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Full Paper

DFT能量分解和氮苄叉基苯胺分子的取代基效应

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摘要 为了研究取代基效应对氮苄叉基苯胺分子内p电子离域的影响, 本文在B3LYP/6-311G(d)水平下, 把十一个氮苄叉基苯胺类分子的垂直离域能D$E^{V}(q)$分成了p和s部分. 计算结果显示, 当分子带有供电子集团-OH时, 垂直离域能升高， D$E^{V}(q)$比母体分子更失稳定; 而当带有吸电子集团-NO_2时, 其D$E^{V}(q)$则比母体分子具有较小的失稳定性. 特别是当供电子集团-OH位于片断-N=CH-Ar苯环的邻位时, 分子的垂直离域能具有最大的失稳定性. 对于大部分取代NBA分子来说, 垂直离域能的失稳定性主要取决于失稳定的s骨架, 而不是稳定的p电子体系. 当-NO_2基位于片断-N=CH-Ar苯环的对位时, 分子的p电子体系最稳定, 而s体系最失稳定. 然而, 当-NO_2基位于左边苯环的对位时, 分子具有最小的垂直离域能.

关键词 密度泛函能量分解, 氮苄叉基苯胺类分子, 定域片断分子轨道基组, 垂直离域能, 取代基效应

分类号

Substituent Effect on *N*-Benzylideneanilines by DFT Energy Partition

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Abstract To investigate the substituent effect on p-electron delocalization of the *N*-benzylideneaniline (NBA), the vertical resonance energies D$E^{V}(\theta)$ of eleven substituted NBAs were separated into π and σ parts at the B3LYP/6-311G (d) level of the Density Functional Theory (DFT). When substi-tuted with an electron-releasing group —OH, the calculated D$E^{V}(\theta)$ of NBA was increased, indicative of more resonance destabilization than the mother molecule. However, when substituted with an electron-withdrawing group —NO_2, the calculated D$E^{V}(\theta)$ values indicated less resonance destabilization. The most destabilizing effect was observed especially when the —OH group located at the *ortho*-position of the aromatic ring in the fragment —N＝CH—Ar. For most of the substituted NBA molecules, it was the destabilized σ framework that determined the destabilizing feature of the vertical resonance energy, instead of the stabilized π system. When the —NO_2 substituent at the *para*-position of the aromatic ring of the —N＝CH—Ar group, the π system had the highest stabilizing ef-fect while the s framework exhibited the highest destabilizing effect. While the —NO_2 substituent was at the *para*-position of the left aromatic ring (Ar—), the NBA had the least vertical resonance energy value.

Key words DFT energy partition *N*-benzylideneaniline localized fragment molecular orbital vertical resonance energy substituent effect

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