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联氮杂芳环含能化合物研究进展

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摘要: 联氮杂芳环化合物是一类重要的富氮含能化合物, 是国内外含能材料研究领域热点之一。氮杂芳环可通过 N—N、C—N 单键等不同键合方式而获得种类繁多的联氮杂芳环含能化合物, 主要包含对称型与非对称型两类结构, 也可按双环、三环及多环等环系特征进行分类。综述了咪唑、多氮唑等富氮环系通过 N—N、C—N 单键键合所形成的联氮杂芳环含能化合物研究进展, 重点评述了联氮杂芳环的构建方法及其含能化合物合成技术途径探索, 同时, 简要介绍了典型联氮杂芳环含能化合物的物化与爆轰性能。发展简捷、高效及条件温和的新型环系合成方法, 引入新型高能基团, 设计新型联氮杂芳环含能化合物应是今后该领域研究的重点。

关键词: 联氮杂芳环; 富氮含能化合物; 合成与性能; 综述

中图分类号: TJ55; O62

文献标志码: A

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1 引言

咪唑、氧化咪唑、三唑、四唑及四嗪等氮杂芳环含有大量氮氮及碳氮键, 生成焓较高^[1-3]且燃烧产物清洁; 依据 Hückel 分子轨道理论^[4], 氮杂芳环体系的 π 电子数符合 $[4n+2]$ 规则且缺电子效应明显, 化学稳定性较高^[5], 因此, 富氮含能化合物多数具有氮杂芳环结构单元。现代战争对武器装备高效毁伤能力提出了更高要求, 而获得更高能量密度及氮含量水平的新型化合物则是提高含能材料性能的物质基础。目前, 氮杂单环含能化合物能量水平有限, 不能满足高能量密度材料发展的需求, 故迫切需要发展氮杂多环结构的新型含能化合物。目前获得氮杂多环高能化合物的技术途径主要有三类^[6-7]: (1) 氮杂稠环含能化合物; (2) 氮杂笼型含能化合物; (3) 联氮杂芳环含能化合物。氮杂稠环及氮杂笼型含能化合物国内外已有较多研究^[8-9]。近年, 数个氮杂芳环通过 C—C、C—N 及 N—N 单键键合形成的联氮杂芳环含能化合物成为氮杂多环高能化合物研究的新热点。

联氮杂芳环键合方式多样, 依据不同双环结构可分为对称型的双咪唑与双氧化咪唑含能化合物, 双四唑含能化合物, 双三唑含能化合物, 双咪唑含能化合物, 双异咪唑含能化合物; 非对称型的咪唑联四唑含能化合物, 四唑联三唑含能化合物等。除双环结构外还包含氮杂多咪唑含能化合物及其他氮杂多环含能化合物。较单环类型富氮芳环含能化合物, 联氮杂芳环体系的氮含量有所增加, 生成焓显著提升^[10], 同时现代有机合成化学的发展为各类富氮芳环间通过 C—C、C—N 及 N—N 单键键合提供了高效便捷的途径^[11-12], 令此类新型含能化合物的结构多样性构建成为可能。以 5,5'-联四唑-1,1'-二氧二羟胺 (HATO or TKX-50)^[13-14]、1,1'-二羟基-3,3'-二硝基-5,5'-联-1,2,4-三唑二羟胺盐 (MAD-X1)^[15] 及 3,4-双(4-硝基咪唑-3-基)-氧化咪唑 (DNMF)^[16] 为代表的一批联氮杂芳环含能化合物因合成较为简捷且综合性能突出, 成为近年来含能材料领域的标志性研究成果。但总体而言, 相关环系构建策略仍较为有限, 实现更为高效、多样的环系构建方法及键合模式仍是该领域研究进一步的发展方向。为此, 本文综述了目前联氮杂芳环含能化合物的环系构建方法, 从不同类型键合单键和环系特征的角度对联氮杂芳环结构体系进行了梳理, 同时就典型联氮杂芳环含能化合物的性能及应用前景进行了讨论, 以期对此类新型含能化合物的进一步研发提供参考。

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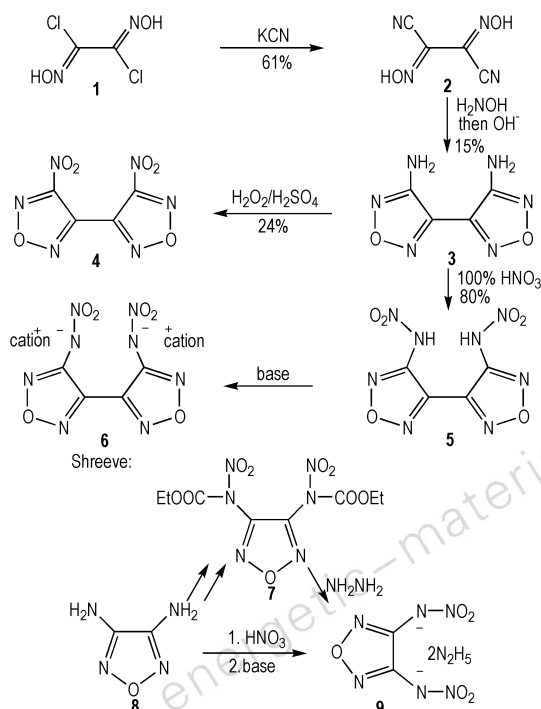
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2 含能富氮双环化合物

2.1 对称型富氮双环含能化合物

2.1.1 双呋咱与双氧化呋咱含能化合物

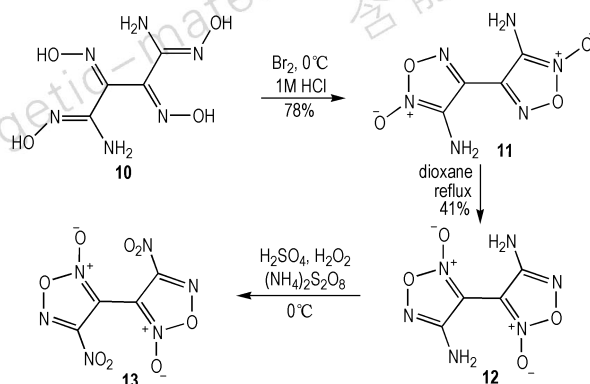
呋咱、氧化呋咱是重要的含能化合物结构单元^[17-19],在分子中引入呋咱、氧化呋咱可以显著提高含能化合物的密度^[20]并改善氧平衡^[21]。1985年Coburn等^[22]通过二氯乙二肼制备二氰基乙二肼,之后经羟胺进攻并环化构建4,4'-二氨基-3,3'-二呋咱**3**,将氨基通过双氧水氧化生成3,3'-二硝基-4,4'-二呋咱**4**。Coburn等为此类对称二环体系的研究做出了开创性工作,2014年,Klapötke等^[23]在化合物**3**基础上制备出多种的含能离子盐(Scheme 1),其中羟胺盐爆轰性能优异(爆速9363 m·s⁻¹,密度1.93 g·cm⁻³,摩擦感度288 N,撞击感度11 J,静电感度0.1 J)。2015年,Shreeve等^[24]首次实现了类似单环体系3,4-二硝胺呋咱合成,通过路线优化发展了安全性可接受的工艺过程,进一步证实了呋咱硝胺化化合物的潜在应用前景。



Scheme 1 Synthesis of nitramines with furazan structure^[22-24]

富氮芳环间通过C-C单键键合有可能提高分子密度。2014年,Klapötke等^[25]对对称型双硝基氧化呋咱结构的合成进行了探索(Scheme 2):化合物**10**经环化,重排得到4,4'-二氨基-3,3'-二氧化呋咱**12**,之后氧化发现仅痕量的**13**可被高分辨质谱检测到。

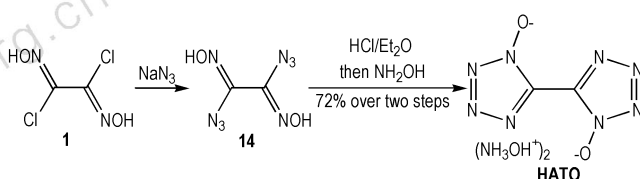
化合物**13**结构高度紧凑,计算结果表明其晶体密度173 K下达到2.007 g·cm⁻³,氧平衡为零,理论爆速为9525 m·s⁻¹,整体能量水平与RDX^[25]相近(90 K下密度1.858 g·cm⁻³,氧平衡-22,理论爆速8855 m·s⁻¹),但鉴于化合物**12**中氨基所连接的氧化呋咱环电子云密度过低,其有效氧化尚有待继续研究。



Scheme 2 Synthesis of diaminobisfuroxane^[25]

2.1.2 双四唑含能化合物

二氯乙二肼中氯原子可被多种负离子取代并成环,如2012年毕福强^[13]及Klapötke等^[14]利用NaN₃取代二氯乙二肼中氯原子并环化制备HATO(Scheme 3),其密度近1.9 g·cm⁻³,爆速9698 m·s⁻¹,静电感度0.1 J,略高于RDX,HMX(表1)。HATO合成简捷且能量水平优异,摩擦感度和撞击感度较低,在高能炸药领域具有较好的应用前景。2014年,赵廷兴等^[26]实现了HATO的50 g量级制备,近期西安近代化学研究所完成了其10 kg级工程化制备。



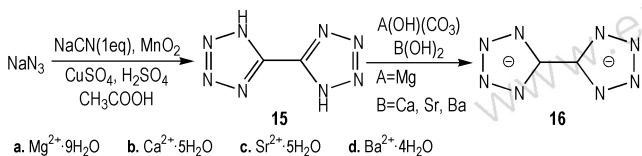
Scheme 3 Synthesis of HATO^[13-14]

2008年,Klein等^[27]实现了5,5'-联四唑双负离子**16**与部分稀土金属成盐产物,之后2011年Klapötke等^[28]系统研究了5,5'-联四唑双负离子**16**与碱土金属成盐产物(Scheme 4),其中35%的Sr-BT,40% NH₄NO₃,18%金属Mg及7%乙烯醇酯树脂(VAAR)混合体系**16c**和30% Ba-BT,35% NH₄NO₃,11%金属Mg,17% PVC及7% VAAR混合体系**16d**燃烧分别快速呈现高强度无烟红色和白色火焰,燃烧后无任何残留,是潜在的绿色高能烟火剂。

表 1 HATO 与部分高能炸药性能比较^[14]Table 1 Performance comparison of HATO and some high energy explosives^[14]

explosive	impact sensitivity/J	friction sensitivity /N	$\rho/\text{g} \cdot \text{cm}^{-3}$	oxygen balance/%	$T_{\text{dec}}/^\circ\text{C}$	$D_{\text{det}}/\text{m} \cdot \text{s}^{-1}$	$\Delta H_f/\text{kJ} \cdot \text{mol}^{-1}$
TNT	15	353	1.648	-73.96	290	7459	-55.5
RDX	7.5	120	1.806	-21.61	210	8983	86.3
HMX	7	112	1.904	-21.61	279	9221	116.1
CL-20	4	48	2.035	-10.95	215	9455	365.4
HATO	20	120	1.877	-27.10	221	9698	446.6

Note: ρ is density; T_{dec} is temperature decomposition; D_{det} is detonation velocity; ΔH_f is enthalpy of formation.

Scheme 4 Synthesis of alkaline earth metal salts of 5,5'-bistetrazole^[28]

BT 胺化无法通过成环后直接引入胺基实现,为实现 BT 氮原子的胺化,2014 年,Klapötke 等^[29]采取迂回的方式构建含胺基的前体后环化,硝化中和得到 5,5'-联四唑-1,1'-二胺二钾盐 (K_2 DNABT) (Scheme 5)。2015 年,Yedukondalu 等^[30]就 K_2 DNABT 的结构稳定性等进行了研究。 K_2 DNABT 密度 $1.93 \text{ g} \cdot \text{cm}^{-3}$,爆速 $9967 \text{ m} \cdot \text{s}^{-1}$ 且感度较高(摩擦感度 $<1 \text{ N}$,撞击感度

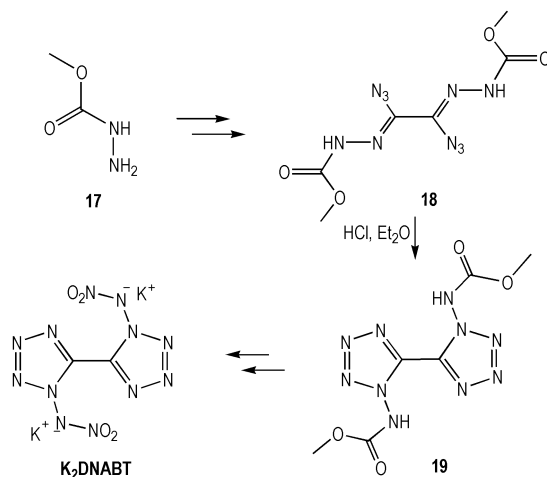
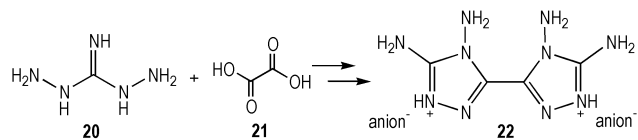
表 2 K_2 DNABT 与 PbN_3 部分爆轰及计算性能比较^[29]Table 2 Comparison of the some detonation properties data and the calculated performance ones of lead azide and K_2 DNABT^[29]

explosive	impact sensitivity/J	friction sensitivity/N	$r/\text{g} \cdot \text{cm}^{-3}$	oxygen balance/%	$T_{\text{dec}}/^\circ\text{C}$	$D_{\text{det}}/\text{m} \cdot \text{s}^{-1}$	$\Delta H_f/\text{kJ} \cdot \text{mol}^{-1}$
PbN_3	2.5-4	0.1-1	4.8	-11.0	315	5920	450.1
K_2 DNABT	1	<1	2.17	-4.8	200	8330	326.4

2.1.3 双三唑含能化合物

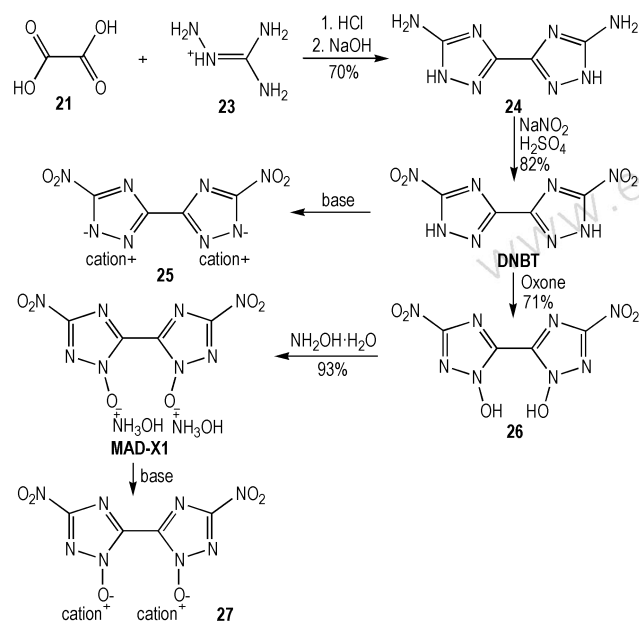
2015 年,Klapötke 等^[31]利用廉价的二氨基胍(盐酸盐)与草酸(二水合物)为原料一步法合成出高热稳定性的化合物 22,通过复分解反应所得离子盐 4,4',5,5'-四氨基-3,3'-双-1,2,4-三唑阳离子体系与不同富氧阴离子配对,合成了多种高热稳定性的含能离子盐 (Scheme 6)。其成盐产物密度可达 $1.826 \text{ g} \cdot \text{cm}^{-3}$,热分解温度 $342 \text{ }^\circ\text{C}$,生成热 $301.5 \text{ kJ} \cdot \text{mol}^{-1}$,理论爆速 $9053 \text{ m} \cdot \text{s}^{-1}$,与 TNT 相容性良好且摩擦、撞击及静电感度(5 J,360 N,0.8 J)适宜^[31],可作为潜在的廉价绿色高能钝感含能材料。

1 J),在高效起爆药领域具有一定的应用前景(表 2)。

Scheme 5 Synthesis of potassium 1,1'-dinitramino-5,5'-bistetrazolate^[29]Scheme 6 Synthesis of bis(3,4-diamino-1,2,4-triazolium) cation^[31]

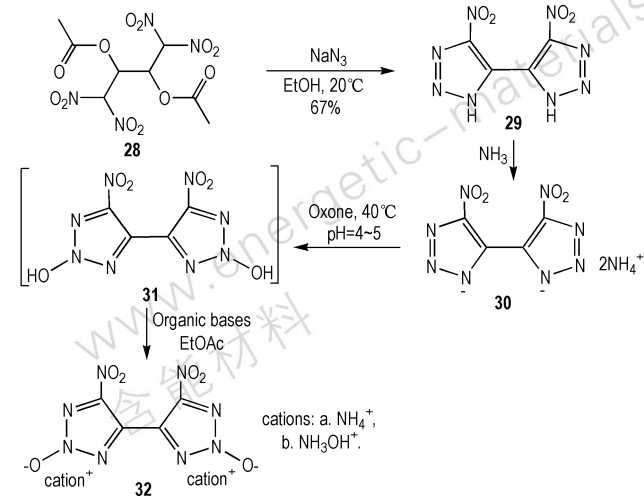
2013 年,Klapötke 等^[15]利用乙二酸为起始原料缩合环化及重氮化取代实现了 5,5'-二硝基-3,3'-联-1,2,4-三唑(DNBT)制备,DNBT 氧化可制备 1,1'-二羟基-3,3'-二硝基-5,5'-联-1,2,4-三唑二羟胺盐

(MAD-X1)。2015年,罗义芬等^[32]进一步对该MAD-X1的合成进行了探讨。MAD-X1经复分解反应获得一系列含能离子盐(Scheme 7)。Klapötke等的研究比较了MAD-X1与RDX的密度、爆速和爆压^[15],表明MAD-X1具有一定潜在的替代RDX作为无烟CMDB推进剂的应用前景。



Scheme 7 Synthesis of MAD-X1^[15]

1992年,Baryshnikov等^[33]利用消除及环化反应实现了4,4'-双(5-硝基-1,2,3-二氢-三唑)的合成,Shreeve等^[34]则于2014年在此基础上采取与MAD-X1研究工作相似策略,经Oxone的作用实现氧化。其含能离子盐32a与32b(Scheme 8)整体能量水平与RDX接近(表3),有望作为RDX替代品。



Scheme 8 Synthesis of nitro-1,2,3-triazoles^[33-34]

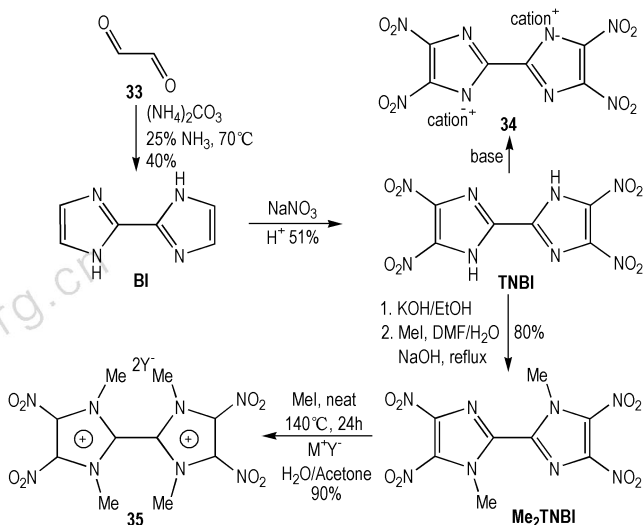
表3 32a和32b物理化学性质与RDX比较^[33]

Table 3 Comparison of the physicochemical properties of compounds 32a-b and RDX^[33]

explosive	impact sensitivity/J	ρ /g · cm ⁻³	oxygen balance/%	T_{dec} /°C	D_{det} /m · s ⁻¹	ΔH_f /kJ · mol ⁻¹
RDX	7.5	1.80	-21.61	210	8983	86.3
32a	>40	1.81	-10.9	251	8744	152.2
32b	-	1.88	0	172	9171	271.9

2.1.4 双咪唑含能化合物

1983年,Bernaducci等^[35]报道了乙二醛与氨缩合形成2,2'-联咪唑(BI)的方法,2012年,Klapötke等^[36]对BI进行硝化合成出4,4',5,5'-四硝基-2,2'-二咪唑(TNBI)同时制备了一系列的含能离子化合物(Scheme 9),而在2011年,Srinivasan等^[37]即对TNBI进行了计算化学研究。2015年,Lewczuk等^[38]对利用TNBI作为配体构建的铜离子配合物进行了研究,获得了该类化合物的配合物体系含能化合物。正离子胍含能离子盐具有优异的热稳定性($T_{dec} = 328$ °C)和较好的能量性能($D_{det} = 8070$ m · s⁻¹),可作为六硝基芪(HNS)^[39-40]的潜在替代品,在耐高温爆破器材等领域应用前景广阔。

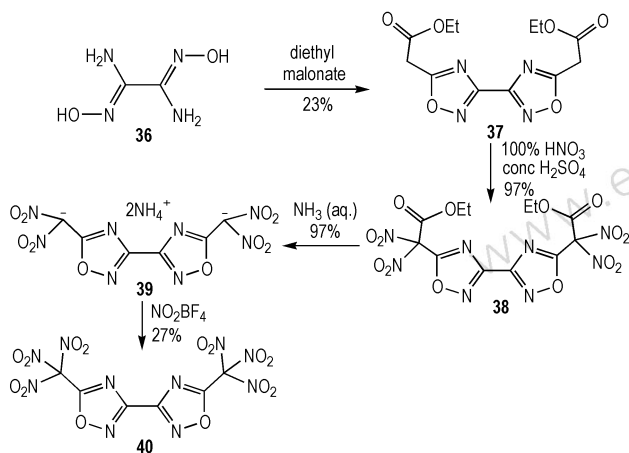


Scheme 9 Synthesis of 4,4',5,5'-tetranitro-2,2'-bisimidazole^[35-36]

2.1.5 双异咪唑含能化合物

富含含能杂环骨架连接硝仿基团研究较为有限,这与硝仿基的引入方法相对特殊有关^[41]。1991年,Kiseleva等^[42]实现了二氨乙二腈与丙二酸二乙酯环化构建对称结构37的工作。Klapötke等^[43]于2014年在此基础上利用不同硝化试剂对酯基邻位进行二硝

化反应,之后脱羧及再次硝化成功构建了硝仿基团 (Scheme 10)。100 K 下化合物 **40** 的密度高达 $2.02 \text{ g} \cdot \text{cm}^{-3}$,原因可能是分子内及分子间大量的氮原子与氧原子间的静电作用,而相关的爆轰参数尚未见报道。该研究为类似体系硝仿基团的引入提供了重要的参考。

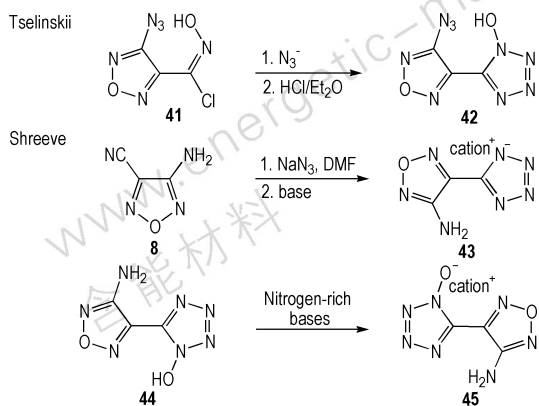


Scheme 10 Synthesis of bis(hydroxylammonium) 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolate)^[43]

2.2 非对称型双环含能化合物

2.2.1 呔咱联四唑含能化合物

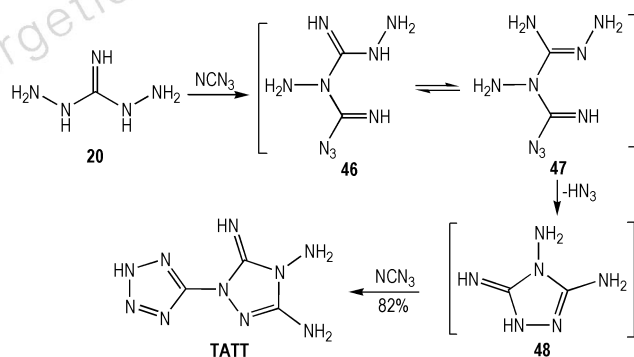
2001年 Tselinskii 等^[44]通过叠氮化钠与4-氨基-1,2,5-二氮唑基-3-氯羟胺**41**发生环化反应实现了呔咱与氧化四唑的连接。2015年,Shreeve 等^[45]利用该类结构制备了氨基取代呔咱联氧化四唑类含能离子化合物,与其之前所发展的氨基取代呔咱联四唑结构^[46]相比(Scheme 11)。氧化四唑与氨基呔咱所存在的分子间氢键大大增强了体系的稳定性,是潜在的不敏感高能炸药,也为类似不敏感材料的设计提供了借鉴。



Scheme 11 Synthesis of furazan-tetrazole structures^[44-46]

2.2.2 四唑联三唑含能化合物

1965年,Child 等^[47]利用氰基叠氮与二氨基胍**20**一锅煮实现3,4,5-三氨基-1-四唑基-1,2,4-三唑(TATT)的制备,但未能提出反应机理。2009年,Shreeve 等^[48]对该反应进行了深入机理探讨,认为氰基叠氮两次参与成环历程(Scheme 12)。TATT生成焓较高,热稳定性好且感度较低(表4),具有良好应用前景。



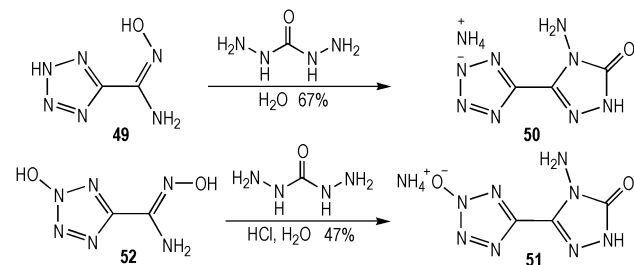
Scheme 12 Synthesis of TATT^[48]

表4 TATT与TNT, HMX及TATB性能比较^[48]

Table 4 Comparison of the properties of TATT with TNT, HMX and TATB^[48]

explosive	impact sensitivity / J	ρ / $\text{g} \cdot \text{cm}^{-3}$	oxygen balance / %	T_{dec} / $^{\circ}\text{C}$	D_{det} / $\text{m} \cdot \text{s}^{-1}$	ΔH_f / $\text{kJ} \cdot \text{mol}^{-1}$
TNT	15	1.648	18.50	290	7459	-55.5
HMX	7	1.904	37.84	279	9221	116.1
TATB	50	1.937	32.55	318	8114	-140
TATT	>60	1.685	76.90	324	8423	440

2014年, Klapötke 等^[49]合成了含能离子配体HATT,同年, Klapötke 等^[50]进一步通过ATT及HATT与金属离子 Cu^{2+} 及 Co^{2+} 形成相应的金属络合物(Scheme 13),而这两类化合物均可作为潜在的起爆药。

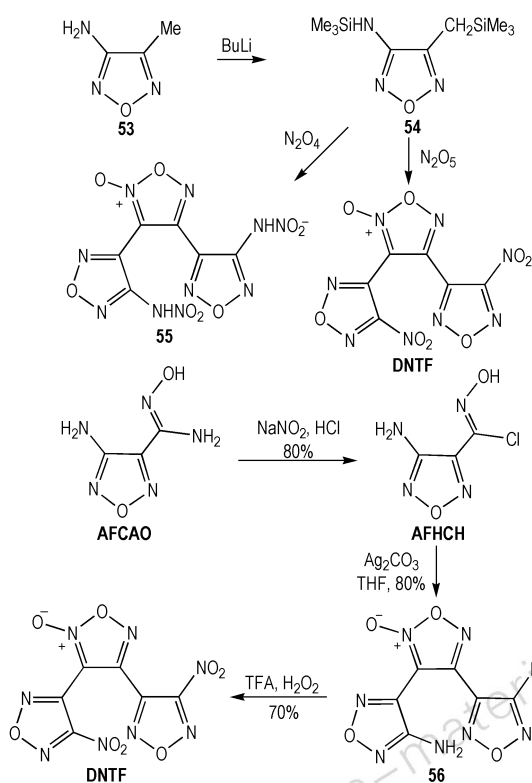


Scheme 13 Synthesis of 5-(4-amino-1,2,4-triazol-3-on-5-yl)-1H-tetrazole^[49] and 5-(4-amino-1,2,4-triazol-3-on-5-yl) tetrazole^[50]

3 氮杂多环含能化合物

3.1 多咪唑含能化合物

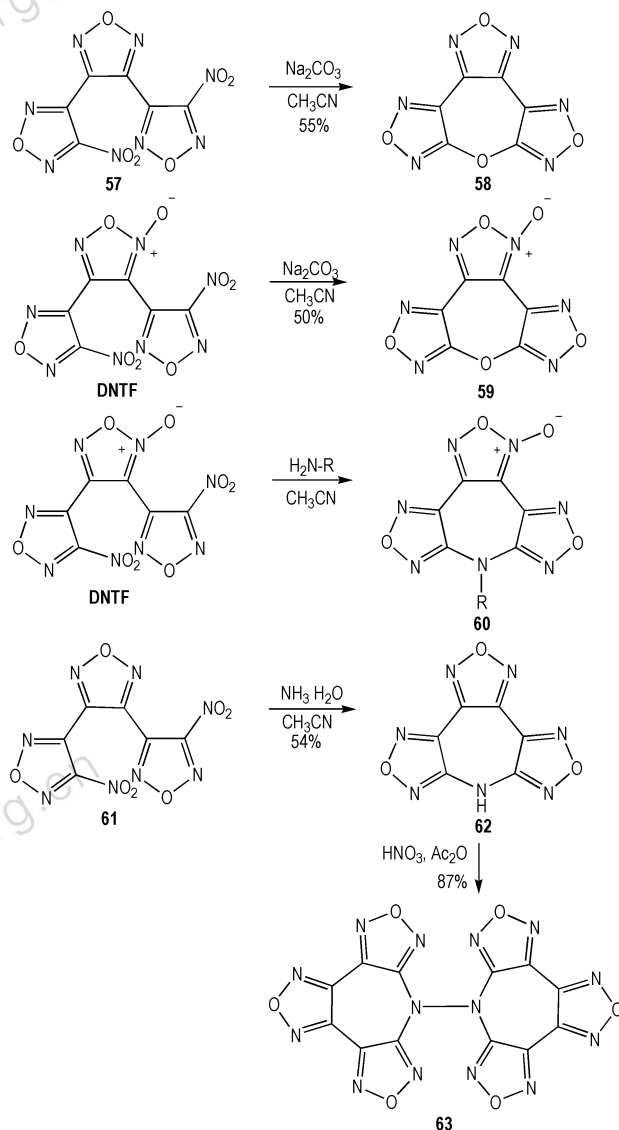
C—C 单键连接数个咪唑及氧化咪唑所形成的氮杂多环含能化合物具有较高的能量水平和较低的感受度。作为能量水平与 CL-20 接近的三代单质炸药, DNTF 分子较低(110 °C)的熔点和较为钝感的性质使其在熔铸炸药领域独具优势,针对 DNTF 的合成及性能已有相关综述报道^[16]。DNTF 分子及其类似物合成策略的核心是对其中咪唑及氧化咪唑体系的有效构建。2005 年, Sheremetev 等^[51] 利用甲基氨基咪唑为原料合成了 DNTF, 但产率仅 12%。2015 年, Tsyshevsky 等^[52] 报道了 DNTF 分子合成, 总收率 37%。(Scheme 14)。



Scheme 14 Synthesis of DNTF^[51-52]

咪唑醚类含能化合物具有熔点低、能量高、可塑性强的优点,2012 年,王锡杰等^[53] 及周彦水等^[54] 报道了三咪唑并氧杂环庚三烯(TFO)分子和双咪唑并[3,4-b:3',4'-f]氧化咪唑并[3'',4''-d]氧杂环庚三烯(BFFO)分子的结构及合成方法,该类方法分别以 3,4-双(3'-硝基咪唑-4'-基)咪唑(BNTF)及 DNTF 为原料进行分子内硝基醚化反应,实现了咪唑环醚的构建。

TFO 与 BFFO 熔点分别为 77 °C 和 92 °C,理论密度 1.935 g·cm⁻³ 及 1.866 g·cm⁻³,计算爆速分别为 8646 m·s⁻¹ 和 8256 m·s⁻¹,均有望作为熔铸炸药中的液相载体组份,也可作为固体推进剂中的含能增塑剂与氧化剂。与咪唑醚类研究类似,Stepanov 等^[55] 则以胺或胍作为亲核试剂与 BNFF 发生取代反应,合成了氮杂环庚三烯衍生物的结构,贾思媛等^[56] 利用类似的方法通过 HNO₃ 进一步将两个不同的氮杂环庚三烯进行了偶联(Scheme 15)。

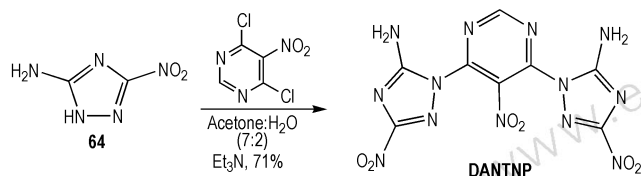


Scheme 15 Synthesis of TFO, BFFO and other analogues^[53-56]

3.2 其他氮杂多环含能化合物

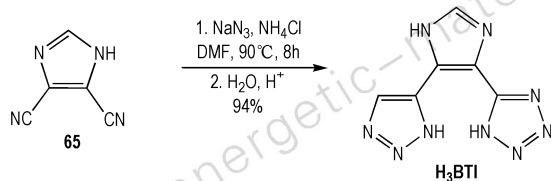
1989 年,Laval 等^[57] 利用 4,6-二氯-5-硝基嘧啶(DCNP)与 3-硝基-5-氨基-1,2,4-三唑(ANTA)钠盐

反应得到 5-硝基-4,6-双(5-氨基-3-硝基-三唑)咪啉(DANTNP)。DANTNP 密度为 $1.86 \text{ g} \cdot \text{cm}^{-3}$, 熔点大于 320°C , 爆速约为 $8600 \text{ m} \cdot \text{s}^{-1}$, 撞击感度达到 50 cm (Type 12), 是良好的高能、低感及耐热炸药^[58]。2008 年, 贾思媛等^[59]对其合成方法进行了改进(Scheme 16), 同年, 王伯周等^[60]利用计算化学辅助, 探讨了该分子热分解机理, 发现热分解始于 N—H 键的断裂。



Scheme 16 Synthesis of DANTNP^[57, 59]

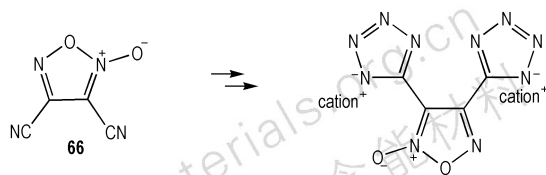
2008 年, Dinca 等^[61]人通过 Click 反应合成了 H_3BTI , 并以其为配体, 通过与 CoCl_2 在碱性条件下的自组装反应获得了一种具有混合价态的新型钴化合物(Scheme 17)。4,5-二(1H-四唑-5-基)-1H-咪唑(H_3BTI)的氮含量达到 68.61%, 分解产物氮气含量较高, 在低特征信号推进剂或气体发生剂领域具有潜在应用前景。2013 年, 毕福强等^[62]对其合成及热分解行为进行了研究: 结果表明, H_3BTI 无熔化过程, 324.6°C 时的放热峰为固相分解过程, 分解热约为 $208 \text{ kJ} \cdot \text{mol}^{-1}$ 。以不同升温速率的 DSC 研究了 H_3BTI 的非等温反应动力学, 研究结果表明, 热分解反应受随机成核和随后生长控制, 反应机理服从 $n=3/4$ 的 Avrami Erofeev 方程, 临界爆炸温度为 $T_{cr} = 556.38 \text{ K}$, 峰温处热分解反应的活化焓和活化自由能分别为 $193.66 \text{ kJ} \cdot \text{mol}^{-1}$ 和 $173.33 \text{ kJ} \cdot \text{mol}^{-1}$ 。



Scheme 17 Synthesis of H_3BTI ^[61-62]

2011 年, 周智明等^[63]利用二氰基取代的氧化咪唑, 通过 Click 反应快速构建了相应四唑-氧化咪唑-四唑的含能双负离子盐化合物(Scheme 18), 密度为 $1.56 \sim 1.85 \text{ g} \cdot \text{cm}^{-3}$, 爆速为 $7939 \sim 8915 \text{ m} \cdot \text{s}^{-1}$ 。该组合模式并未如化合物 DNTF(密度 $1.86 \text{ g} \cdot \text{cm}^{-3}$, 爆

速 $8930 \text{ m} \cdot \text{s}^{-1}$)那样具有较高的能量水平^[64], 因而极大限制了其应用研究的潜力。



Scheme 18 Synthesis of 3,4-bis(1H-5-tetrazolyl) furoxan^[63]

4 结论与展望

氮杂含能芳环因其结构中存在较多高能碳氮及氮氮键, 故氮含量及生成焓均较高, 燃烧产物清洁。氮杂单芳环通过 C—C、C—N 等单键进行键合, 合成了种类繁多的联氮杂芳环含能化合物, 有利于实现相关含能化合物的多样性合成。合成性能更为优异的联氮杂芳环含能化合物对含能材料领域的发展影响深远, 目前相关环系构建策略仍然较为有限, 在一定程度上限制了结构多样性的合成探索研究。下一步该领域研究应侧重以下两点。

(1) 富氮芳环体系结构多样, 发展简捷、高效及条件温和的新型环系合成方法将直接推动该类含能材料的发展, 引入 α -多硝甲基氧化偶氮基团^[65-67]等新型高能基团设计完成新型联氮杂芳环含能化合物应是下一阶段研究的重点。

(2) 不同环系的组合对联氮杂芳环含能化合物整体能量密度水平及稳定性有怎样的影响需进行深入的研究探索, 得出具有一定指导意义的理论数据和规律特点将直接影响此类含能化合物结构设计和性能预估。

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Review on the Aza-polyaromatic Ring Energetic Compounds

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Abstract: Aza-polyaromatic ring energetic compounds are a kind of important nitrogen-rich energetic compounds, which are one of the hotspots in the research field of energetic materials at home and abroad. A wide variety of various aza-polyaromatic ring energetic compounds were obtained via different bonding methods of C—C or C—N single bond etc of aza-aromatic rings. These compounds mainly contain two kinds of symmetrical and nonsymmetrical structures. Their classification is also performed according to ring system characteristics of bicyclic, tricyclic and polycyclic structures. The synthesis of aza-polyaromatic ring compounds is simple. Currently, a large number of new high energy density compounds with excellent properties were obtained. In this paper, the research progresses on aza-polyaromatic ring energetic compounds consisted of furazans or azoles etc nitrogen-rich ring system, which are connected by C—C or C—N single bond, were summarized. The construction methodologies of aza-polyaromatic ring and the synthesis technology route of aza-polyaromatic ring energetic compounds are emphatically reviewed, at same time, the physicochemical and detonation performances of typical aza-polyaromatic ring energetic compounds were briefly introduced. Developing the synthesis method of new ring system with simple, efficient and mild reaction conditions, introducing new energetic groups and designing new aza-polyaromatic ring energetic compounds should be the emphasis of research in this field in the next stage.

Key words: aza-polyaromatic compound; nitrogen-rich energetic compound; synthesis and performance; review

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