3,6-二肼基-1,2,4,5-四嗪及其盐的合成与表征

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摘要: 以三氨基胍盐酸盐和 2,4-戊二醛为原材料, 通过成环反应, 氧化脱氢, 肼基取代, 三步合成了 3,6-二肼基-1,2,4,5-四嗪的含能盐的合成进行了研究。对文献报道的反应路线进行了适当的放大研究。通过红外光谱分析, 色谱分析和 'HNMR 对产物的结构特征进行了鉴定。

关键词: 有机化学; 3,6-二肼基-1,2,4,5-四嗪; 含能; 含能化合物

1 引言
3,6-二肼基-1,2,4,5-四嗪及其盐作为一类高氮杂环含能材料, 具有高能量、低特征信号、燃烧无残渣、无污染等优点, 可广泛用于炸药、推进剂和烟火技术领域。此外, 其因具有高氮量且高密度性能而有希望成为叠氮化合物的替代物而被用于安全气囊中。国外关于 3,6-二肼基-1,2,4,5-四嗪的合成报道较多。

但按文献介绍的合成条件, 一次合成的产品太少, 不能满足固体推进剂配方研究的要求, 因此我们在保持反应物配比不变的情况下, 将投料量放大进行研究, 并对合成出的 3,6-二肼基-1,2,4,5-四嗪进行了结构表征。同时还对 3,6-二肼基-1,2,4,5-四嗪的含能盐进行了合成研究和结构表征。

2 合成与表征

2.1 仪器与试剂

仪器: EQUINOX 55 型傅立叶变换红外光谱仪, 德国 Bruker 公司; Vario El III 型元素分析仪, 亮公司; GCT CA137 型质谱分析仪, 英国 waters 公司; 数字熔点仪, 上海精密仪器有限公司; DSC 2920 型高压差示扫描量热仪, 美国 TA 公司。

试剂: 一水合肼、2,4-戊二醛、1-甲基-2-吡咯烷酮、双氰胺, 均为分析纯。

2.2 实验步骤

2.2.1 一盐酸三氨基胍的合成

将 272 ml 水合肼和 600 ml 蒸馏水加入到 5000 ml 的三口烧瓶中, 在搅拌条件下, 缓慢滴加 1003 ml 盐酸 (37%) 至溶液呈中性, 然后加入 504.5 g 双氰胺和 1090 ml 一水合肼, 升温至 80~90℃, 在此温度下反应 4 h, 再用冰水冷却 8 h, 溶液被冷却并用水冲洗, 再用冰水冲洗, 得白色晶体。产率 84%, 熔点 230℃。

2.2.2 3,6-双(3,5-二甲基吡唑基)-1,2-二氢-1,2,4,5-四嗪的合成

将 200 g 一盐酸三氨基胍溶解在 3000 ml 水溶液中, 将 527 g 2,4-戊二醛, 在 1500 ml 1-甲基-2-吡咯烷酮溶剂中搅拌, 其温度保持在 80~90℃, 再用冰水冷却 8 h, 过滤, 滤液经用冰水冲洗, 再用冰水冲洗, 得白色晶体。产率 65%, 熔点 230℃。

2.2.3 3,6-双(3,5-二甲基吡唑基)-1,2,4,5-四嗪的合成

采用文献[5]报道的合成路线合成母体化合物

3,6-双(3,5-二甲基吡唑基)-1,2,4,5-四嗪。
体，冒泡10～20 min，反应完毕后，过滤溶液，用1-M基2-吡啶酮冲洗，干燥后得到浅红色粉末。产率94%。熔点224℃。

元素分析（%）C2H6N4: 实测值（计算值）C 53.40 (53.33), H 5.25 (5.18), N 39.94 (41.48)。IR谱图（KBr ς/cm⁻¹）1578 (—C=C—), 1079 (—C=CN—)。

2.2.4 3,6-二肼基-1,2,4,5-四嗪的合成

采用文献[2]报道的合成路线合成3,6-二肼基-1,2,4,5-四嗪。

在三口烧瓶中，将136 g 3,6-双(3,5-二甲基吡啶基-1)-1,2,4,5-四嗪溶液于1600 ml乙腈中，然后缓慢滴加40 ml一水合肼，待一水合肼滴加完毕，继续搅拌溶液，回流30 min，然后将溶液冷却至室温，过滤溶液，用乙腈冲洗，干燥后得暗红色粉末，产率77%。DSC分解峰温为160.37℃。

IR谱图（KBr ς/cm⁻¹）：3294 (NH2), 3222 (NH2), 3027(NH2), 1639(NH2), 1540 (NH2), 1053 (—C==N—), 941 (—N==N—)。元素分析（%）C2H6N4: 实测值（计算值）C 16.9 (16. 90), H 4.4 (4.23), N 77.59 (78.87); 质谱分析：m/z 142.07 (分子离子峰 M), 112.05 (失去 HNNH2), 84.04 (失去 N2)。

感度测试：3,6-二肼基-1,2,4,5-四嗪的撞击感度为H0=3.5 cm, I=2.65 J, σ=0.18 kg (锤重2 kg, 试样重0.2 g, 参照标准QJ3039-98)；摩擦感度为100% (测试角度66°, 测试压强2.5 MPa, 参照标准QJ2913-97); 真空定容爆热：7710.0 kJ·kg⁻¹ (参照标准QJ1359-88)。

3 结 论

（1）以3,6-双(3,5-二甲基吡啶基-1)-1,2,4,5-四嗪为母体合成了3,6-二肼基-1,2,4,5-四嗪及其盐，对文献报道的实验条件进行适当的放大研究，并利用IR、元素分析、质谱分析和'H NMR等方法鉴定了结构。

（2）3,6-二肼基-1,2,4,5-四嗪的冲击感度和摩擦感度都很低，具有很高的安全性。

参考文献:
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The Technology of the Strong Light Blindness Ammunition

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Abstract: The radiation mechanism, formulation composition, properties test and the disturbance on night vision equipment with strong flash blindness ammunition are studied. The results show that the trinary formulation containing KClO₄, Al and epoxy resin (mass ratio is 50: 50: 3) has higher radiation and lower sensitivities. The ammunition security is greatly improved when 1% micro-powder graphite is added into the trinary formulation. When 80 g charge amount of trinary formulation (the mass ratio of KClO₄, Al and epoxy resin is 50: 50: 3) is loaded into the simulation bomb, the luminesced intensity at visible region is more than 5.0 × 10⁻⁴ cd and the radiation intensity at near-infrared band exceeds 2.1 × 10⁷ W·sr⁻¹. Moreover, 40 g charge amount of the trinary formulation has obvious disturbance on night vision equipment at 37 m.

Key words: military chemistry and pyrotechnics; strong light blindness ammunition; radiation intensity; micro-powder graphite; sensitivity; pattern bomb

Numerical Simulation of Blasting Warheads Exploding Based on ALE Method

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Abstract: Using the Arbitrary Lagrangian-Eulerian (ALE) algorithm, the numerical simulation of the blasting warheads exploding in the air is realized. During the modeling process, the explosive was plotted with ALE elements, the shell with Lagrange elements and the air with Euler elements, the ALE meshes of the initial void were created in which the explosive products could flow, the meshes of explosive and the initial void were joined with common nodes, and the fluid-structure interaction was defined between the meshes of the explosive, shell and air. The diffusion of explosive products and the pressure distribution were obtained. The overpressure values at different distance to the explosion center were presented. The results show that the relative errors between the simulation results of overpressure and the experimental results at different distance to explosion center is less than 10%.

Key words: explosion mechanics; blasting warhead; explosion effect; numerical simulation; ALE algorithm

Synthesis and Characterization of 3,6-Dihydrazine-1,2,4,5-tetrazine and its Energetic Salts

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Abstract: 3,6-Dihydrazine-1,2,4,5-tetrazine and its energetic salts were synthesized from the easily available starting materials like triaminoguanidine and 2,4-penatane dine. The synthesis route in literature was magnified properly. Moreover, the synthesized compounds were characterized by spectra analysis (IR, NMR, EA and MS) and the explosive properties (impact and friction sensitivity) and thermal properties (TGA/DTG) were studied.

Key words: organic chemistry; 3,6-dihydrazine-1,2,4,5-tetrazine; synthesis; tetrazine; high-nitrogen energetic material