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多氰基立方烷生成热的**DFT-B3LYP**和半经验**MO**研究

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摘要 运用密度泛函理论(DFT)B3LYP方法和半经验MO(MINDO/3,MNDO,AM1和PM3)方法系统计算了全部21种多氰基立方烷的生成热，首先，在DFT-B3LYP/6-31G^*水平下通过不破裂立方烷笼状骨架(亦即选择立方烷为参考物)的等键反应设计，精确计算了9种多氰基立方烷的生成热；发现B3LYP/6-31G^*结果分别地均与上述四种半经验MO方法求得的生成热之间存在良好的线性关系(相关系数均在0.9994以上)，且以AM1生成热与B3LYP/6-31G^*计算值最为接近，其次，其它12种多氰基立方烷的精确生成热借助上述线性关系通过校正对应的AM1结果而获得，多氰基立方烷的生成热很高，且随-CN基数目的增加而线性地增大，表明它们属于极具潜力的“新一低高能炸药”而具开发价值。

关键词 氰基 立方烷 等键反应 生成热 半经验方程 密度函数 炸药 多氰基立方烷

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Studies on heats of formation for polycyanocubanes with density functional theory B3LYP method and semiempirical MO methods

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Abstract The heats of formation (HOF) for all of the 21 polycyanocubanes are calculatedsystematicaly with density functional theory (DFT) B3LYP and semiempirical MO(MINO/3, MNDO, AM1 and PM3) methods. First, the accurate HOFs for the 9 titled compounds are obtained by means of designed isodesmic reactions at DFT-B3LYP/6-31G^* level, and the cubane cage skeletonhas not been broken (i.e. choosing cubane as a reference compound) to produced more accurate and reliable results. It is found that there are good linear relationships between the HOFs calculated using the B3LYP/6-31G^* and four semiempirical MO methods, respectively, and the linear correlation coefficient are all more than 0.999 4. The HOFs from AM1 calculation are the closest to the corresponding HOFs from B3LYP/6-31G^* results. Then, the accurate HOFs at B3LYP/6-31G^* level of other 12 polycyanocubanes are obtained by systematically correcting their AM1-calculated HOFs. Polycyanocubanes have very high HOFs, and the HOFs increase linearly with increasing in the number of cyano groups in a molecule. The results show that polycyanocubanes are the new generation explosives with high potentials and exploitable values.

Key words CYANO GROUP CUBANE FORMATION HEAT SEMIEMPIRICAL EQUATIONS EXPLOSIVES

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