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多硝基金刚烷生成热和稳定性的理论研究

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摘要 在密度泛函理论（DFT）B3LYP/6-31G水平下，通过不破裂金刚烷分子骨架（即 选择金刚作为参考物）的等键反应设计，比较精确地计算了系列多硝基金金刚烷的 生成热。经验性基团加和法和半经验MO法（AM1，PM3，MNDO，MNDO/3）均不适用于 标题生成熟的估算。4种半经验MO方法中，以MP3计算结果略好些。探讨了生成热和 分子结构的关系，发现桥头C上硝基使生成热减小，而偕二硝基使生成热增大。运 用生成热、前沿轨道能级差和C-NO_2键级等计算结果，阐明了标题的相对稳定性， 为新一代高能量密度材料（HEDM）的分子设计提供了基础数据和规律性。

关键词 多硝基金刚烷 生成热 密度泛函理论 前线轨道理论 稳定性

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Theoretical Studies on Heat of Formation and Stability for Polynitroadamantanes

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Abstract The heat of formation (HOF) for a series of polynitroadamantanes was calculated systematically by using density functional theory (DFf) at B3LYP/6-31G* level by means of designed isodesmic reactions without breaking the adamantane skeleton (i.e. choosing adamantane as a reference compound). Empirical group addition method and semi-empirical MO (AMI, PM3, MNDO and MINDO/3) methods did not produce more accurate and reliable results for HOFs of the title compounds. The result from PM3 calculation is the best in tire four MO methods. The relationship between HOFs and molecular structures was discussed. It is found that the nitro group on the bridge C decreases HOF, whereas gem-dinitro groups increase HOF. The relative stability of the title compounds was illustrated according to the results calculated by HOFs, the energy gaps between the frontier orbitals and the bond order of C- NO_2. The obtained results provide basic data and regularity for the molecular design of new type of high energetic density materials.

Key words polynitroadamantane FORMATION HEAT DFT FRONTIER ORBITAL THEORY STABILITY

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