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亚胺基桥连的平面型富氮含能化合物的合成与性能

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摘要: 为了合成平面型的高能钝感富氮类含能化合物,以6-(3,5-二甲基吡唑)-[1,2,4]三唑[4,3-*b*][1,2,4,5]四嗪(1)为底物,与2,6-二氨基-3,5-二硝基吡嗪(2)在碱性条件下反应,合成了一NH—桥联的基于稠杂环体系的6-(2,6-二氨基-3,5-二硝基吡嗪)-1,2,4-三唑[4,3-*b*][1,2,4,5]四嗪(3),收率为81.3%。采用核磁、红外、X射线衍射等分析手段对化合物3的结构进行表征;利用差示扫描量热(DSC)研究了化合物3的热分解过程,其初始分解温度高达254.6℃;采用Gaussian 09 D.01和Explo5 V6.05.02软件计算化合物3的爆速和爆压分别为7568 m·s⁻¹和23.5 GPa;采用BAM法测得化合物3的撞击感度和摩擦感度分别为12.5 J和240 N。结果表明化合物3具有较好的爆轰性能和较低感度,同时较高的分解温度表明化合物3可以作为耐热性炸药。

关键词: 平面型;亚胺基桥联;富氮;含能材料

中图分类号: TJ55; O64

文献标志码: A

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1 引言

设计制备具有高能量密度、高稳定性和低感度的化合物一直是含能材料领域的主要研究内容。在新型含能化合物的分子设计中,将不同的取代基通过桥联的方式进行连接,从而提高爆轰性能和稳定性,是一种行之有效的手段,其中以—(CH₂)_n—^[1]、—N—N=N—N—^[2-5]、—N=N—^[6-7]、—NH—^[8-9]等进行桥联最为常见。—(CH₂)_n—为桥联的方式使得分子的含氮量降低,从而一定程度上降低了材料的爆轰性能。通过—N—N=N—N—键桥联的化合物,由于—N—N=N—N—键较长,稳定性较低,分子间的堆积较为稀疏,使得化合物通常热稳定性差,且密度低,不利能量的存储。以—N=N—和—N(O)=N—进行桥联,由于其自身的不稳定性,使材料的稳定性通常较差,大大降低了实际应用价值^[10]。亚胺基桥联是一种优异的桥联方式,—NH—

的存在一方面有利于形成分子内和分子间氢键,增强的分子间和分子内相互作用,使得材料形成紧密堆积,从而改善化合物的密度,另一方面可以通过氮上的孤对电子和相连的富氮杂环形成sigma-pi超共轭进而提高化合物的稳定性,能够有效地平衡爆轰性能和感度之间的矛盾。因此,采用亚胺基桥连是获得高能钝感含能材料的有效策略之一^[11]。

构造平面型的分子结构也是得到高密度,低感度的含能材料的方法之一^[12-15]。含有氨基和硝基官能团的平面芳族或杂芳族体系组成的含能化合物通常具有高能钝感的优异性能^[16-17],例如典型的1,3,5-三氨基-2,4,6-三硝基苯(TATB)和2,6-二氨基-3,5-二硝基吡嗪-1-氧(LLM-105)。TATB和LLM-105的平面结构^[18],使得材料的感度大大降低,导致这类化合物具有较高的机械感度。此外,—NO₂和—NH₂的大量存在能够提高炸药的含氮量,有利于爆轰性能的提升。尤其是,当—NO₂与—NH₂处于邻位时,可形成分子内氢键,从而在稳定分子和提高化合物密度中起着重要作用^[19-21]。

本研究拟以—NH—为桥,连接两个富氮模块,形成平面型含能分子,同时在富氮模块上引入邻位的—NO₂和—NH₂,从而得到高能钝感的含能化合物。以6-(3,5-二甲基吡唑)-[1,2,4]三唑[4,3-*b*][1,2,4,5]四嗪(化合物1)为底物,与2,6-二氨基-3,5-二硝

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基吡嗪(化合物2)在碱性条件下反应,合成了-NH-桥联的具有稠杂环体系的6-(2,6-二氨基-3,5-二硝基吡嗪)-[1,2,4]-三唑[4,3-*b*][1,2,4,5]四嗪(化合物3),该化合物含有邻位的—NO₂和—NH₂官能团。对该化合物的分子进行结构表征与晶体分析,研究其分子间堆积方式对化合物性能的影响,并且计算其爆轰性能,探究其作为含能材料的潜质。

2 实验部分

2.1 试剂与仪器

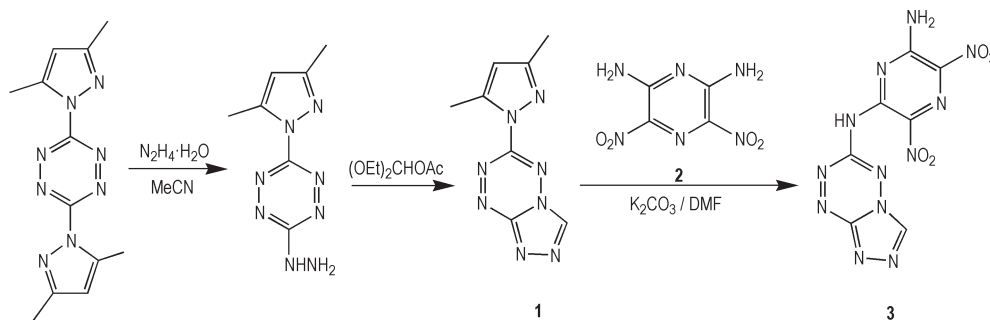
Bruker Avance III 500 MHz 数字化核磁共振仪, DSC-25 型差示扫描量热仪, Thermo Nicolet AVATAR 370 红外光谱仪, 2000 Bruker-AXS X-射线单晶衍射仪, Vario MICRO cube Elementar Analyser 元素分析仪, Micromeritics 全自动气体置换法真密度仪 ACCUPYCI1345, FSKM 10 BAM 摩擦感度仪, BFH 12 BAM 撞击感度仪。

碳酸钾(分析纯), 出自阿拉丁; DMF, 36% 盐酸,

乙腈, 乙醚, 均为分析纯, 出自沪试; 6-(3,5-二甲基吡嗪)-[1,2,4]三唑[4,3-*b*][1,2,4,5]四嗪(1), 2,6-二氨基-3,5-二硝基吡嗪(2)参照文献[22-23]制备。

2.2 实验过程

合成过程如 Scheme 1 所示, 化合物 1 (1.20 g, 6.0 mmol) 和碳酸钾 (0.83 g, 6.0 mmol) 加入 10 mL DMF 中, 室温搅拌 1.5 h, 加入化合物 2 (1.08 g, 5.0 mmol), 升温 60 °C, 保温 4 h 后, 加大量水, 10% 稀盐酸调至 pH=1, 析出大量黄绿色固体, 过滤, 滤饼用水、乙腈、乙醚淋洗, 干燥得到 1.3 g 黄绿色固体^[24], 收率为 81.3%。¹H NMR (500 MHz, DMSO-*d*₆, 25 °C) δ: 8.66 (s, 1H), 9.11 (s, 1H), 9.76 (s, 1H), 11.90 (br); ¹³C NMR (125 MHz, DMSO-*d*₆, 25 °C) δ: 127.4, 128.1, 137.5, 145.5, 149.5, 150.3, 151.3; IR (KBr, ν/cm^{-1}): 3420, 3320, 1635, 1585, 1536, 1490, 1430, 1401, 1367, 1326, 1257, 1232, 1192, 1122, 1025, 973, 951, 887, 835, 763, 653, 633, 602, 516; Anal. Calcd. for C₇H₄N₁₂O₄ (%): C 26.26, H 1.26, N 52.49; Found: C 26.29, H 1.23, N 52.41。



Scheme 1 Synthetic route of compound 1 and 3

3 结果与讨论

3.1 化合物 3·CH₃CN 的晶体结构

利用乙腈作为溶剂将 6-(2,6-二氨基-3,5-二硝基吡嗪)-[1,2,4]-三唑[4,3-*b*][1,2,4,5]四嗪(化合物3)配制成饱和溶液,于室温下缓慢挥发得到符合测试标准的单晶。选取尺寸为 0.19 mm×0.13 mm×0.06 mm 的单晶于 2000 Bruker-AXS X-射线单晶衍射仪上,采用经石墨单色化的 MoK_α 射线($\lambda=0.143 \text{ nm}^{-1}$) 在 173(2) K 温度下收集单晶衍射数据。在 $5.61^\circ \leq 2\theta \leq 46.534^\circ$ 下,共收集衍射点 15620 个,其中独立衍射点 3693 个。晶体结构用全矩阵最小二乘法修正,最终偏离因子 $R_1=0.0558$, $wR_2=0.1571$ 。

3·CH₃CN 晶体的分子结构和堆积图分别为图 1

和图 2, 3·CH₃CN 部分键长、键角的数据列于表 1 和表 2。化合物 3·CH₃CN 为单斜空间群 P2₁/c, 每个晶胞有八个分子 (Z=8), 晶体学参数为 $a=16.417(4) \text{ \AA}$, $b=17.260(4) \text{ \AA}$, $c=9.538(2) \text{ \AA}$, $\alpha=90^\circ$, $\beta=102.811(8)^\circ$, $\gamma=90^\circ$ 。其中, N(1)—C(2), N(2)—C(1), N(3)—C(1), N(3)—C(2), N(4)—C(2), N(5)—C(3), N(6)—C(3), N(8)—C(4), N(8)—C(7), N(9)—C(5), N(9)—C(6) 的键长分别为 1.320(6), 1.328(7), 1.356(6), 1.361(6), 1.361(6), 1.406(6), 1.304(5), 1.320(6), 1.318(6), 1.330(5) Å 和 1.344(6) Å, 介于 N—C 单双键 (1.28~1.47 Å) 之间; N(1)—N(2), N(3)—N(6), N(4)—N(5) 的键长分别为 1.366(5) Å, 1.368(5) Å 和 1.286(5) Å, 介于 N—N 单双键 (1.30~1.47 Å) 之间; C(4)—C(5), C(6)—C(7) 的键长分别为 1.421(6) Å 和 1.428(6) Å,

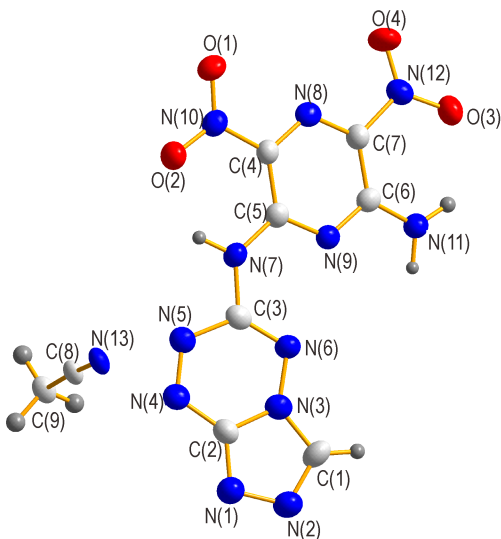


图1 3·CH₃CN 分子结构图

Fig.1 Molecular structure of 3·CH₃CN

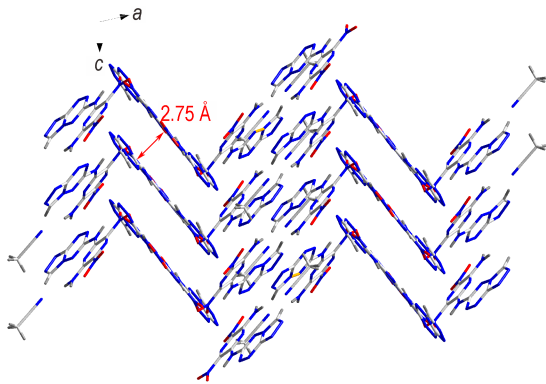


图2 化合物3·CH₃CN 沿 b 轴的堆积方式

Fig.2 Packing diagram of 3·CH₃CN viewed from b axis

表1 化合物3·CH₃CN 的部分键长

Table 1 Selected bond lengths of 3·CH₃CN

bond	length / Å	bond	length / Å
N(1)—C(2)	1.320(6)	N(8)—C(7)	1.318(6)
N(2)—C(1)	1.328(7)	N(9)—C(5)	1.330(5)
N(3)—C(1)	1.356(6)	N(9)—C(6)	1.344(6)
N(3)—C(2)	1.361(6)	N(1)—N(2)	1.366(5)
N(4)—C(2)	1.361(6)	N(3)—N(6)	1.368(5)
N(5)—C(3)	1.406(6)	N(4)—N(5)	1.286(5)
N(6)—C(3)	1.304(5)	C(4)—C(5)	1.421(6)
N(8)—C(4)	1.320(6)	C(6)—C(7)	1.428(6)

表2 化合物3·CH₃CN 的部分扭转角

Table 2 Selected torsion angles of 3·CH₃CN

torsion angles	angle / (°)
N(1)—C(2)—N(3)—N(6)	179.897(4)
N(4)—C(2)—N(3)—C(1)	-178.135(4)
C(3)—N(7)—C(5)—C(4)	-178.610(4)
C(3)—N(7)—C(5)—N(9)	2.196(7)

说明三唑并四嗪的稠环和吡嗪环均形成了共轭的大π键,降低电子云密度,形成稳定的分子结构。

从表2(3·CH₃CN 的部分扭转角)可知,N(1)—C(2)—N(3)—N(6)=179.897(4)°,N(4)—C(2)—N(3)—C(1)=-178.135(4)°,C(3)—N(7)—C(5)—C(4)=-178.610(4)°,C(3)—N(7)—C(5)—N(9)=2.196(7)°,表明化合物3为近平面结构,而平面型分子有利于构成分子的紧密堆积,分子间层间距为2.75 Å(图2)。图3展现了化合物3·CH₃CN 的分子间和分子内氢键,由图可知,相邻的氨基和硝基之间形成分子内氢键,另外,相邻的分子之间形成了分子间氢键,大量氢键的存在使得化合物沿 b 轴形成了波浪型堆积。

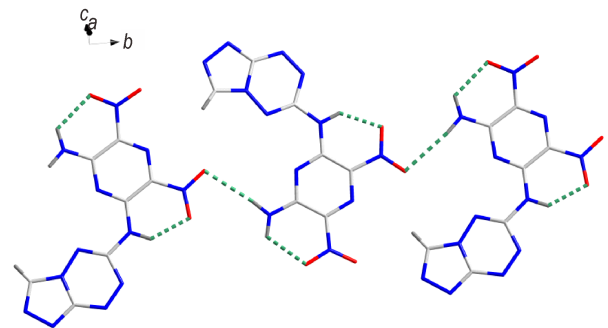


图3 化合物3 的分子间和分子内氢键

Fig.3 Inter-/intra- molecular hydrogen bonds of compound 3

3.2 热稳定性及爆轰性能

采用差示扫描量热仪研究化合物3的热稳定性(氮气气氛,密封盘,升温速率5 °C·min⁻¹),获得了化合物3在40~400 °C条件下的DSC曲线。如图4所示,在250~300 °C范围内,化合物3有两个峰型尖锐的分解热峰,放热过程较为集中且迅速。由图4可知,化合物3具有较高的起始分解温度(T_d=254.6 °C),优于传统的含能材料RDX(210 °C),且符合作为耐热性炸药的要求(T_d>250 °C)^[25]。通过设计等键反应,运用密度泛函理论DFT/B3LYP,采用6-311g(d,p)基组^[26]可计算得化合物3的生成焓为757.2 kJ·mol⁻¹,远远高于TNT^[27](-67.0 kJ·mol⁻¹)和RDX^[27](80.0 kJ·mol⁻¹)。

根据所得的生成焓(757.2 kJ·mol⁻¹),和采用排惰性气体(氮气,25 °C)测得的实际密度(1.70 g·cm⁻³),运用EXPLO5 V6.05.02软件^[28]计算得到化合物3的爆速为7568 m·s⁻¹,爆压为23.5 GPa,其爆轰性能优于TNT(爆速6824 m·s⁻¹)。化合物3的撞击感度和摩擦感度依据BAM标准测试法^[29]测定:样品量20 mg,落锤5 kg,得化合物3的撞击感度和摩擦感度分别为12.5 J和240 N,其感度均优于RDX(撞击感度7.4 J;

摩擦感度 120 N)。

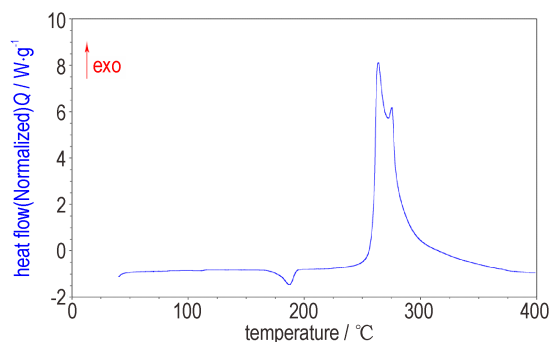


图4 化合物3的DSC曲线(5 °C·min⁻¹)

Fig.4 DSC curve of 3 at 5 °C·min⁻¹

表3 化合物3, TNT和RDX的物理特性和爆炸性能

Table 3 Physical and detonation properties of compound 3, TNT and RDX

compound	T_d / °C	ρ / g·cm ⁻³	$\Delta_f H$ / kJ·mol ⁻¹	D / m·s ⁻¹	P / GPa	IS / J	FS / N
3	255	1.70	757.2	7568	23.5	12.5	240
TNT ^[27]	295	1.65	-67.0	6881	19.5	15.0	/
RDX ^[27]	210	1.82	80.0	8748	34.9	7.4	120

Note: T_d is the thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C·min⁻¹). ρ is the measured density, gas pycnometer at room temperature. $\Delta_f H$ is the calculated heat of formation. D is the calculated detonation velocity. P is the calculated detonation pressure. IS is the impact sensitivity. FS is the friction sensitivity.

4 结论

(1) 含有氨基和硝基官能团的平面杂芳环化合物通常具有高能钝感的优异性能, 再通过—NH—键桥联高氮的稠环结构, 设计合成了一种具有平面型结构的含能化合物。

(2) 以 6-(3, 5-二甲基吡唑)-[1, 2, 4]三唑[4, 3-*b*][1, 2, 4, 5]四嗪为底物, 通过亲核取代反应得到 6-(2, 6-二氨基-3, 5-二硝基吡唑)-[1, 2, 4]三唑[4, 3-*b*][1, 2, 4, 5]四嗪, 并采用核磁、红外、元素分析和X射线单晶衍射进行结构表征, 6-(2, 6-二氨基-3, 5-二硝基吡唑)-[1, 2, 4]三唑[4, 3-*b*][1, 2, 4, 5]四嗪分子属于单斜空间群 $P2_1/c$, 实测密度为 1.70 g·cm⁻³。利用 Gaussian 09 和 Explo5 软件计算得到其爆轰性能, 其爆速为 7568 m·s⁻¹, 爆压为 23.5 GPa。

(3) 6-(2, 6-二氨基-3, 5-二硝基吡唑)-[1, 2, 4]三唑[4, 3-*b*][1, 2, 4, 5]四嗪较高的分解温度(255 °C)和较低感度(撞击感度 12.5 J, 摩擦感度 240 N), 使得其可以作为耐热性炸药应用于民用行业中。

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Synthesis and Properties of Imine-bridged Planar Nitrogen-rich Energetic Materials

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Abstract: Planar heteroaromatic compounds containing amino and nitro functional groups usually have excellent detonation performances. Hereby, the —NH— bond bridging two high-nitrogen fused rings was adopted aiming at constructing a nitrogen-rich energetic compound with a planar structure. The resulting compound is expected to have a regular packing in crystal and favorable detonation performance and stabilities. Reaction of 2,6-diamino-3,5-dinitropyrazine (**2**) with K_2CO_3 gives rise to 6-(2,6-diamino-3,5-dinitropyrazine)-1,2,4-triazole[4,3-b][1,2,4,5]tetrazine (**3**) in a high yield of 81.3%. Compound **3** was characterized by NMR, IR, single crystal X-ray diffraction. The thermal decomposition process of **3** was studied by differential scanning calorimetry (DSC), and its decomposition temperature (onset) is as high as 254.6 °C. The detonation performances of **3** ($D=7568 \text{ m}\cdot\text{s}^{-1}$, $P=23.5 \text{ GPa}$) were calculated by Gaussian 09 and Explo5 software.

Key words: planar; imino bridge; nitrogen-rich; energetic materials

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