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含能五唑离子盐的能量性能预估

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摘　要： 为了在同一水平上比较含能五唑离子盐的密度、生成热、爆速和爆压，采用密度泛函理论，对近两年合成的五大类16个非金属N_5^-离子盐进行了研究。结果表明在MP2/6-311++G(d,p)理论水平上，根据Born-Haber能量循环计算的五唑离子盐的生成热为95.2~1362.0 kJ·mol^{-1}，三唑类N_5^-离子盐的平均生成热最高。这些五唑离子盐的密度为1.395~1.650 g·cm^{-3}(298.15 K)，远远低于理论预测的全氮化合物的密度。通过Kamlet-Jacobs公式计算的爆速和爆压结果与EXPLO5的计算结果吻合良好，大部分五唑含能离子盐的爆速为6500~8000 m·s^{-1}；爆压为15~26 GPa，低于RDX的爆速和爆压。N_5^-的缩二胍盐、羟胺盐和肼盐的理论爆轰性能突出，它们的爆速(8622~9032 m·s^{-1})与RDX持平或者略高，爆压(29.5~32.3 GPa)均低于RDX，并未展现出全氮阴离子衍生物的明显优势，也远未达到对它们超高能量的预期。

关键词： 五唑负离子；生成热；密度；爆轰性能；含能离子盐

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1　引言

五唑负离子(N_5^-)的研究始于1903年[1]。1956年，Huisgen和Ugi[2-5]首次解决了芳基五唑(Ar-N_5)合成的难题，为N_5^-的合成奠定了基础。2017年南京理工大学的Hu和Lu[6]在Science上报道了一种甘氨酸亚铁和间氯过氧苯甲酸体系氧化切断Ar-N_5中的C—N键制备含N_5^-的固体化合物的方法。这是首次分离出室温稳定、含有N_5^-离子的复合盐$(N_5)_6(H_3O)_3(NH_4)_4Cl$，虽然这个含$N_5^-$的复合盐的晶体结构和相关表征存在争议[7-10]，但它标志着具有116年研究历史的N_5^-离子在凝聚相的成功合成，是全氮化合物史上具有里程碑意义的一步。

之后，大量关于N_5^-的研究成果如雨后春笋般涌现出来。首先是金属—N_5^-化合物的合成，包括$[Na(H_2O)(N_5)]\cdot 2H_2O$[11]、$[Na_8(N_5)_8(H_2O)_3]_n$[12]、MPF-1[13]、$[M(H_2O)_4(N_5)_2]\cdot 4H_2O$(M = Mn、Fe、Co、Zn)[11,14]、$[Mg(H_2O)_6(N_5)_2]\cdot 4H_2O$[11]、$[LiNa(N_5)_2(H_2O)_4]\cdot H_2O$[15]、$[Ba(N_5)(NO_3)(H_2O)_3]_n$[16]、$[NaBa_3(N_5)_6(NO_3)(H_2O)_3]_n$[16]、$[Cu(N_5)(N_3)]_n$[16]、$[Ag(N_5)]_n$[16]、$[Ag(NH_3)_2]^+[Ag_3(N_5)_4]^-$[17]、$[Na_5(CH_6N_3)(N_5)_9]^{3-}$[18]和$[(NaN_5)_2(C_2H_4N_4)]$[18]。但金属—$N_5^-$化合物的能量有限，为了追求更高的能量水平，一系列不含金属的含能五唑离子盐被开发出来[19-23]。根据与N_5^-离子配对的阳离子的类型，16个含能离子盐大体可以分为铵、肼、羟胺、胍和三唑五大类(图1)。然而上述文献报道的能量参数的计算方法不尽相同，相互比较存在一定困难。专门针对具有新型释能方式的全氮或者高氮化合物能量参数计算的方法也未开发出来。考虑到这些含能五唑离子盐中的绝大部分仍然具有传统含能材料的特点，本研究采用Gaussian09软件在同一理论水平计算了这16个含能离子盐的生成热，然后根据其

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298.15 K下的计算密度利用文献[24]计算其爆轰性能参数并进行比较。旨在通过本研究客观评价现有五唑离子盐的能量水平，并促进更高能量的五唑基化合物的开发。

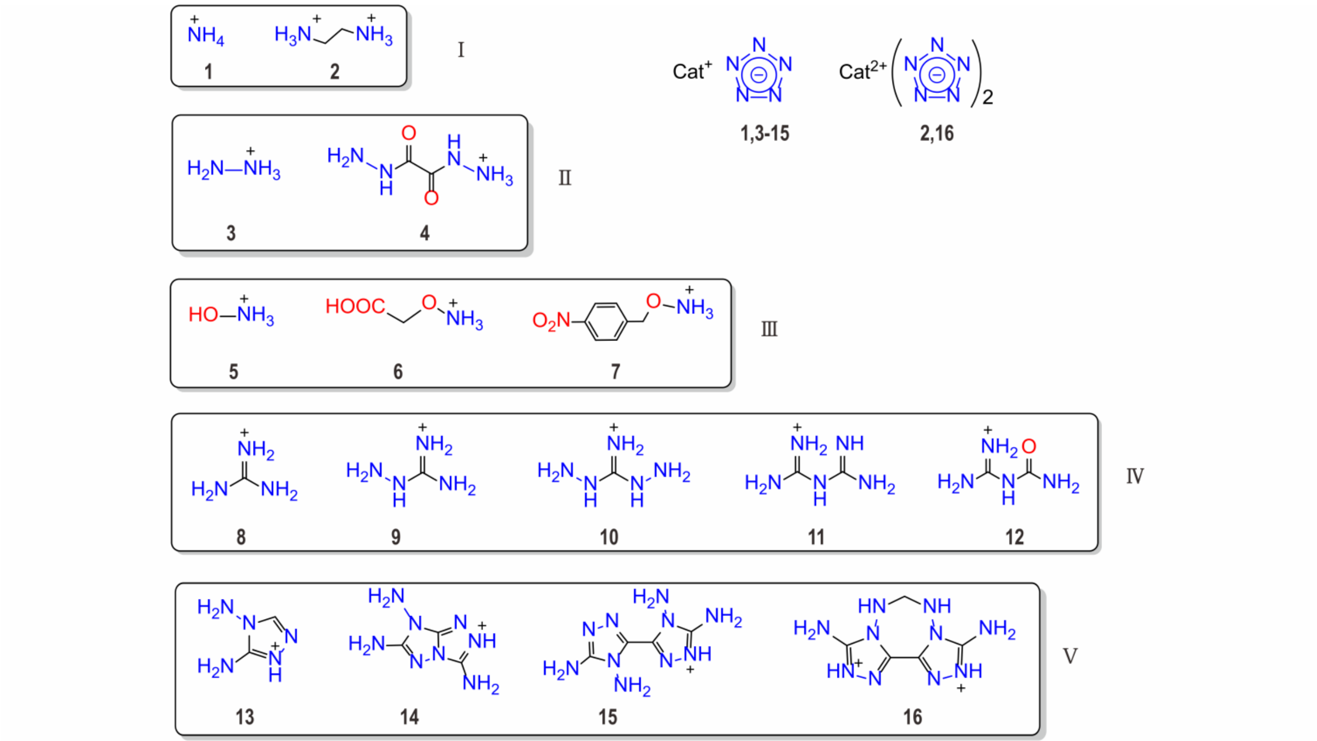

图1 五类含能五唑离子盐[19-23]及其结构

Fig.1 Five kinds of energetic pentazolatesalts[19-23] and their structures

2 计算方法

本研究使用Gaussian09软件[25]进行密度泛函理论（DFT）计算。运用B3LYP方法和6-31++G(d,p)基组，基于单晶结构进行几何结构的无约束优化和频率分析，以确保其势能面上的最小值且振动分析无虚频，即稳态结构，然后在MP2/6-311++G(d,p)水平上进行单点能计算。所涉及的离子生成热则通过相应的质子化反应计算得到。含能离子盐的固态生成热根据Born-Haber能量循环[26]（图2）可以简化为式(1)。

$$\Delta H_f^0(\text{salt}, 298\ \text{K}) = \Delta H_f^0(\text{cation}, 298.15\ \text{K}) + \Delta H_f^0(\text{anion}, 298.15\ \text{K}) - \Delta H_L \qquad (1)$$

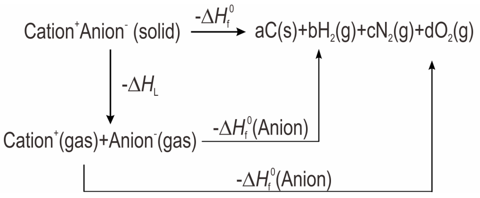

图2 含能离子盐形成反应的Born-Haber能量循环

Fig.2 Born-Haber cycle for the formation of energetic salts

式中，ΔH_L是离子盐M_pX_q的晶格能，kJ·mol⁻¹，根据Jenkins等[27]提出的公式(2)预测。

$$\Delta H_L = U_{POT} + \left[p\left(\frac{n_M}{2} - 2\right) + q\left(\frac{n_X}{2} - 2\right)\right]RT \qquad (2)$$

式中，n_M和n_X取决于离子M^{q+}和X^{p-}的性质，单原子离子等于3，线性多原子离子等于5，非线性多原子离子等于6。U_{POT}为晶格势能，kJ·mol⁻¹，通过式(3)计算。

$$U_{POT} = \gamma\left(\frac{\rho}{M}\right)^{\frac{1}{3}} + \delta \qquad (3)$$

式中，ρ是密度，g·cm⁻³；M是每摩尔离子盐的质量，g；γ和δ为系数，当q=p=1时，γ=1981.2 kJ·mol⁻¹·cm、δ=103.8 kJ·mol⁻¹；当q=2、p=1时，γ=6764.3 kJ·mol⁻¹·cm、δ=365.4 kJ·mol⁻¹[28]。

大部分离子盐（2和15除外）在298.15 K下的密度（$\rho_{298.15\ \text{K}}$）根据式(4)计算得到[29]。

$$\rho_{298.15\ \text{K}} = \frac{\rho_{cry}}{1 + 1.5 \times 10^{-4}(298.15 - T_{XRD})} \qquad (4)$$

式中，ρ_{cry}为单晶密度，g·cm⁻³；T_{XRD}为单晶衍射的温度，K。对于离子盐2和15，其密度通过式(5)计算[30]。

$$\rho = 1.026\frac{M}{V_{\text{corrected}}} + 0.0514\frac{V_S^+}{4.18585A_S^+} + 0.0419\frac{V_S^-}{4.18585A_S^-} + 0.0227 \qquad (5)$$

式中，M为每摩尔离子盐的质量，g；V_S^+和V_S^-分别代表阳离子表面正电势和阴离子表面负电势的平均值，kJ·mol^{-1}；A_S^+和A_S^-分别代表阳离子表面具有正电势部分和阴离子表面具有负电势部分的面积，Å^2；静电势相关参数通过Multiwfn软件计算[31]；$V_{\text{corrected}}$为校正体积，通过式(6)计算[32]。

$$V_{\text{corrected}} = V_{\text{uncorrected}} - [0.6763 + 0.9418 \times n_H] \qquad (6)$$

式中，$V_{\text{uncorrected}}$为阳离子与阴离子的体积之和，cm^3，通过式(7)计算[32]；n_H为离子盐中H原子的数目。单个离子的体积($V_{M^{q+}}$或$V_{X^{p-}}$)可通过DFT方法估算。

$$V_{\text{uncorrected}} = pV_{M^{q+}} + qV_{X^{p-}} \qquad (7)$$

五唑离子盐的爆速和爆压通过Kamlet-Jacobs公式[33]计算。所涉及到的生成热和密度为上述方法计算所得。最后得到的爆速和爆压偏大，因为实际装药密度远远达不到晶体密度。

3 结果与讨论

3.1 含能盐的密度

这些五唑离子盐的密度为1.395~1.650 g·cm^{-3}(表1)，远低于理论预测的全氮化合物的密度(2.0~3.9 g·cm^{-3})[34]，甚至低于三硝基甲苯(TNT)的密度[35](1.65 g·cm^{-3})。据文献报道，这些阳离子形成的含能离子盐中不乏高密度者，比如3-二硝基甲基-1，2，4-三唑酮羟胺盐[36](1.910 g·cm^{-3})、二硝胺基呋咱肼盐[37](1.873 g·cm^{-3})、1-三硝基甲基-3-硝基-5-硝胺基三唑铵盐[38](1.88 g·cm^{-3})和1-硝胺基-2，4-二硝基咪唑肼盐[39](1.93 g·cm^{-3})。所以，N_5^-的低密度以及它与阳离子的作用特性[40]是造成这些五唑离子盐密度较低的主要原因。这几类五唑离子盐中，平均密度较高的是第Ⅴ类，它们的共同点是阳离子均为几乎呈平面结构的环状三唑衍生物。稠合三环阳离子比双环阳离子更有利于提高五唑离子盐的密度，单环三唑阳离子的离子盐密度最低。另外，对比化合物**11**和**12**发现，含氧的阳离子有利于提高五唑离子盐的密度。这一点也从化合物**4**~**6**的密度上得到验证。

3.2 含能盐的生成热

对于含能五唑离子盐，它们的生成热在其潜在性能的评估中起关键性作用。298.15 K下N_5^-的生成热为255.9 kJ·mol^{-1}，与文献在G3(MP2)(269.6 kJ·mol^{-1})[42]，CCSD (T)/aug-cc-pVTZ (249.37 kJ·mol^{-1})[43]，MP2 (FU)/6-31G (d) (254.6 kJ·mol^{-1})[44]，CCSD (T)/6-311+G(3df)((260±15) kJ·mol^{-1})[45]，和RI-MP2-fc/TZVPP(263.59 kJ·mol^{-1})[46]基组水平下的计算结果相吻合。阳离子的生成热、离子盐的晶格能和离子盐的生成热结果见表2。这些离子盐的生成热为0.59~7.91 kJ·g^{-1}，均为正值且高于TNT(−0.35 kJ·g^{-1})[35]和环三亚甲基三硝胺(RDX，0.36 kJ·g^{-1})[36]的生成热。其中第Ⅴ类——三唑衍生物阳离子的N_5^-离子盐的平均生成热最高，充分体现出环状的多氮阳离子在提高N_5^-离子盐生成热方面比链状或者简单阳离子更具有优势。

表1 五类含能五唑离子盐的密度

Table 1 The densities of the five kinds of energetic pentazolate salts

comp.		T_{XRD} / K	ρ_{cry} / g·cm^{-3}	$\rho_{298.5\ K}$ / g·cm^{-3}	reference
Ⅰ	**1**	150	1.519	1.486	[22]
		153	1.520	1.488	[21]
	2	100	1.462 (**2**·H_2O)	1.395	[23]
Ⅱ	**3**	150	1.618	1.583	[22]
		153	1.620	1.586	[21]
	4	173	1.681	1.650	[19]
Ⅲ	**5**	153	1.636	1.601 (1.71)$^{1)}$	[21]
	6	205	1.666	1.643	[23]
	7	150	1.547	1.513	[23]
Ⅳ	**8**	153	1.515	1.483 (1.60)$^{1)}$	[21]
	9	150	1.476	1.444	[22]
	10	173	1.465	1.438	[22]
	11	150	1.524	1.491	[22]
	12	173	1.596	1.567	[19]
Ⅴ	**13**	150	1.618	1.583	[22]
	14	173	1.645	1.615	[22]
	15	173	1.520 (**15**·3H_2O)	1.624	[20]
	16	173	1.660	1.629	[19]

Note: 1) Values in brackets are from the Ref. [41].

对于离子盐**5**和**8**，陆明[41]教授曾在其合成之前就预估了它们的生成热数据(262.2 kJ·mol^{-1}和186.9 kJ·mol^{-1})，但未公布计算方法和基组水平。根据本研究的计算，之前的预估结果偏低。

3.3 含能盐的爆轰性能

含能五唑离子盐的爆轰性能的预估对于判断这些已合成的离子盐是否具有应用潜力和工艺放大的必要性具有重要意义。五类含能五唑离子盐的爆速(D)和

爆压(p)结果以及文献值如表3所示。本研究的结果与文献[19-23]中EXPLO5软件计算的结果吻合较好，并且略低于EXPLO5软件计算的结果。大部分五唑含能离子盐的爆速为6500~8000 m·s^{-1}；爆压为15~26 GPa，低于RDX[36]的爆速和爆压(8748 m·s^{-1}；34.9 GPa)。离子盐11的爆轰性能最高，其次为离子盐5和3，它们的爆速(8622~9032 m·s^{-1})与RDX持平或者略高；爆压(29.5~32.3 GPa)均低于RDX。

表2 五类含能五唑离子盐的生成热

Table 2 The heats of formation of the five kinds of energetic pentazolate salts

comp.		ΔH_f(cation, 298.15 K) / kJ·mol^{-1}	ΔH_L / kJ·mol^{-1}	ΔH_f(salt) / kJ·mol^{-1}	ΔH_f(salt) / kJ·g^{-1}
Ⅰ	1	626.4 (639.2)$^{2)}$	613.2 (589.4)$^{2)}$	269.1 (308.1)$^{2)}$	3.06
	2	1709.0	1664.7	556.1	2.75
Ⅱ	3	770.0 (776.1)$^{2)}$	596.3 (563.0)$^{2)}$	429.6 (471.3)$^{2)}$	4.17
	4	645.1	512.9	388.1	2.05
Ⅲ	5	669.5 (681.9)$^{2)}$	597.8 (568.9)$^{2)}$	327.6 (262.2)$^{1)}$ (371.7)$^{2)}$	3.15
	6	373.0	533.7	95.2	0.59
	7	961.9	471.4	746.4	3.12
Ⅳ	8	566.7 (583.5)$^{2)}$	551.0 (529.9)$^{2)}$	271.6 (186.9)$^{1)}$ (312.3)$^{2)}$	2.09
	9	667.4	531.2	392.1	2.70
	10	769.0	516.9	508.0	3.17
	11	1618.0	511.9	1362.0	7.91
	12	465.5	518.0	203.4	1.17
Ⅴ	13	905.6	521.8	639.7	3.76
	14	1085.0	487.1	853.8	3.79
	15	1266.6	463.5	1059.0	3.96
	16	2314.2	1484.8	1341.2	3.83

Note: 1) Values in brackets are from the Ref.[41]. 2) Values in brackets are from the Ref.[42].

表3 五类含能五唑离子盐的爆轰性能

Table 3 The detonation properties of the five kinds of energetic pentazolate salts

comp.		$\rho_{298.5\ K}$ / g·cm^{-3}	ΔH_f(salt) / kJ·g^{-1}	D / m·s^{-1}	p / GPa	OB (CO_2) / %
Ⅰ	1	1.487$^{1)}$	3.06	7511 (7757)$^{2)}$ (9280)$^{5)}$	22.1 (23.2)$^{2)}$ (27.3)$^{5)}$	−36.36
	2	1.395	2.75	6736 (6896)$^{3)}$	17.0 (17.5)$^{3)}$	−71.29
Ⅱ	3	1.585$^{1)}$	4.17	8622 (8796)$^{2)}$ (10400)$^{5)}$	29.5 (30.8)$^{2)}$ (37.0)$^{5)}$	−38.83
	4	1.650	2.05	8055 (8320)$^{4)}$	26.8 (27.1)$^{4)}$	−46.53
Ⅲ	5	1.601	3.15	8779 (9005)$^{2)}$(9930)$^{5)}$	31.5 (32.7)$^{2)}$ (35.8)$^{5)}$	−15.38
	6	1.643	0.59	7726 (7870)$^{3)}$	26.4 (26.0)$^{3)}$	−39.48
	7	1.513	3.12	7197 (7121)$^{3)}$	19.7 (20.1)$^{3)}$	−103.68
Ⅳ	8	1.483	2.09	6573 (7960)$^{5)}$	16.9 (20.1)$^{5)}$	−61.54
	9	1.444	2.70	6938 (7189)$^{2)}$	18.9 (19.6)$^{2)}$	−60.69
	10	1.438	3.17	7310 (7505)$^{2)}$	21.0 (21.2)$^{2)}$	−60.00
	11	1.491	7.91	9032 (9257)$^{2)}$	32.3 (33.0)$^{2)}$	−74.42
	12	1.567	1.17	6816 (6920)$^{4)}$	18.7 (18.9)$^{4)}$	−60.07
Ⅴ	13	1.583	3.76	7701 (7824)$^{2)}$	23.5 (24.5)$^{2)}$	−65.88
	14	1.615	3.79	7515 (7791)$^{2)}$	24.1 (24.6)$^{2)}$	−67.56
	15	1.624	3.96	7638 (7741)$^{6)}$	25.2 (24.8)$^{6)}$	−74.84
	16	1.629	3.83	7520 (7615)$^{4)}$	23.3 (23.6)$^{4)}$	−68.52

Note: 1) Average value. 2) Values in brackets are from the Ref.[22]. 3) Values in brackets are from the Ref.[23]. 4) Values in brackets are from the Ref.[19]. 5) Values in brackets are from the Ref.[42]. 6) Values in brackets are from the Ref.[20].

4 结论

（1）采用Gaussian09软件在MP2/6-311++G(d,p)理论水平上对已合成的五大类16个非金属五唑含能离子盐进行了生成热计算；根据低温下的晶体密度计算了298.15 K下五唑含能离子盐的密度；通过Kamlet-Jacobs公式计算了五唑含能离子盐的爆速和爆压。

（2）环状、平面型和含氧的阳离子有利于提高N_5^-含能盐的密度；环状的多氮阳离子有利于提高N_5^-含能盐的生成热。目前合成的非金属五唑含能离子盐的密度均低于TNT，生成热均大于RDX，综合爆轰性能参数在小于或等于RDX的水平。

（3）N_5^-缩二胍盐的能量性能超过了其羟胺盐和肼盐，在目前合成的所有N_5^-离子盐中性能较为突出，但远未达到对N_5^-含能化合物超高能量的预期。

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Prediction of the Energetic Performance of Pentazolate Salts

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Abstract: In order to compare the densities, heats of formation, detonation velocities, and detonation pressures of the energetic pentazolate salts at the same level, density functional theory (DFT) method was used to study the sixteen N_5^- based nonmetallic energetic salts synthesized in the past two years. According to the Born-Haber energy cycle, the calculated heats of formation of the pentazolate salts are between 95.2 kJ·mol^{-1} and 1362.0 kJ·mol^{-1} at the MP2/6-311++G(d,p) level. The average heat of formation of the salts formed by the triazole-containing cation and N_5^- is the highest among the five types of N_5^- salts. The densities (at 298.15 K) of these pentazolate salts range from 1.395 g·cm^{-3} to 1.650 g·cm^{-3}, which are much lower than the theoretical densities of all-nitrogen compounds. The detonation velocities and detonation pressures calculated by the Kamlet-Jacobs formula agree well with the calculation results from EXPLO5. Most of the N_5^--containing ionic salts have detonation velocities between 6500 m·s^{-1} and 8000 m·s^{-1} and detonation pressures between 15 GPa and 26 GPa, which are lower than RDX. The theoretical detonation performance of biguanidinium, hydroxylammonium, and hydrazinium pentazolates are outstanding. Their detonation velocities (8622-9032 m·s^{-1}) are equal or slightly higher than that of RDX, and their detonation pressures (29.5-32.3 GPa) are lower than that of RDX. Thus, their predicted performance are not revolutionary. They do not exhibit the distinct advantages of all-nitrogen anion derivatives, and are far from the expectation of their ultra-high energy.

Key words: pentazolate anion; heat of formation; density; detonation performance; energetic ion salt

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