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二苯并噻吩及其氧化物与离子液体相互作用的理论研究

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Theoretical study on the interactions between dibenzothiophene/dibenzothiophene sulfone and ionic liquids

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摘要 采用密度泛函理论方法比较了DBT/$DBTO_2$和$[BMIM]^+[PF_6]^-$/$[BMIM]^+[BF_4]^-$的相互作用。对最稳定的$[BMIM]^+[PF_6]^-$、$[BMIM]^+[PF_6]^-$-DBT、$[BMIM]^+[PF_6]^-$-$DBTO_2$、$[BMIM]^+[BF_4]^-$、$[BMIM]^+[BF_4]^-$-DBT、$[BMIM]^+[BF_4]^-$-$DBTO_2$进行了NBO和AIM分析。结果表明,DBT和$[BMIM]^+[PF_6]^-$/$[BMIM]^+[BF_4]^-$中的咪唑环彼此相互平行,NBO和AIM分析表明它们之间发生了π-π相互作用。H1'和H9'形成的F…H氢键有利于π-π堆积作用的形成。$DBTO_2$倾向于趋近C2-H2和甲基基团形成O…H相互作用;$DBTO_2$优先吸附在$[BMIM]^+[PF_6]^-$/$[BMIM]^+[BF_4]^-$。在模拟油中,$[BMIM]^+[PF_6]^-$和$[BMIM]^+[BF_4]^-$离子液体对$DBTO_2$的萃取能力大于DBT,其原因是可能是$DBTO_2$具有较大的极性和O…H与F…H的氢键作用。

关键词： 密度泛函理论 二苯并噻吩 二苯并噻吩氧化物 离子液体

Abstract： The interactions between sulfur-containing compounds of dibenzothiophene (DBT) and dibenzothiophene sulfone ($DBTO_2$) and ionic liquids of 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM]^+[PF_6]^-$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM]^+[BF_4]^-$) were comparatively studied by using density functional theory. The most stable structures of $[BMIM]^+[PF_6]^-$, $[BMIM]^+[PF_6]^-$-DBT, $[BMIM]^+[PF_6]^-$-$DBTO_2$, $[BMIM]^+[BF_4]^-$, $[BMIM]^+[BF_4]^-$-DBT, and $[BMIM]^+[BF_4]^-$-$DBTO_2$ systems were obtained by natural bond orbitals (NBO) and atoms in molecules (AIM) analyses. The results indicated that DBT and [BMIM] rings of $[BMIM]^+[PF_6]^-$/$[BMIM]^+[BF_4]^-$ are parallel to each other. There is a strong π-π interaction between them in terms of NBO and AIM analyses. The H1' and H9' involved F…H hydrogen bonding interactions may favor the formation of π-π stacking interactions. The $DBTO_2$ preferentially locates near the C2-H2 and methyl group of $[BMIM]^+$ to form O…H interactions. The predicted geometries and interaction energies imply the preferential adsorption of $DBTO_2$ on $[BMIM]^+[PF_6]^-$/$[BMIM]^+[BF_4]^-$. The $[BMIM]^+[PF_6]^-$/$[BF_4]^-$ have better extracting ability to remove $DBTO_2$ than DBT, possibly due to the larger polarity of $DBTO_2$ and stronger interactions between $[BMIM]^+[PF_6]^-$/$[BF_4]^-$ and $DBTO_2$.

Key words： density functional theory dibenzothiophene dibenzothiophene sulfone ionic liquid

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. Theoretical study on the interactions between dibenzothiophene/dibenzothiophene sulfone and ionic liquids[J]. J Fuel Chem Technol, 2012, 40(12): 1444-1453.

[1] BOSMANN A, DATSEVICH L, JESS A, LAUTER A, SCHMITZ C, WASSEERSCHEID P. Deep desulfurization of diesel fuel by extraction with ionic liquids[J]. Chem Commun, 2001, 23(23): 2494-2495.

[2] LO W-H, YANG H-Y, WEI G-T. One-pot desulfurization of light oils by chemical oxidation and solvent extraction with room temperature ionic liquids[J]. Green Chem, 2003, 5(5): 639-642.

[3] WANG J-L, ZHAO D-S, ZHOU E-P, DONG Z. Desulfurization of gasoline by extraction with *N*-alkyl-pyridinium-based ionic liquids[J]. J Fuel Chem Technol, 2007, 35(3): 293-296.

[4] ZHANG C, WANG F, PAN X-Y, LIU X-Q. Study of extraction-oxidation desulfurization of model oil by acidic ionic liquid[J]. J Fuel Chem Technol, 2011, 39(9): 689-693.

[5] ANANTHARAJ R, BANERJEE T. Phase behavior of 1-ethyl-3-methylimidazolium thiocyanate ionic liquid with catalytic deactivated compounds and water at several temperatures: Experiments and theoretical predictions[J]. Int J Chem Eng, 2011, 2011(1):1-13.

[6] KUMAR A A P, BANERJEE T. Thiophene separation with ionic liquids for desulphurization: A quantum chemical approach[J]. Fluid Phase Equilib, 2009, 278(1/2): 1-8.

[7] ANANTHARAJ R, BANERJEE T. Liquid-liquid equilibria for quaternary systems of imidazolium based ionic liquid + thiophene + pyridine + iso-octane at 298.15 K: Experiments and quantum chemical predictions[J]. Fluid Phase Equilib, 2011, 312(1): 20-30.

[8] SANTIAGO R S, SANTOS G R, AZNAR M. UNIQUAC correlation of liquid-liquid equilibrium in systems involving ionic liquids: the DFT-PCM approach[J]. Fluid Phase Equilib, 2009, 278(1/2): 54-61.

[9] HANKE C G, JOHANSSON A, HARPER J B, LYNDEN-BELL R M. Why are aromatic compounds more soluble than aliphatic compounds in dimethylimidazolium ionic liquids? A simulation study[J]. Chem Phys Lett, 2003, 374(1/2): 85-90.

[10] KEDRA-KROLIK K, FABRICE M, JAUBERT J. Extraction of thiophene or pyridine from *n*-heptane using ionic liquids, gasoline and diesel desulfurization[J]. Ind Eng Chem Res, 2011, 50(4): 2296-2306.

[11] ANANTHARAJ R, BANERJEE T. Quantum chemical studies on the simultaneous interaction of thiophene and pyridine with ionic liquids[J]. AIChE J, 2011, 57(3): 749-764.

[12] LU R, QU Z, YU H, WANG F, WANG S. Comparative study on interactions between ionic liquids and pyridine/hexane[J]. Chem Phys Lett, 2012, 532(4): 13-18.

[13] DONG K, ZHANG S, WANG D, YAO X. Hydrogen bonds in imidazolium ionic liquids[J]. J Phys Chem A, 2006, 110(31): 9775-9782.

[14] HEIMER N E, del SESTO R E, MENG Z, WILKES J S, CARPER W R. Vibrational spectra of imidazolium tetrafluoroborate ionic liquids[J]. J Mol Liq, 2006, 124(1/3): 84-95.

[15] BHARGAVA B L, BALASUBRAMANIAN S. Insights into the structure and dynamics of a room-temperature ionic liquid: Ab initio molecular dynamics simulation studies of 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and the [bmim][PF_6]-CO_2 mixture[J]. J Phys Chem B, 2007, 111(17): 4477-4487.

[16] MORROW T I, MAGINN E J. Molecular dynamics study of the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate[J]. J Phys Chem B, 2002, 106(49): 12807-12813.

[17] KATSYUBA S A, DYSON P J, VANDYUKOVA E E, CHERNOVA A V, VIDIS A. Molecular structure, vibrational spectra, and hydrogen bonding of the ionic liquid 1-ethyl-3-methyl-1H-imidazolium tetrafluoroborate[J]. Helv Chim Acta, 2004, 87(10): 2556-2565.

[18] MICAELO N M, BAPTISTA A M, SOARES C M. Parametrization of 1-butyl-3-methylimidazolium hexafluorophosphate/nitrate ionic liquid for the GROMOS force field[J]. J Phys Chem B, 2006, 110(29): 14444-14451.

[19] TALATY E R, RAJA S, STORHAUG V J, DOLLE A, CARPER W R. Raman and infrared spectra and ab initio calculations of C_{2-4}MIM imidazolium hexafluorophosphate ionic liquids[J]. J Phys Chem B, 2004, 108(35): 13177-13184.

[20] PERDEW J P, WANG Y. Accurate and simple analytic representation of the electron-gas correlation energy[J]. Phys Rev B, 1992, 45(23): 13244-13249.

[21] DELLEY B. An all-electron numerical method for solving the local density functional for polyatomic molecules[J]. J Chem Phys, 1990, 92 (1): 508-517.

[22] DELLEY B. From molecules to solids with the $DMol^3$ approach[J]. J Chem Phys, 2000, 113(18): 7756-7764.

[23] CASTELLANO O, GIMON R, SOSCUN H. Theoretical study of the σ-π and π-π interactions in heteroaromatic monocyclic molecular complexes of benzene, pyridine, and thiophene dimers: Implications on the resin-asphaltene stability in crude oil[J]. Energy Fuels, 2011, 25(6): 2526-2541.

[24] REED A E, CURTISS L A, WEINHOLD F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint[J]. Chem Rev, 1988, 83(6): 899-926.

[25] BIEGLER-KONIG F, SCHONBOHM J. Update of the AIM2000 program for atoms in molecules[J]. J Comput Chem, 2002, 23(15): 1489-1494.

[26] BIEGLER-KONIG F, SCHONBOHM J, BAYLES D. AIM2000 - A program to analyze and visualize atoms in molecules[J]. J Comput Chem, 2001, 22(5): 545-559. 3.0.CO;2-Y target="_blank">

[27] INADA Y, ORITA H. Efficiency of numerical basis sets for predicting the binding energies of hydrogen bonded complexes: Evidence of small basis set superposition error compared to Gaussian basis sets[J]. J Comput Chem, 2008, 29(2): 225-232.

[28] ROZAS I, ALKORTA I, ELGUERO J. Bifurcated hydrogen bonds: three-centered interactions[J]. J Phys Chem A, 1988, 102(48): 9925-9932.

[29] PADIYAR G S, SESHADRI T P. Trifurcated (four-center) hydrogen bond in solid state crystal structure of 5'-amino-5'-deoxyadenosine *p*-toluenesulfonate[J]. Nucleos Nucleot, 1996, 15(4): 857-865.

[30] SINNOKROT M O, VALEEV E F, SHERRILL C D. Estimates of the ab initio limit for π-π interactions: The benzene dimmer[J]. J Am Chem Soc, 2002, 124(36): 10887-10893.

[31] HUNTER C A, SANDERS J K M. The nature of π-π interactions[J]. J Am Chem Soc, 1990, 112(14): 5525-5534.

[32] DESIRAJU G R. Hydrogen bridges in crystal engineering: Interactions without borders[J]. Acc Chem Res, 2002, 35(7): 565-573.

[33] BADER R F W. A quantum theory of molecular structure and its applications[J]. Chem Rev, 1991, 91(5): 893-928.

[34] CHECINSKA L, GRABOWSKI S J, MALECKA M. An analysis of bifurcated H-bonds: Crystal and molecular structures of *O,O*-diphenyl 1-(3-phenylthioureido) pentanephosphonate and *O,O*-diphenyl 1-(3-phenylthioureido) butanephosphonate[J]. J Phys Org Chem, 2003, 16(4): 213-219.

[35] ESPINOSA E, SOUHASSOU M, LACHEKAR H, LECOMTE C. Topological analysis of the electron density in hydrogen bonds[J]. Acta Cryst, 1999, B55(4): 563-574.

[36] NETZEL J, van SMAALEN S. Topological properties of hydrogen bonds and covalent bonds from charge densities obtained by the maximum entropy method (MEM)[J]. Acta Cryst, 2009, B56(5): 624-638.

[1] 贾建波, 李风海, 曾凡桂, 郭红玉. 四氢化萘热解中甲基茚满生成机理的密度泛函计算[J]. 燃料化学学报, 2012, 40(10): 1188-1193.

[2] 王梅, 张立麒, 刘浩, 张军营, 郑楚光. 咪唑类离子液体混合物吸收CO_2性能研究[J]. 燃料化学学报, 2012, 40(10): 1264-1268.

[3] 黄金保, 童红, 曾桂生, 谢宇, 李伟民. 丁醇醛和丁醇酸热解形成CO和CO_2机理的密度泛函理论研究[J]. 燃料化学学报, 2012, (08): 979-984.

[4] 杜梅芳, 张影, 樊俊杰, 吴高贺, 侯宁普, 鲁贵林, 张忠孝. 气体再燃低NO_x燃烧中NO与NH_i的反应机理研究[J]. 燃料化学学报, 2012, (08): 935-942.

[5] 黄金保, 刘朝, 曾桂生, 谢宇, 童红, 李伟民. 左旋葡聚糖热解机理的密度泛函理论研究[J]. 燃料化学学报, 2012, 40(07): 807-815.

[6] 张薇, 丁永萍, 宫敬, 宋溪明. 羧基功能化离子液体催化二苯并噻吩氧化脱硫[J]. 燃料化学学报, 2012, 40(05): 626-629.

[7] 李翠清, 邓明亮, 王虹, 葛明兰, 郭志武, 孙桂大. 含磷铝单元的AIMCM-41负载的磷化钨催化剂DBT HDS性能[J]. 燃料化学学报, 2012, (04): 501-506.

[8] 刘兴武, 李永旺, 王建国, 霍春芳. 第一性原理研究C在Fe(111)表面和次表面的积炭机理[J]. 燃料化学学报, 2012, 40(02): 202-209.

[9] 袁金焕, 滕波涛, 赵越, 赵云, 罗孟飞. 贵金属原子在CeO_2(111)表面吸附的密度泛函理论研究[J]. 燃料化学学报, 2012, 40(01): 124-128.

[10] 赵训华, 李永旺, 王建国, 霍春芳. Fe(100)表面Cu单层膜上CO的吸附|解离以及C－C偶合反应[J]. 燃料化学学报, 2011, 39(12): 956-960.

[11] 李翠清, 潘雅妹, 李继文, 王 虹, 靳广州, 孙桂大. 含镍WP/MCM-41催化剂二苯并噻吩加氢脱硫性能[J]. 燃料化学学报, 2011, 39(12): 930-935.

[12] 刘理华, 刘摇迪, 刘摇宾, 李广慈, 柳云骐, 刘晨光. NiMo 催化剂上MoS2 形貌与其DBT 加氢脱硫选择性的关系[J]. 燃料化学学报, 2011, 39(11): 838-843.

[13] 程时富, 安 莹, 司晓娟, 付贤磊, 高国华. Ti-MWW分子筛催化叔丁基过氧化氢氧化脱硫[J]. 燃料化学学报, 2011, 39(10): 771-775.

[14] 范洪富, 马 军. 离子液体处理含油污水实验研究[J]. 燃料化学学报, 2011, 39(1): 33-36.

[15] 张 存, 王 峰, 潘小玉, 刘晓勤. 酸性离子液体萃取-氧化模拟油品脱硫研究[J]. 燃料化学学报, 2011, 39(09): 689-693.