

研究论文

TATB二聚体分子间作用力及其气相几何构型研究

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摘要 采用对称性匹配微扰理论(SAPT)定量地求得TATB分子间的静电、交换排斥、诱导和色散等分子间作用能项,从理论上揭示了TATB分子间作用本质;在此基础上,阐明了密度泛函在研究TATB二聚体时的适合性问题.结果表明:(1)在有分子间氢键的TATB二聚体中,库仑力足以与交换排斥力相抗衡,起主导作用.(2)

含分子间氢键的气相TATB二聚体的合理几何构型为平面型结构,此结构的产生与色散力无关,因此不管泛函是否含有近程色散作用,均应预测到这种强极性的平面型结构.(3)

在无分子间氢键的TATB二聚体中,库仑力难以与交换排斥力相抗衡,色散作用起到了关键作用;(4)在这种情况下,未含有近程色散作用的密度泛函不可能给出合理构型.恰好相反,含有近程色散作用的密度泛函PBE0却能正确地预测到具有“平行重叠”结构且呈微弱极性的TATB二聚体,色散力是导致这种构型产生的根本原因.

“平行重叠”TATB二聚体是典型的色散体系,其色散力占绝对主导地位并极有可能起源于两个TATB分子上 π 电子的相互作用.(5)对于所有TATB二聚体,色散力或很显著或起主导作用.由于密度泛函或未含有近程色散,或只能部分地把近程色散表达出来,这样使得当前所有密度泛函不可能精确求得这些二聚体的作用能.

关键词 [分子间作用](#) [密度泛函理论\(DFT\)](#) [对称性匹配微扰理论\(SAPT\)](#) [1,3,5-三氨基-2,4,6-三硝基苯\(TATB\)](#)

分类号

Intermolecular Forces and Gas Geometries of TATB Dimers

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Abstract The coulomb, exchange-repulsion, induction and dispersion components between 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) molecules were quantitatively derived utilizing symmetry adapted perturbation theory (SAPT), and for the first time the nature of the intermolecular interaction of TATB was unraveled. On this basis, the appropriateness of density functionals for investigation of TATB dimers was also elucidated. The results are shown as follows: (1) In the hydrogen bonded TATB dimers, Coulomb force has an enough ability to counteract exchange-repulsion force and plays a leading role. (2) A reasonable geometry of the gas hydrogen bonded TATB dimer takes on a planar structure whose existence has nothing to do with the dispersion. Therefore, the density functionals, whether or not to include the dispersion, should have a correct prediction of the strong polarization plane structure. (3) In the TATB dimers free of any intermolecular hydrogen bonds, Coulomb force has an inability to resist the exchange-repulsion, but the dispersion performs a key function. (4) In this case, it is impossible for the density functionals without a near short-range dispersion to yield a reasonable geometry for TATB dimers of this kind. Just the opposite, the functional PBE0 with the near short-range dispersion is able to predict correctly a weakly polar “parallel-eclipsed” structure, and the dispersion is responsible for the existence of such a structure, which is a classical dispersion dominated dimer. The dispersion taking up an absolutely leading position originates most likely from the interaction between the π electrons on the two different TATB molecules. (5) For all TATB dimers, dispersion either is remarkable or plays a leading role. However, density functionals either exclude the near short-range dispersion or include partially the dispersion. In this way, it is unlikely that all of current density functionals should derive the accurate interaction energies of the dimers. (6) The geometries similar to those of the TATB dimer in the crystallite will not likely exist stably in gas.

Key words [intermolecular interaction](#) [density functional theory](#) [symmetry adapted perturbation theory](#) [1](#) [3](#) [5-triamino-2](#) [4](#) [6-trinitrobenzene](#)

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