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面向高通量含能分子设计筛选的三种生成焓计算方法评估

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摘要: 高通量含能分子设计需要兼顾准确性与效率的性能预测方法。结合原子化方案,对常见的3种不同水平的理论方法(半经验PM6方法、密度泛函理论方法B3LYP/6-31G(d,p)和高精度的完全基组CBS-4M方法)用于高通量含能分子设计筛选的生成焓(HOF)计算适宜性进行了评估。计算并比较了20种含能分子的固相HOF,发现不同理论水平预测结果存在较大差异;而基于10种常见含能分子的不同水平下的HOF,实验密度和Kamlet-Jacobs(K-J)、Becker-Kistiakowsky-Wilson(BKW)与Virial-Wu(VLW)3种模型预测的爆轰性能差别不大。其中B3LYP方法具有最佳适宜性,具有较高的计算效率且爆轰性能预测结果同CBS方法接近,如基于BKW模型计算的爆速和爆压的平均相对偏差仅为0.4%和1.2%。而低精度的PM6方法和高耗时的CBS方法难以满足兼顾高通量含能分子设计筛选中的精度和效率的要求。这表明,在高通量的含能分子设计筛选中,可考虑中等精度的方法进行快速的HOF预测。

关键词: 生成焓;爆轰性能;高通量含能分子设计;含能材料;生成焓计算

中图分类号: TJ55; O64

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1 引言

含能材料是储存大量化学能的亚稳态物质,包括炸药、推进剂和烟火药^[1-5],广泛应用于军事和民用领域。作为军事武器的能量来源,含能材料优异的爆轰性能和较低感度决定了军事装备的先进性。过去几十年里,诸多致力于追求高性能含能材料分子设计的策略已被提出,如设计具有高张力键的笼形硝基化合物^[6-7]和分子中含有大量的N—N键和N—C键的高氮化合物^[8-10]。此外,为了缓解能量与感度间的矛盾,人们提出了在分子中引入氢键的策略,改善分子的堆积模式以在晶体水平上缓解能量-安全性间矛盾^[11-12]。随着计算机技术的快速发展和各种预测模型的建立,

高通量分子设计正逐步成为材料设计的主流^[13-19],含能材料也将不会例外^[20-23]。

爆轰性能包括爆热、爆速、爆压、爆温和爆容,是含能材料的基本性能,也是含能分子高通量设计要首先考虑的问题之一。生成焓(HOF)是化合物的基本热力学性质与爆轰性能正相关^[24-25],是预测爆轰性能的必要参数。目前,等键反应结合密度泛函理论(DFT)计算的方案^[26-27]已经能够给出化学精度的HOF;但是,基于优化的等键反应方案的HOF计算程序开发难度较高,目前还只能手动进行。原子化方案^[28-31]通过计算分子内能和组成原子的气态标准HOF获得分子的HOF,能够很方便地实现程序化;因此,高通量HOF计算通常采用原子化方案。然而,原子化方案须同昂贵的高水平量子化学方法相结合才能准确计算分子和原子的内能。常用的量子化学方法有半经验方法,Gong等^[32]用PM6法和PM3法对56种高能材料的生成焓进行了预测,预测偏差较大,其均方根偏差分别为42.09 kJ·mol⁻¹和58.83 kJ·mol⁻¹;高精度从头算的完全基组方法CBS, Montgomery等^[33]基于CBS-Q方法对中小分子进行热化学计算,精度可达4.18~8.36 kJ·mol⁻¹,该方法计算精度较高,但所耗时较多,不适用于大分子体系。

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BAO Fu-cheng, PENG Ru-fang, ZHANG Chao-yang. Evaluation of Three Heat of Formation Calculation Methods for High-throughput Energetic Molecule Design and Screening[J]. Chinese Journal of Energetic Materials (Hanneng Cailiao), 2022, 30(7):726-735.

目前密度泛函理论方法得到广泛认可和使用, Rice等^[34]在B3LYP/6-31G(d)水平上计算了35种CHNO分子的HOF, 预测气相分子HOF与实验值的均方根偏差为 $12.97 \text{ kJ}\cdot\text{mol}^{-1}$, 最大偏差为 $25.52 \text{ kJ}\cdot\text{mol}^{-1}$ 。然而, 在高通量分子设计筛选中, 高精度方法会急剧增加计算成本, 而半经验方法又难以满足计算精度需要。

因此, 为给高通量筛选的理论方法选择提供依据, 一方面须加快基于等键反应方案的HOF计算的程序化进程; 另一方面, 须评估不同理论水平基于原子化方案计算HOF的偏差对爆轰性能的影响程度。基于此, 本研究对3种不同水平理论方法, 半经验PM6方法、密度泛函理论方法B3LYP/6-31G(d,p)和高精度的完全基组CBS-4M方法, 在面向高通量含能分子设计筛选的爆轰性能预测中的适宜性进行了评估, 以满足高

通量筛选所要求的程序化、预测精度与计算效率。

2 研究方法

本研究旨在获得高通量的计算方法, 而不是要进行高通量的分子设计。研究的对象为20种CHNO类含能分子, 涵盖了硝基化合物炸药、硝胺炸药、硝酸酯炸药、咪唑类、噁类及叠氮类炸药等, 它们的分子结构如图1所示。选用的CHNO含能分子, 一方面有实验HOF值, 便于比较, 能确定计算方法的准确性; 另一方面, 结构上具有代表性和多样性, 如链状、环状与笼形的分子结构, 同时具有C-NO₂、N-NO₂和O-NO₂官能团, 待进行高通量设计的分子大多具有这一类似的结构。

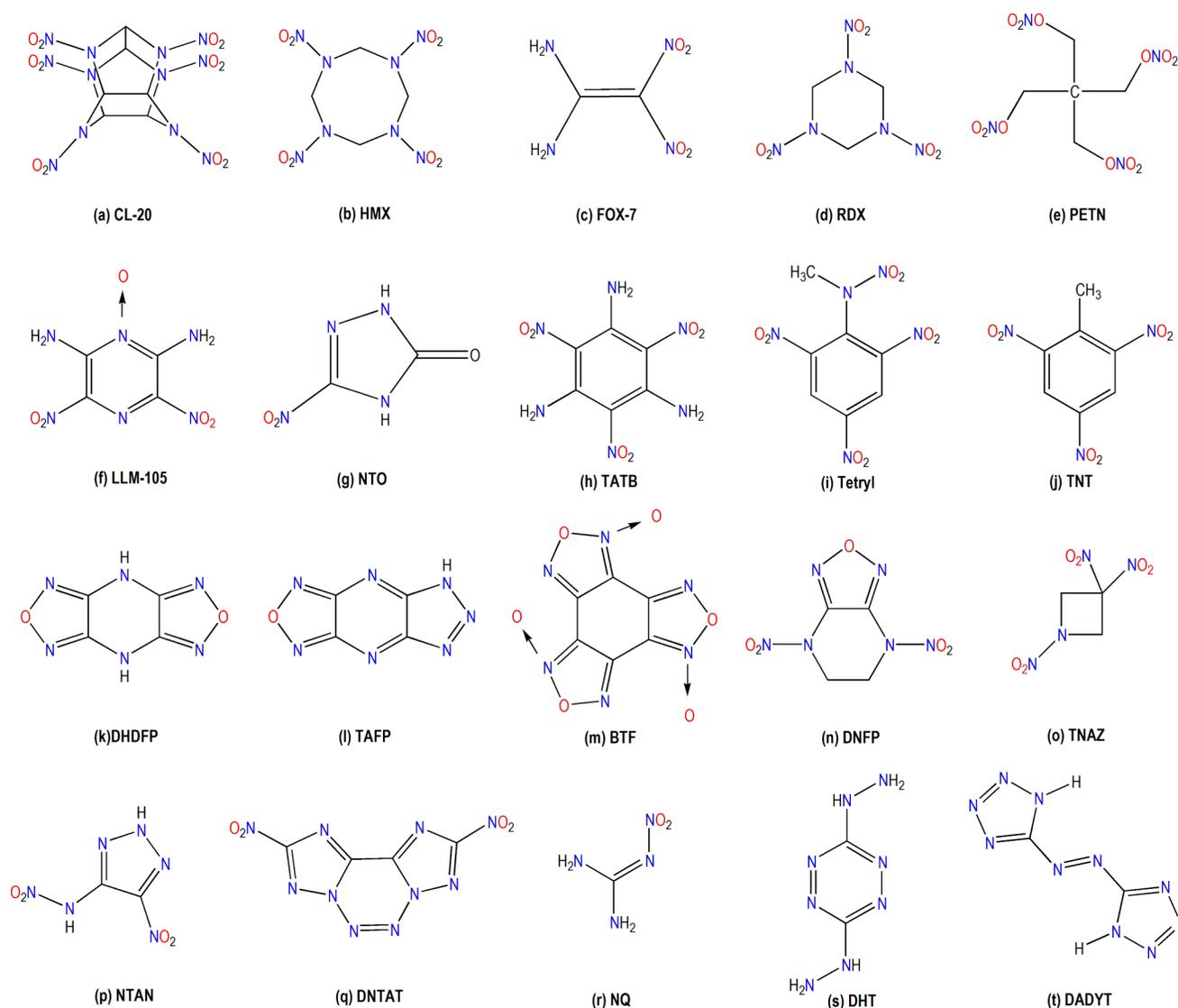


图1 20种含能分子的结构

Fig.1 Structures of twenty energetic molecules

由于计算方法对CHNO体系的可行性没有结构上的限制,因此3种不同水平的方法可计算得到以上20种含能分子标准状态下的气相HOF($\Delta_f H_m^\circ(M, g, 298.15 K)$)。对于 $\Delta_f H_m^\circ(M, g, 298.15 K)$,采用PM6方法(VAMP程序包)计算便可直接获得;而采用DFT-B3LYP/6-31G(d, p)和CBS-4M方法(Gaussian 03程序包)计算时,结合了原子化方案。基于原子化方案计算 $\Delta_f H_m^\circ(M, g, 298.15 K)$ 方法简要介绍如下^[28-31]:

(1) 参考了文献[31]构造M原子化反应。



式中, x_1, x_2, x_3, x_4 表示原子个数。

(2) 采用上述量子化学方法对分子M进行结构优化,频率计算无虚频确认势能面上稳定的结构。

(3) 计算原子化反应能($\sum D_0(M)$),即,产物与反应物的内能差, $\text{kJ}\cdot\text{mol}^{-1}$ 。再通过式(1)计算获得0 K条件下的标准摩尔HOF($\Delta_f H_m^\circ(M, g, 0 K)$)。

$$\Delta_f H_m^\circ(M, g, 0 K) = \sum x \Delta_f H_m^\circ(X, g, 0 K) - \sum D_0(M) \quad (1)$$

式中, $\Delta_f H_m^\circ(X, g, 0 K)$ 表示原子X在0 K下的HOF, $\text{kJ}\cdot\text{mol}^{-1}$;C、H、N和O原子的 $\Delta_f H_m^\circ(X, g, 0 K)$ 分别为711.19、216.02、470.82 $\text{kJ}\cdot\text{mol}^{-1}$ 和246.81 $\text{kJ}\cdot\text{mol}^{-1}$ 。

(4) 通过式(2)进行温度从0 K到298.15 K的HOF校正。

$$\Delta_f H_m^\circ(M, g, 298.15 K) = \Delta_f H_m^\circ(M, g, 0 K) + (H_M^\circ(298.15 K) - H_M^\circ(0 K)) - \sum x (H_X^\circ(298.15 K) - H_X^\circ(0 K)) \quad (2)$$

式中, $H_M^\circ(298.5 K) - H_M^\circ(0 K)$ 和 $H_X^\circ(298.5 K) - H_X^\circ(0 K)$ 分别是分子M和原子X在0 K到298.15 K下的焓校正,分子的焓校正可由量子化学频率计算直接给出,C、H、N和O原子的焓校正分别为1.05、4.23、4.35 $\text{kJ}\cdot\text{mol}^{-1}$ 和4.35 $\text{kJ}\cdot\text{mol}^{-1}$ 。

含能分子M爆轰性能计算需要的HOF参数为固相标准摩尔HOF($\Delta_f H_m^\circ(M, s, 298.15 K)$),可用标准状态下的气相HOF($\Delta_f H_m^\circ(M, g, 298.15 K)$)减去升华焓($\Delta H_m^\circ(\text{sub})$)得到。对于 $\Delta H_m^\circ(\text{sub})$,则按照经验式(3)计算^[35-36]。

$$\Delta H_m^\circ(\text{sub}) = \alpha A^2 + \beta(\nu\sigma_{\text{total}}^2)^{1/2} + \gamma \quad (3)$$

式中, A, ν 和 σ_{total}^2 分别表示分子表面积、分子表面正负静电势平衡常数与总表面静电势的方差,可由Bulat等^[37]提出的计算方法计算获得。常数 $\alpha=11.171 \times 10^{-4} \text{ kJ}\cdot\text{mol}^{-1}$, $\beta=6.904 \text{ kJ}\cdot\text{mol}^{-1}$, $\gamma=12.409 \text{ kJ}\cdot\text{mol}^{-1}$ 。计算 $\Delta_f H_m^\circ(M, g, 298.15 K)$ 与 $\Delta H_m^\circ(\text{sub})$ 的差值,便可得到

$\Delta_f H_m^\circ(M, s, 298.15 K)$ 。

基于上述HOF和实验密度,分别采用K-J经验方程式见式(4)~(5)^[38-40]、BKW模型^[41-44]和VLW模型^[45]对10种典型CHNO含能分子的爆轰性能进行计算。

$$D(\text{km}\cdot\text{s}^{-1}) = 1.01[N^{0.5}M_{\text{ave}}^{0.25}Q^{0.25}(1 + 1.30\rho)] \quad (4)$$

$$\rho(\text{MPa}) = 1558[NM_{\text{ave}}^{0.5}Q^{0.5}\rho^2] \quad (5)$$

式中, N 表示每克炸药爆炸产生的气体摩尔数, $\text{mol}\cdot\text{g}^{-1}$; M_{ave} 为气体爆轰产物的平均摩尔质量, $\text{g}\cdot\text{mol}^{-1}$; ρ 为炸药的装载密度, $\text{g}\cdot\text{cm}^{-3}$; Q 为爆热, $\text{kJ}\cdot\text{g}^{-1}$ 。

3 结果和讨论

3.1 计算机时对比

研究所用CPU是2.6 GHz的Intel, Gold 6142。不同精度的量子化学方法计算HOF所耗时不同,3种方法的不同机时如图2所示,由图2可见,PM6半经验方法所需时间最短,且无明显分子大小依赖性,计算平均机时仅约 5.0×10^{-4} 核时。DFT(B3LYP)方法所耗时较PM6方法高约3个数量级,平均机时0.36核时。而CBS方法耗时最大,20种分子计算的平均机时为每分子1.06核时,特别是对大分子体系计算所耗时巨大,如大分子CL-20所需的机时较其他小分子体系高约1个数量级。仅从计算机时考虑,PM6方法能够在最低的成本下进行高效的高通量筛选,而CBS方法耗时较大,计算成本高,不利于高通量筛选。

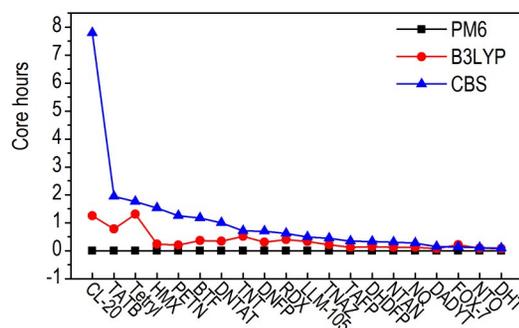


图2 3种方法的计算机时对比

Fig.2 Comparison of the machine-time by three calculation methods

3.2 生成焓的计算偏差

表1列出了20种含能分子的实验密度(ρ)、升华焓($\Delta H_m^\circ(\text{sub})$)。研究通过3种理论方法获得298.15 K下的气相HOF和固相HOF,结果也见表1。由表1可以看出,3种不同精度的方法计算结果差异较大,而B3LYP方法与CBS方法计算结果较为接近。以高精度的CBS方法获得的固相HOF为标准,基于PM6和

B3LYP法获得的固相HOF的绝对偏差如图3a所示,从图3a中可以看出,不同精度的方法计算获得的HOF绝对差值较大。总体上PM6计算结果的偏差最大,如图3a中红色显示,除分子较大的CL-20外,B3LYP方法获得的HOF偏差较小,如图3a中蓝色显示。3种方法计算结果对比中,PM6方法相对于CBS方法的平均绝对偏差为65.1 kJ·mol⁻¹,绝对偏差最大的分子是DNTAT,为151.5 kJ·mol⁻¹,绝对偏差最小的分子是TNAZ,为4.2 kJ·mol⁻¹。而B3LYP方法相对于CBS方

法的平均绝对偏差为34.2 kJ·mol⁻¹,绝对偏差最大的分子是CL-20,为132.6 kJ·mol⁻¹,绝对偏差最小的分子是RDX,为-1.3 kJ·mol⁻¹。此外,计算了分子的HOF在单位质量的绝对偏差和单位体积的绝对偏差如图3b~3c所示,基于PM6方法和B3LYP方法获得平均单位质量的HOF偏差分别为0.30 kJ·g⁻¹和0.15 kJ·g⁻¹,平均单位体积的HOF偏差分别为0.37 kJ·Å⁻³和0.19 kJ·Å⁻³,尽管这些含能分子基于不同方法获得的HOF具有较高的偏差值,但其偏差在后续Q的计算结果中占比较小。

表1 20种CHNO含能分子的实验密度、升华焓及3种方法计算所得气相生成焓 $\Delta_f H_m^\circ(g)$ 和固相生成焓 $\Delta_f H_m^\circ(s)$

Table 1 The experiment density, calculated enthalpy of sublimation, gas-phase heat of formation $\Delta_f H_m^\circ(g)$ and solid-state heat of formation $\Delta_f H_m^\circ(s)$ calculated based on three methods for twenty energetic molecules

compounds	ρ	$\Delta H_m^\circ(\text{sub})$	$\Delta_f H_m^\circ(g)$			$\Delta_f H_m^\circ(s)$		
			PM6	B3LYP	CBS	PM6	B3LYP	CBS
CL-20	2.044 ^[6]	174.5	341.8	585.8	453.1	167.3	411.3	278.6
HMX	1.894 ^[46]	200.4	142.3	233.9	216.7	-58.1	33.5	16.3
RDX	1.806 ^[47]	146.4	65.7	172.8	174.1	-80.7	26.4	27.7
PETN	1.781 ^[48]	152.3	-524.3	-402.9	-406.3	-676.6	-555.2	-558.6
FOX-7	1.893 ^[49]	178.2	-33.1	-15.1	12.1	-211.3	-193.3	-166.1
LLM-105	1.919 ^[50]	165.7	206.3	95.0	120.9	40.6	-70.7	-44.8
NTO	1.918 ^[51]	138.9	38.1	-12.1	-17.6	-100.8	-151	-156.5
TATB	1.937 ^[52]	188.3	-82.0	-12.6	9.2	-270.3	-200.9	-179.1
Tetryl	1.731 ^[53]	141.0	160.2	174.5	106.3	19.2	33.5	-34.7
TNT	1.654 ^[54]	129.7	59.4	61.5	9.2	-70.3	-68.2	-120.5
DHDFP	2.008 ^[55]	146.6	587.9	507.5	543.9	441.3	360.9	397.3
DNTAT	1.901 ^[56]	132.6	995.8	882.0	844.3	863.2	749.4	711.7
BTF	1.932 ^[57]	89.1	677.4	697.1	760.2	588.3	608.0	671.1
NTAN	1.919 ^[58]	127.1	319.7	309.2	312.1	192.6	182.1	185.0
NQ	1.752 ^[59]	143.4	43.5	32.2	49.8	-99.9	-111.2	-93.6
DADYT	1.774 ^[60]	150.4	1078.6	1017.1	1094.5	928.2	866.7	944.1
DNFP	1.829 ^[61]	143.9	362.8	381.2	397.9	218.9	237.3	254.0
TNAZ	1.861 ^[62]	113.7	95.8	120.5	91.6	-17.9	6.8	-22.1
DHT	1.729 ^[63]	211.3	572.0	635.5	652.3	360.7	424.2	441.0
TAFP	1.834 ^[64]	112.7	809.2	696.2	727.6	696.5	583.5	614.9

Note: the ρ , enthalpy of sublimation ($\Delta H_m^\circ(\text{sub})$), heat of formation in gas state ($\Delta_f H_m^\circ(g)$) and solid state ($\Delta_f H_m^\circ(s)$) are in g·cm⁻³, kJ·mol⁻¹, kJ·mol⁻¹ and kJ·mol⁻¹, respectively.

3.2 生成焓计算偏差对爆轰性能的影响评估

为了评估3种不同精度的理论方法在高通量筛选中的适宜性,兼顾高通量筛选的精度和效率,研究了基于3种理论水平下含能分子的固相HOF偏差对爆轰性能的影响程度,包括 Q 、 D 和 p 。由于采用的3种爆轰性能预测模型对新型富氮杂环体系的适宜性还受到质疑^[65],以下爆轰性能预测只选取10种传统CHNO含能分子作为研究对象。Kamlet

和Jacobs提出的爆炸反应气体产物规则认为,化合物中的N全部转化为N₂,H转化为H₂O(g)或H₂(g),C转化为CO₂(g)、CO(g)和C(s),O被全部用于H和C的氧化,爆炸产物遵循的步骤为:(a)氢原子全部转化为H₂O(g);(b)使用剩余的氧生成CO₂(g);(c)没有CO(g)产生^[38,66-67]。根据爆热的计算公式^[65]:

$$Q = \frac{1}{M_x} [\sum \Delta_f H_m^\circ(\text{products}) - \Delta_f H_m^\circ(\text{explosive})],$$

基

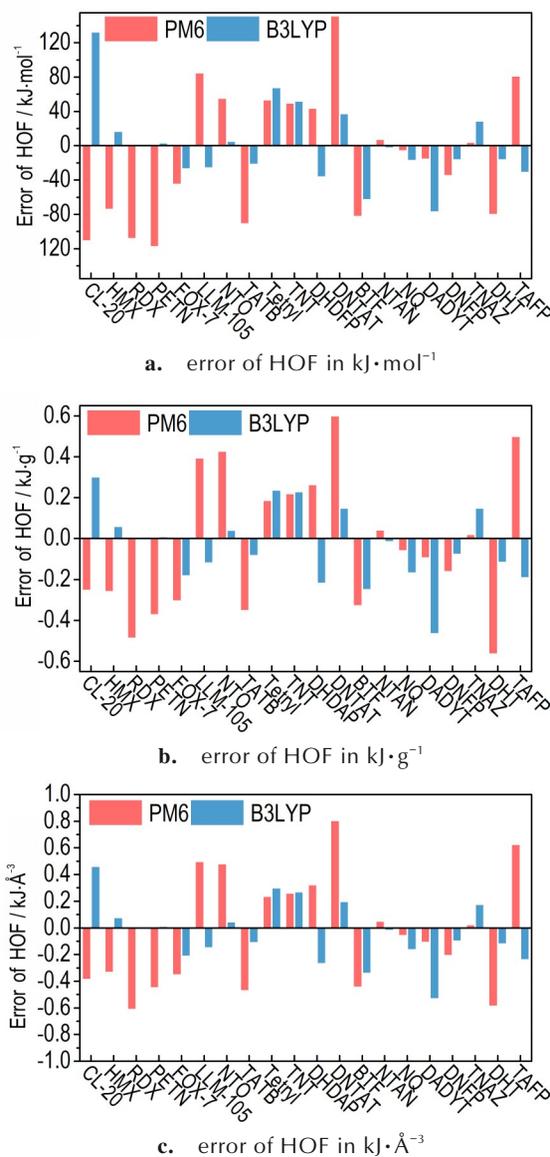


图3 相对于CBS方法的PM6与B3LYP的HOF的计算偏差
Fig.3 Error of the HOF calculated by PM6 and B3LYP compared with the CBS method

于3种方法获得的固相HOF,可计算得到的 Q 及相对偏差(RE),结果如图4所示。由图4b可以看出,以基于CBS方法计算结果为标准,我们发现PM6结果的RE大于B3LYP。其中,基于PM6方法计算 Q 的平均RE为6.5%,最大RE为11.3%,而B3LYP的平均RE要小一些,仅为2.8%,最大RE仅为4.8%。另外,基于PM6方法获得HOF绝对偏差最大的PETN($-118.0\text{ kJ}\cdot\text{mol}^{-1}$),其 Q 的RE仅有 -6.9% ,基于B3LYP方法获得HOF绝对偏差最大的CL-20($132.6\text{ kJ}\cdot\text{mol}^{-1}$),其 Q 的RE仅有4.8%。研究发现尽管采用不同方法获得10种含能分子的HOF的偏差较大,但其偏差对 Q 的影响较小。究

其原因,影响含能材料 Q 的大小包括两部分,一是分子本身HOF的大小,其次是爆炸产物HOF的大小。对于传统CHNO含能材料来说,基于K-J规则的爆炸产物仅有 $\text{CO}_2(\text{g})$ 和 $\text{H}_2\text{O}(\text{g})$ 对HOF有贡献,而单质气体的HOF为 $0\text{ kJ}\cdot\text{mol}^{-1}$,因此当有更多 $\text{CO}_2(\text{g})$ 和 $\text{H}_2\text{O}(\text{g})$ 产生时,产物的HOF在其 Q 中占比较大,含能材料本身的HOF的偏差对 Q 的影响较小。

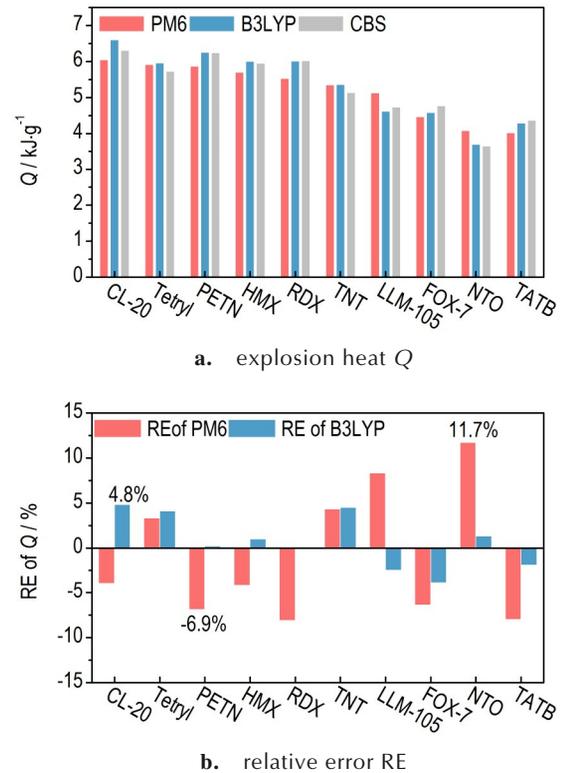


图4 基于3种方法计算获得的10种含能分子的爆热 Q 及其相对偏差RE

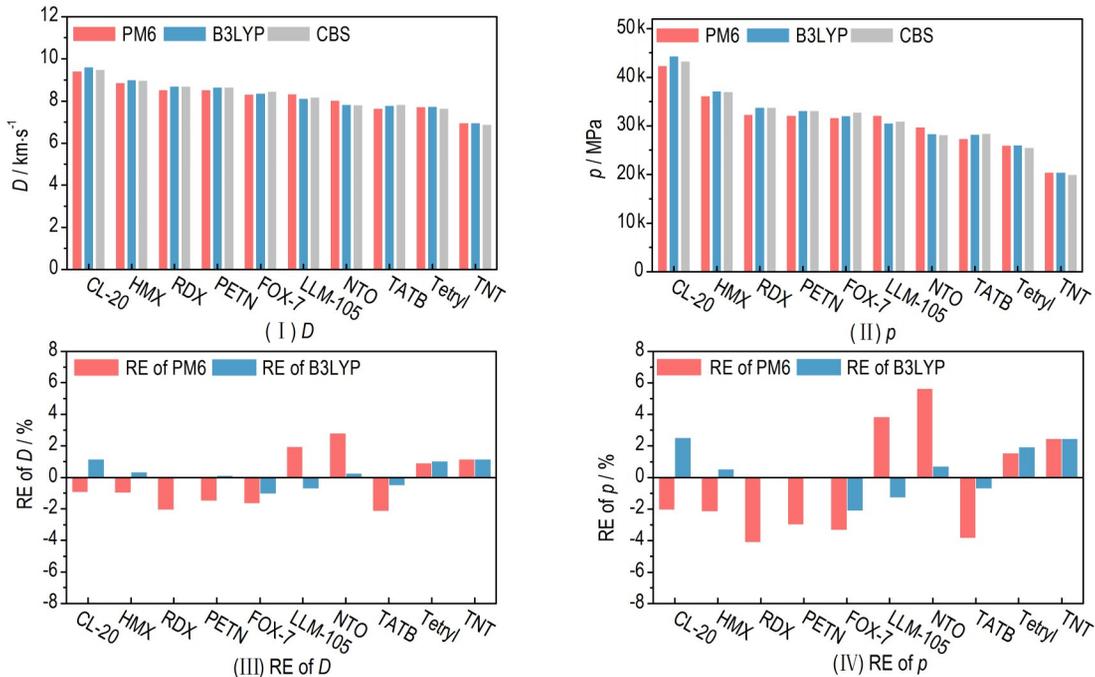
Fig.4 Explosive heat Q and relative error RE of ten energetic molecules calculated based on three methods

基于3种方法获得的固相HOF、实验密度和K-J、BKW与VLW模型预测得到10种含能分子的 D 和 P 如图5a I~5c II所示。根据K-J经验方程知 D 和 p 与 Q 密切相关,因此HOF的大小在一定程度上会影响 D 、 p 的大小。对于相同的含能分子,基于不同理论方法获得的HOF计算的爆轰性能不同,例如CL-20,B3LYP法获得的HOF最大($585.8\text{ kJ}\cdot\text{mol}^{-1}$),基于BKW模型计算得到最大的 D ($9.8\text{ km}\cdot\text{s}^{-1}$)和 p (45200 MPa),而PM6法获得的HOF最低($341.8\text{ kJ}\cdot\text{mol}^{-1}$),其 D 和 p 相对较小,分别为 $9.6\text{ km}\cdot\text{s}^{-1}$ 和 43500 MPa 如图5b I和5b II所示。因此,HOF的计算偏差对含能材料的爆轰性能预测有一定的影响。

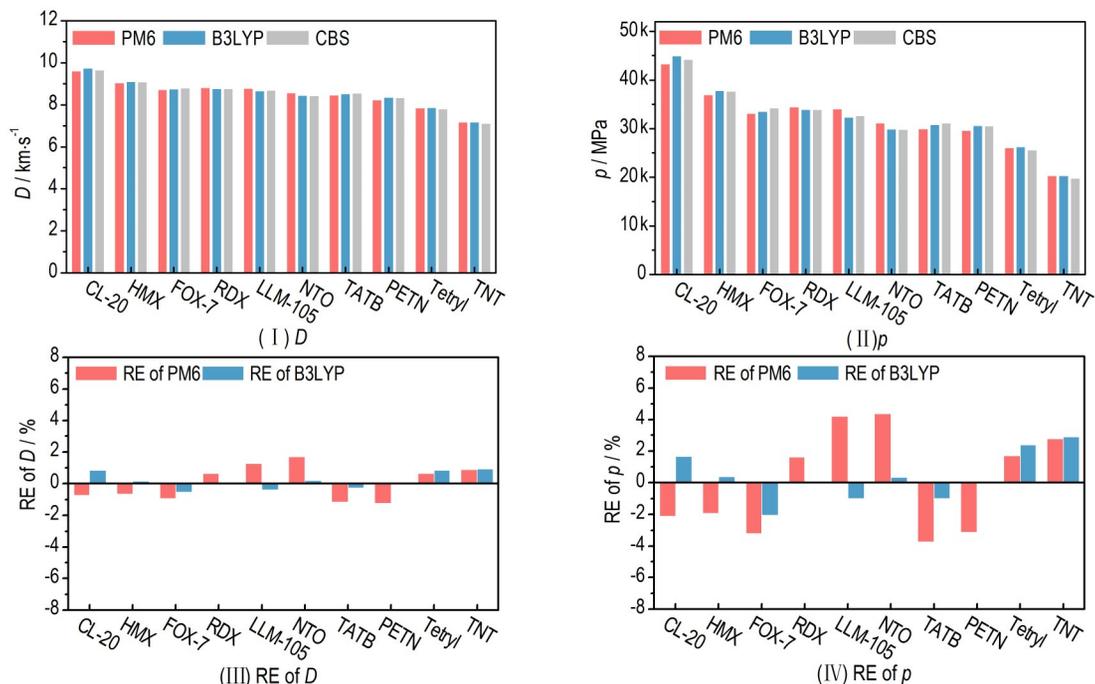
基于PM6和B3LYP法获得的HOF预测得到的爆轰性能与基于CBS结果的RE如图5aⅢ~5cⅣ所示,尽管不同精度的计算方法获得的HOF绝对偏差较大,但预测得到爆轰性能的RE较小,如基于PM6方法获得的HOF和K-J方程、BKW模型、VLW模型预测 D 的平均RE分别为1.6%、1.0%和1.5%,预测 p 的平均RE分别为3.2%、2.9%和5.3%。基于B3LYP方法获得的

HOF和K-J方程、BKW模型、VLW模型预测 D 的平均RE分别为0.6%、0.4%和0.6%,预测 p 的平均RE分别为1.2%、1.2%和1.9%。

对比基于3种模型预测的爆轰性能结果可以看出,基于PM6方法计算得到的HOF预测的爆轰性能偏差最大,在高通量分子设计筛选中难以满足计算精度要求,而基于B3LYP方法计算得到的HOF预测的爆



a. K-J



b. BKW

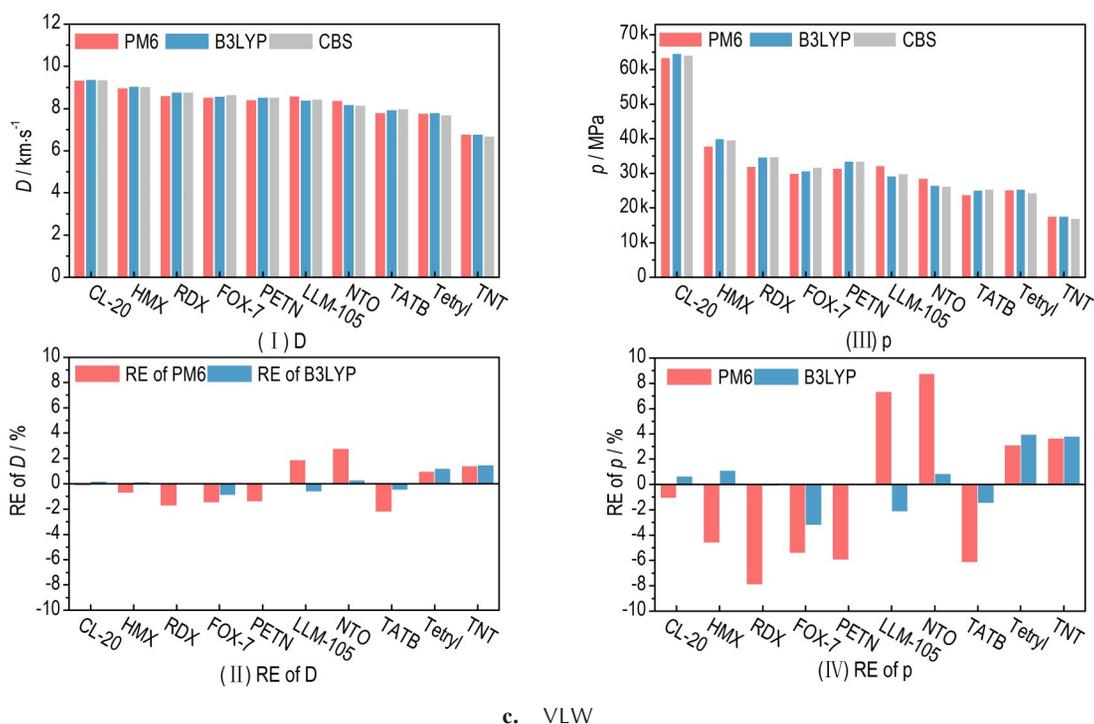


图5 基于3种不同模型计算获得10种含能分子的爆速、爆压及相对偏差

Fig.5 Detonation velocity, detonation pressure, and relative error of ten energetic molecules calculated by three different models

轰性能的偏差在可接受的范围内。此外,通过比较HOF偏差和爆轰性能偏差发现,尽管基于3种精度获得10种含能分子的HOF偏差较大,但该偏差对 Q 、 D 及 p 的影响较小。究其原因,一方面CHNO类含能分子的 Q 除了与分子本身HOF大小相关外,还与爆炸产物的种类和数量相关,产物HOF大小对 Q 的影响不可忽略;另一方面,根据K-J经验方程,密度对 D 和 p 的影响远大于 Q 对 D 和 p 的影响,即 $D \sim Q^{0.25}$, $p \sim Q^{0.5}$, $D \sim \rho$, $p \sim \rho^2$ 。因此,在高通量含能分子设计筛选中,选择中等水平的B3LYP方法即可满足HOF计算的精度需要,而选择合适的爆炸反应气体规则和准确预测密度的方法需要我们重点关注。

4 结论

基于3种量子化学计算方法和原子化方案计算获得了20种含能分子的气相HOF,结合升华焓获得了其固相HOF,基于实验密度、固相HOF和3种方法预测了10种常见含能分子爆轰性能,讨论了HOF的计算偏差对爆轰性能的影响程度。评估了面向高通量含能分子筛选的3种方法的适宜性,结论如下:

(1)用于HOF计算的3种不同精度的方法所耗时

时差别较大,PM6方法能够快速获得所需的结果, B3LYP方法的计算机时也在可接受范围内,而CBS方法耗时巨大,不满足高通量分子设计筛选中高效的要求。

(2)3种不同精度计算的HOF差别较大,以高精度的CBS方法为标准,PM6方法计算结果的平均绝对偏差为 $65.1 \text{ kJ} \cdot \text{mol}^{-1}$,而B3LYP方法计算结果的平均绝对偏差为 $34.2 \text{ kJ} \cdot \text{mol}^{-1}$ 。

(3)研究表明传统CHNO类含能材料的爆轰产物对爆热 Q 的贡献较大,故其HOF的计算偏差对 Q 的影响较小,其中基于PM6方法获得的HOF计算 Q 的平均RE为6.5%,而基于B3LYP方法获得的HOF计算 Q 的平均RE仅为2.8%。

(4)采用K-J、BKW和VLW模型预测了10种含能分子的 D 和 p ,发现在较大HOF的绝对偏差下,基于PM6方法获得的HOF计算 D 和 p 的平均RE分别小于1.6%和5.3%,基于B3LYP方法获得的HOF计算 D 和 p 的平均RE分别小于0.6%和1.9%。

综上所述,在高通量含能分子筛选中,HOF的预测采用中等精度的B3LYP方法即可满足高通量分子设计的筛选需要,已将此方法置于了含能材料高通量

计算平台 EM Studio 1.0, 作为默认的 HOF 计算方法^[68]。当然, 随着完善的基于等键反应方案的 HOF 程序的出现, 准确与效率兼顾的 HOF 计算方法将更有利于高通量含能分子筛选。

参考文献:

- [1] BADGUJAR D M, TALAWAR M B, ASTHANA S N, et al. Advances in science and technology of modern energetic materials: An overview [J]. *Journal of Hazardous Materials*, 2008, 151: 289-305.
- [2] MILLAR R, HAMID J, ENDSOR R, et al. Selection and synthesis of energetic heterocyclic compounds suitable for use in insensitive explosive and propellant compositions [J]. *Propellants Explosives Pyrotechnics*, 2010, 33(1): 66-72.
- [3] SCHMITT D, EYERER P, ELSNER. Insensitive high-performance energetic materials-applied research for optimized products[J]. *Propellants, Explosives, Pyrotechnics*, 1997, 22: 109-111.
- [4] GAO Hai-xiang, SHREEVE J M. Azole-based energetic salts[J]. *Chemical Reviews*, 2011, 111(11): 7377-7436.
- [5] BEHNLEIN-MAUSS J, KROEBER H. Technology of foamed propellants[J]. *Propellants, Explosives, Pyrotechnics*, 2009, 34: 239-244.
- [6] NIELSEN A T, CHAFIN A P, CHRISTIAN S L, et al. Synthesis of polyazapolycyclic caged polynitramines [J]. *Tetrahedron*, 1998, 54: 11793-11812.
- [7] DR M, EATON P E, DR R G. Hepta-and octanitrocubanes[J]. *Angewandte Chemie International Edition*, 2000, 39 (2) : 401-404.
- [8] ZHANG Wen-quan, ZHANG Jia-heng, DENG Mu-cong, et al. A promising high-energy-density material[J]. *Nature Communications*, 2017, 8(1):181.
- [9] ZHANG Q, SHREEVE J M. Growing catenated nitrogen atom chains [J]. *Angewandte Chemie International Edition*, 2013, 52(34): 8792-8794.
- [10] HE P, ZHANG J G, WANG K, et al. Combination multinitrogen with good oxygen balance: Molecule and synthesis design of polynitro-substituted tetrazolotriazine-based energetic compounds [J]. *Journal of Organic Chemistry*, 2015, 80 (11) : 5643.
- [11] BU Rupeng, XIONG Ying, ZHANG Chaoyang. II-II Stacking contributing to the low or reduced impact sensitivity of energetic materials[J]. *Crystal Growth Design*, 2020, 20: 2824-2841.
- [12] ZHANG Chaoyang, JIAO Fangbao, LI Hongzhen. Crystal engineering for creating low sensitivity and highly energetic materials[J]. *Crystal Growth Design*, 2018, 18:5713-5726.
- [13] 张朝阳. 含能材料研发的新模式——含能材料基因组研究计划 (EMGI)[J]. 含能材料, 2016, 24(6):520-522.
ZHANG Chao-yang. A new model for the research and development of energetic materials-energetic materials genome initiative (EMGI) [J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2016, 24(6):520-522.
- [14] 刘利民. 材料基因工程: 材料设计与模拟[J]. 新型工业化, 2015, 5(012):71-88.
LIU Li-ming. Genetic engineering of materials: Materials design and simulation[J]. *The Journal of New Industrialization*, 2015, 5(012):71-88.
- [15] LIU Yun, GROSSMAN J C. Accelerating the design of solar thermal fuel materials through high throughput simulations[J]. *Nano Letters*, 2014, 14(12): 7046-7050.
- [16] MARTIN R L, SIMON C M, SMIT B, et al. In silico design of porous polymer networks: High-throughput screening for methane storage materials[J]. *Journal of the American Chemical Society*, 2014, 136(13): 5006-5022.
- [17] VADDI K, WODO O. Metric learning for high-throughput combinatorial data sets [J]. *ACS Combinatorial Science*, 2019, 21(11): 726-735.
- [18] VARLEY J B, MIGLIO A, HA V A, et al. High-throughput design of non-oxide p-type transparent conducting materials: data mining, search strategy, and identification of boron phosphide[J]. *Chemistry of Materials*, 2017, 19(6) : 2568-2573.
- [19] YANG Ke-song, OSES C, CURTAROLO S. Modeling off-stoichiometry materials with a high-throughput ab-initio approach[J]. *Chemistry of Materials*, 2016, 28(16) : 6484-6492.
- [20] WANG Yi, LIU Yu-ji, YANG Zhi-jian, et al. Accelerating the discovery of insensitive high-energy-density materials by a materials genome approach [J]. *Nature Communications*, 2018, 9: 2444.
- [21] WEN Lin-yuan, YU Tao, LAI Wei-peng, et al. Accelerating molecular design of cage energetic materials with zero oxygen balance through large-scale database search [J]. *The Journal of Physical Chemistry Letters*, 2021: 11591-11597.
- [22] SONG Si-wei, CHEN F, WANG Yi, et al. Accelerating the discovery of energetic melt-castable materials by a high-throughput virtual screening and experimental approach [J]. *Journal of Materials Chemistry A*, 2021, 9: 21723-21731.
- [23] WEN Lin-yuan, WANG Bo-zhou, YU Tao, et al. Accelerating the search of CHONF-containing highly energetic materials by combinatorial library design and high-throughput screening [J]. *Fuel*, 2022, 310: 122241.
- [24] 何飘, 杨俊清, 李彤, 等. 含能材料量子化学计算方法综述[J]. 含能材料, 2018, 26(1): 34-45.
HE Piao, YANG Jun-qing, LI Tong, et al. Overview on the quantum chemical methods for energetic materials[J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2018, 26 (1): 34-45.
- [25] ZHANG Xiao-wen, ZHU Wei-hua, XIAO He-ming. Theoretical studies on heats of formation, detonation properties, and bond dissociation energies of monofurazan derivatives [J]. *International Journal of Quantum Chemistry*, 2010, 110 (8) : 1549-1558.
- [26] SANA M, LEROY G, PEETERS D, et al. The theoretical study of the heats of formation of organic compounds containing the substituents CH₃, CF₃, NH₂, NF₂, NO₂, OH and F [J]. *Journal of Molecular Structure Theochem*, 1988, 164 (3-4) : 249-274.
- [27] ZHANG Ji, XIAO He-ming, et al. Theoretical studies on heats of formation for polynitrocubanes using the density functional theory B3LYP method and semiempirical MO methods [J]. *Journal of Physical Organic Chemistry*, 2001, 14: 583-588.
- [28] CURTISS L A, RAGHAVACHARI K, REDFERN P C, et al. Assessment of Gaussian-2 and density functional theories for the computation of enthalpies of formation [J]. *Journal of Chemical Physics*, 1997, 106(3): 1063-1079.
- [29] BYRD E F C, RICE B M. Improved prediction of heats of forma-

- tion of energetic materials using quantum mechanical calculations [J]. *Journal of Physical Chemistry A*, 2006, 110 (3): 1005-13.
- [30] RICE B M, SHARMILA V P. Predicting heats of formation of energetic materials using quantum mechanical calculations [J]. *Combustion and Flame*, 1999, 118: 445-458.
- [31] 邱丽美, 贡雪东, 郑剑, 等. 由原子化反应法估算高能化合物的生成热[J]. 含能材料, 2008, 16(6): 647-651.
QIU Li-mei, GONG Xue-dong, ZHENG Jian, et al. Heats of formation for energetic compounds calculated using atomization reactions[J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2008, 16(6): 647-651.
- [32] GONG C Z, ZENG X L, JU X H. Comparative PM6 and PM3 study on heats of formation for high energetic materials [J]. *Computers and Applied Chemistry*, 2014, 31(4): 445-45.
- [33] MONTGOMERY J A, FRISCH M J, OCHTERSKI J W, et al. A complete basis set model chemistry. VI. Use of density functional geometries and frequencies [J]. *Journal of Chemical Physics*, 1999, 110(6): 2822-2827.
- [34] RICE B M, SHARMILA V P. Predicting heats of formation of energetic materials using quantum mechanical calculations [J]. *Combustion and Flame*, 1999, 118: 445-458.
- [35] PLITZER P, MURRAY J S, GRICE M E. Calculation of heats of sublimation and solid phase heats of formation [J]. *Molecular physics*, 1997, 91(5): 923-928.
- [36] POLITZER P, MURRAY J S. Some perspectives on estimating detonation properties of C, H, N, O compounds [J]. *Central European Journal of Energetic Materials*, 2011, 8(3): 209-220.
- [37] BULAT F A, TORO-LABBÉ A, BRINCK T, et al. Quantitative analysis of molecular surfaces: Areas, volumes, electrostatic potentials and average local ionization energies [J]. *Journal of Molecular Modeling*, 2010, 16(11): 1679-1691.
- [38] KAMLET M J, JACOBS S J. The chemistry of detonations. I. A simple method for calculating detonation properties of CHNO explosives [J]. *Journal of Chemical Physics*, 1968, 48 (1): 23-55.
- [39] KAMLET M J. Chemistry of detonations. III. evaluation of the simplified calculational method for chapman-jouguet detonation pressures on the basis of available experimental information [J]. *Journal of Chemical Physics*, 1968, 48(1): 43-50.
- [40] WANG Y, ZHANG J, SU H, et al. A simple method for the prediction of the detonation performances metal-containing explosives [J]. *Journal of Chemical Physics A*, 2014, 118(25): 4575-81.
- [41] SUČESKA M. Calculation of detonation parameters by EXPLO5 computer program [J]. *Materials Science Forum*, 2004, 465: 325-330.
- [42] SUČESKA M. EXPLO5-computer program for calculation of detonation parameters [C]// International Conference of Ict. Karlsruhe, Germany, 2001, pp. 110/1-110/13
- [43] 托马斯·马蒂亚斯·克拉珀特克. 高能材料化学 [M]. 北京: 北京理工大学出版社, 2016: 083-086.
KLAPÖTKE T M. Chemistry of high-energy materials [M]. Beijing: Beijing Institute of Technology Press, 2016: 083-086.
- [44] 欧育湘. 炸药学 [M]. 北京: 北京理工大学出版社, 2014: 24-30.
OU yu-xiang. Explosives [M]. Beijing: Beijing Institute of Technology Press, 2014: 24-30.
- [45] 吴雄, 龙新平, 何碧, 等. VLW 爆轰产物状态方程 [J]. 中国科学, 2008, 38(12): 1129-1132.
WU Xiong, LONG Xin-ping, HE Bi, et al. VLW equation of state for detonation products [J]. *Science in China*, 2008, 38 (12): 1129-1132.
- [46] CADY H H, LARSON A C, CROMER D T. The crystal structure of α -HMX and a refinement of the structure of β -HMX [J]. *Acta Crystallographica*, 1963, 16: 617-623.
- [47] CHOI C S, PRINCE E. The crystal structure of cyclotrimethylene-trinitramine [J]. *Acta Crystallographica*, 2010, 28 (9): 2857-2862.
- [48] BOOTH A D, LLEWELLYN F J. The crystal structure of pentaerythritol tetranitrate [J]. *Journal of the Chemical Society*, 1947: 837-846.
- [49] JÜRGEN E, THOMAS M K, MAYER P, et al. Alpha- and beta-FOX-7, polymorphs of a high energy density material, studied by X-ray single crystal and powder investigations in the temperature range from 200 to 423 K [J]. *Inorganic Chemistry*, 2006, 45(13): 4996-5007.
- [50] GILARDI R D, BUTCHER R J. 2, 6-Diamino-3, 5-dinitro-1, 4-pyrazine 1-oxide [J]. *Acta Crystallographica Section E*, 2001, 57(7): 0657-0658.
- [51] ZHUROVA E A, PINKERTON A A. Chemical bonding in energetic materials: β -NTO [J]. *Acta Crystallographica Section B Structural Ence*, 2001, 57(Pt 3): 359-365.
- [52] CADY H H, LARSON A C. The Crystal Structure of 1, 3, 5-Triamino-2, 4, 6-Trinitrobenzene [J]. *Acta Crystallographica*, 1965, 18(3): 485-496.
- [53] CADY H H. The crystal structure of N-methyl-N-2, 4, 6-tetraaminoaniline (tetryl) [J]. *Acta Crystallographica*, 1967, 23 (4): 601-609.
- [54] CARPER W R, DAVIS L P, EXTINE M W. Molecular structure of 2, 4, 6-trinitrotoluene [J]. *Journal of Physical Chemistry B*, 1982, 86: 459-462.
- [55] STARCHENKOV I B, MISHNEV V. Chemistry of furazano [3, 4-b] pyrazine. 1. Synthesis and thermodynamic appraisal of 4, 8-dihydrodifurazano [3, 4-b, e] pyrazine and its derivatives [J]. *Chemistry of Heterocyclic Compounds*, 1997, 33(10): 1219-1233.
- [56] CHAVEZ D E, BOTTARO J C, PETRIE M, et al. Synthesis and thermal behavior of a fused, tricyclic 1, 2, 3, 4-tetrazine ring system [J]. *Angewandte Chemie*, 2015, 54: 1293-1295.
- [57] CADY H H, LARSON A C, CROMER D T. The crystal structure of benzotrifuroxan (hexanitrosobenzene) [J]. *Blackwell Publishing Ltd*, 1966, 20(3): 336-341.
- [58] ZHANG Y, PARRISH D A, JEAN'NE M S. Derivatives of 5-nitro-1, 2, 3-2H-triazole-high performance energetic materials [J]. *Journal of Materials Chemistry A*, 2013, 1(3): 585-593.
- [59] CHOI C S. Refinement of 2-nitroguanidine by neutron powder diffraction [J]. *Acta Crystallographica*, 2010, 37 (10): 1955-1957.
- [60] KLAPÖTKE T M, PIERCEY D G, et al. 1, 1'-Azobis(tetrazole): A highly energetic nitrogen-rich compound with a N10 chain [J]. *Inorganic Chemistry*, 2011, 50(7): 2732-2734.
- [61] OYUMI Y, RHEINGOLD A L, BRILL T B. Thermal decomposition of energetic materials. 16. Solid-phase structural analysis and the thermolysis of 1, 4-dinitrofurazano [3, 4-b] piperazine [J]. *Journal of Physical Chemistry*, 1986, 90(19): 4686-4690.

- [62] ARCHIBALD T G, GILARDI R, BAUM K, et al. Synthesis and x-ray crystal structure of 1, 3, 3-trinitroazetidine [J]. *Cheminform*, 1990, 21(41):2920-2924.
- [63] KLAPATKE T M, PREIMESSER A, SCHEDLBAUER S, et al. Highly energetic salts of 3, 6-bishydrazino-1, 2, 4, 5-tetrazine [J]. *Central European Journal of Energetic Materials*, 2013, 10(2): 151-170.
- [64] STARCHENKOV I B, ANDRIANOV V G, MISHNEV A F. Chemistry of furazano [3, 4-b] pyrazine. 5.1, 2, 3-triazolo [4, 5-e] furazano [3, 4-b] pyrazine 6-oxides [J]. *Chemistry of Heterocyclic Compounds*, 1998, 29(11):1355-1359.
- [65] MURAYYEU N V. What shall we do with the computed detonation performance? comment on “1, 3, 4-oxadiazole bridges: A strategy to improve energetics at the molecular level” [J]. *Angewandte Chemie International Edition*, 2021, 60: 11568-11570.
- [66] POLITZER P, MURRAY J S. Impact sensitivity and the maximum heat of detonation [J]. *Journal of Molecular Modeling*, 2015, 21(10): 262.
- [67] POLITZER P, MURRAY J S. The role of product composition in determining detonation velocity and detonation pressure [J]. *China Health Industry*, 2014, 11(4): 459-474.
- [68] Energetic materials high-throughput computing interactive application system V1.0. 2021 [CP]; SR0611735.

Evaluation of Three Heat of Formation Calculation Methods for High-throughput Energetic Molecule Design and Screening

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Abstract: The performance prediction methods for high-throughput energetic molecule design and screening are required to balance accuracy and efficiency. In the present work, the suitability of three common theoretical methods on different levels, including semi-empirical PM6 method, density functional theory method B3LYP/6-31G(d,p), and high-precision complete basis set CBS-4 method, for heat of formation (HOF) prediction under the atomization scheme for high-throughput energetic molecule design and screening were evaluated. The solid HOF of twenty energetic molecules were compared, and the results of different theoretical levels are found to differ greatly. Based on the predicted HOF, experimental density, and three models (K-J, BKW and VLW), the detonation performance of ten common energetic molecules were predicted. The results show that B3LYP method possesses the best suitability and efficiency, and the predicted detonation performance is closed to that obtained by CBS method. For example, the average relative deviation of the detonation velocity and detonation pressure predicted by BKW are only 0.4% and 1.2%, respectively. However, both the low-precision PM6 method and the time-consuming CBS method are difficult to balance the requirements of precision and efficiency in high-throughput energetic molecule design and screening. It suggests that, for the high-throughput design of energetic molecules, a medium-precision method is adequate for rapid HOF prediction.

Key words: heat of formation; detonation performance; high-throughput design for energetic molecules; energetic materials; heat of formation calculation

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