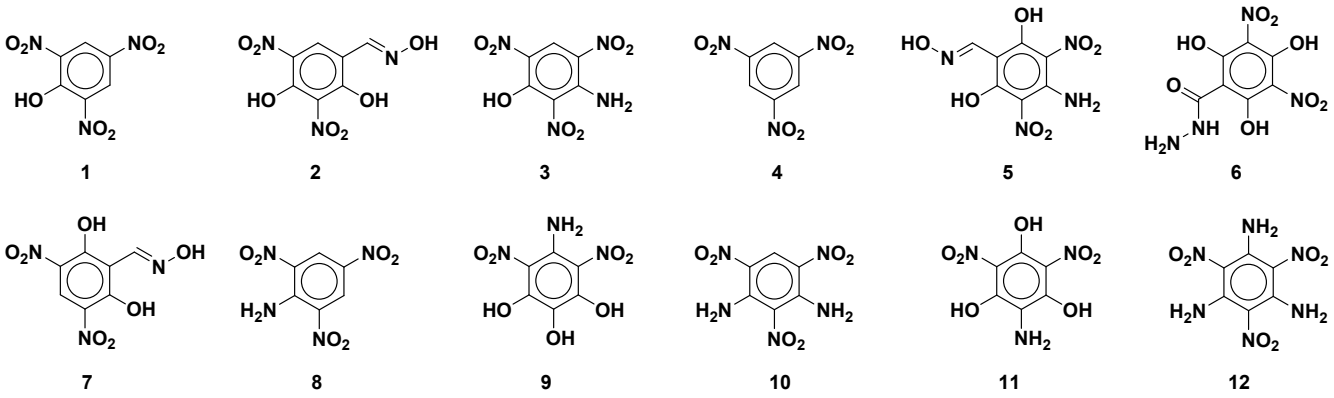


Figure S2. Molecular structures for BDE verification.

S8: References

(1) Lide, D. R., *CRC handbook of chemistry and physics: a ready-reference book of chemical and physical data*. CRC press: 1995.

(2) Atkins, P. W.; De Paula, J.; Keeler, J., *Atkins' physical chemistry*. 2006.

(3) Politzer, P.; Murray, J. S., Some perspectives on estimating detonation properties of C, H, N, O compounds. *Central European Journal of Energetic Materials* **2011,** *8* (3), 209-220.

(4) Rice, B. M.; Byrd, E. F., Evaluation of electrostatic descriptors for predicting crystalline density. *Journal of computational chemistry* **2013,** *34* (25), 2146-2151.

(5) Fei, T.; Du, Y.; Pang, S., Theoretical design and prediction of properties for dinitromethyl, fluorodinitromethyl, and

(difluoroamino)dinitromethyl derivatives of triazole and tetrazole. *RSC Advances* **2018,** *8* (19), 10215-10227.