研究论文

氮苄叉基苯胺分子的平面扭曲驱动力的**DFT**研究

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摘要   为了探索DFT方法中氮苄叉基苯胺分子的扭曲驱动力, 通过把非平面氮苄叉基苯胺(NBA)分子的DFT能量分成π和σ的方法, 分析了垂直离域能$\Delta E^V(\theta)$及σ-π轨道作用能$\Delta E^{\sigma\pi}(\theta)$的失稳定性, 并讨论了在扭曲过程中它们所起的作用. 在B3LYP/6-31G*, 6-311G*, 6-31G(2d), 6-311G(2d)水平下的计算结果显示: 与经典观点不同, π电子的离域是失稳定的, 且平面时失稳定性最强, 是分子扭曲的动力; 但σ-π轨道作用也是失稳定的, 随着扭角的增大其失稳定性增强, 是分子扭曲的阻力. NBA分子的大扭角构象, 是包含π-π, σ-π轨道作用在内的各种电子相互作用共同作用的结果.

关键词   能量分解   密度泛函理论   垂直离域能   σ-π轨道作用能   氮苄叉基苯胺

分类号

DFT Study of Driving Force for Distorting Benzylideneaniline Molecule Away from Planar Geometry

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Abstract In order to understand the nature of the driving force for distorting the non-planar molecule benzylideneaniline (NBA) away from its planar geometry, two energy effects, the vertical resonance energy $DE^V(\theta)$ and the σ-π orbital interaction energy $\Delta E^{\sigma\pi}(\theta)$, were calculated with the DFT method, and then partitioned into their π and σ parts, denoted as $DE^{V\text{-}\pi}(\theta)$ and $DE^{V\text{-}\sigma}(\theta)$, $DE^{(\sigma\pi)\text{-}\pi}(\theta)$ and $DE^{(\sigma\pi)\text{-}\sigma}(\theta)$ respectively. $DE^V(\theta)$ is always destabilizing, and has a tendency to distort NBA molecule away from its planar geometry as far as possible. Similarly, $DE^{\sigma\pi}(\theta)$ is also destabilizing, however, it is most destabilizing at the $\theta=90°$ geometry. NBA molecule would prefer the $\theta=90°$ geometry if there were no interaction between the σ and p systems. The fact $dE^T(\theta)/d\theta=0$ (total energy) around $\theta=40°$ geometry, is a compromise between the various orbital interactions including π-π, σ-π interactions.

Key words   energy separation   density functional theory   vertical resonance energy   σ-π orbital interaction energy   benzylideneaniline

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