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热力学

多氯代二苯并噻吩亚砜热力学性质的密度泛函理论研究

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摘要

在BHandHLYP/6-31G*水平上对135个多氯代二苯并噻吩亚砜(PCDBTOs)系列化合物进行了全优化和振动分析计算，得到各分子在298.15 K、101.3 kPa标准状态下的热力学参数。设计等键反应，计算了PCDBTOs系列化合物的标准生成热(Δ_fH^θ)和标准生成自由能(Δ_fG^θ)。研究了热力学参数S^θ与氯原子的取代位置及取代数目(N_{PCS})之间的关系，结果表明：PCDBTOs系列化合物的S^θ、Δ_fH^θ和Δ_fG^θ与N_{PCS}之间有较好的相关性。根据异构体标准生成自由能的相对大小，从理论上求得异构体的相对稳定性。以Gaussian 03程序的输出文件为基础，采用统计热力学程序计算了PCDBTOs化合物在200～1000 K的摩尔定压热容($c_{p,m}$)，并用最小二乘法求得$c_{p,m}$与温度之间的相关方程，发现$c_{p,m}$与T、T^{-1}和T^{-2}之间有着很好的相关性(R^2=1.000)。同时，根据分子体积推测了化合物的毒性，结果表明：PCDBTOs系列化合物中，毒性最大的异构体可能在4取代中。

关键词

多氯代二苯并噻吩亚砜 密度泛函理论 氯原子取代位置方法 热力学性质 相对稳定性

分类号

DFT study on thermodynamic properties of polychlorinated dibenzothiophene sulfoxide

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Abstract

Fully optimized calculation and frequency analysis of 135 polychlorinated dibenzothiophenes sulfoxide (PCDBTOs) compounds were carried out by using density functional theory(DFT) method at the BHandHLYP/6-31G* level and their thermodynamic parameters in the ideal gas state at 298.15 K and 101.3 kPa were obtained.The isodesmic reactions were designed to calculate standard enthalpy of formation (Δ_fH^θ) and standard free energy of formation (Δ_fG^θ) of PCDBTOs congeners.The relationships of these thermodynamic parameters with the number and the position of Cl atom substitution (N_{PCS}) were established.There exists good correlation between entropy (S^θ)，standard enthalpy of formation (Δ_fH^θ)，standard free energy of formation (Δ_fG^θ) and N_{PCS}.The stability of PCDBTOs congeners was obtained theoretically based on the relative magnitude of their Δ_fG^θ.The values of $c_{p,m}$ were calculated by using statistical thermodynamic calculation program in the temperature range from 200 K to 1000 K based on Gaussian 03 output files.The relative equation between $c_{p,m}$ and temperature was obtained by the least square method.It is found that $c_{p,m}$ and T，T^{-1} and T^{-2} have a very good relationship (R^2=1.000）.Furthermore，based on the relationship of molecular volume and toxicity，it is predicted that the TCDBTO isomers may be the most toxic among the PCDBTOs compounds.

Key words

polychlorinated dibenzothiophenes sulfoxide density functional theory (DFT) method of position of Cl

atom substitution thermodynamic property relative stability

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