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芳环共轭体系光诱导分子内电荷转移机理  
的理论研究

**Theoretical study on photoinduced intramolecular charge  
transfer mechanisms of aromatic conjugated systems**

许 雪 飞

指导教师姓名: 张乾二 教授

曹泽星 教授

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厦门大学博硕士学位论文摘要库

## 摘 要

由电子给体和电子受体部分构成的一系列有机共轭分子可以在光诱导下发生分子内的电荷转移反应,从而具有非线性光学和光-电转化等良好的性质,使其在非线性光学材料以及分子器件制造等领域具有广泛应用。正确理解这些共轭分子体系的光物理特性,对分子材料的光物理和光化学研究具有重要意义。本文通过高水平的量子化学计算,对几类芳香共轭体系的激发态与光诱导分子内电荷转移过程进行了系统的理论研究。获得的结果对建立光诱导分子内电荷转移机理、解决目前在这一研究领域的学术争论有积极意义。

本论文共分三个部分:第一部分即第一章,简要介绍电子转移基本理论以及分子内电荷转移研究现状、学术争论等;第二部分即第二章,重点介绍本论文工作中所用到的处理激发态的量子化学计算方法;第三部分即第三章到第五章,是本论文的重点,通过对一些代表性芳香共轭分子体系的激发态性质与溶剂化效应的计算研究,探讨了光诱导分子内电荷转移 (ICT) 的机制以及相关的光物理和光化学等性质。

主要研究工作包括以下几个方面:

1. 应用密度泛函和从头算计算方法,我们研究了 4-二甲基氨基苯腈 (DMABN) 及其甲基取代的衍生物的低能单、三重电子态的结构和性质。计算表明,苯环上甲基的取代以及氨基基团的扭转对分子激发态的性质有显著影响。一个扭转的分子内电荷转移单态 ( $^1\text{TICT}$ ) 可以由平面构型下具有电荷转移特征的第二激发态 ( $\text{S}_2$ ) 沿氨基扭转坐标驰豫而形成,或者由局域激发单态 ( $^1\text{LE}$ ) 经由分子内的电荷转移反应转化而成。基于计算和态交叉模型,阐明了 DMABN 分子的分子内电荷转移反应及其双重荧

光现象的机制。另外，通过旋-轨耦合计算，对分子内电荷转移三重态的形成以及单、三重态间的系间窜跃过程进行了调查。计算表明，扭转的分子内电荷转移三重态 ( $^3\text{TICT}$ ) 在能量上和扭转的分子内电荷转移单态 ( $^1\text{TICT}$  态) 非常接近，它可以经由内转换过程与最稳定的扭转三重态 ( $^3\text{TT}_1$ ) 相互转换，进而参与失活过程。然而由于它只能瞬时存在，使实验上对它的检测存在困难。我们预测系间窜跃过程是光激发的 4-二甲氨基苯腈分子的主要失活通道。

2. 采用从头算电子相关计算方法，我们对苯基吡咯 (PP) 及其平面刚性的衍生物吡咯并吡啶 (FPP) 分子的低能电子态和分子内的电荷转移 (ICT) 进行了对比研究，结合可极化连续介质模型 (PCM) 评估溶剂极性对电子态能量和性质、以及光物理过程的影响，并基于计算结果对激发态的性质以及可能的双荧光机制进行了阐述。结果表明极性溶剂在双荧光产生机制中扮演了重要的角色，而强吸收的第二垂直激发单态 ( $S_2$ ) 是一系列光物理过程得以发生的关键态。在极性的 MeCN 溶液中， $S_2$  态既可以驰豫到一个较低能的局域激发态，也可以演化成一个较低能的溶剂化的分子内电荷转移态 (S-ICT)。前者发射正常荧光返回到基态，而后者独自负责发射红移荧光带。计算表明，苯基吡咯和吡咯并吡啶分子的 ICT 荧光态具有相似的几何结构特征，即：氮-苯基键增长，连接吡咯环的碳原子锥形化以及苯环成醌式结构。发生分子内的电荷转移并不一定需要分子绕氮-苯基键转动。对于易扭转的苯基吡咯分子来说，连接吡咯环的碳原子发生锥形化的 ICT 态结构在接近  $90^\circ$  扭角处的能量要比其  $0^\circ$  扭角处的形式略微稳定，但是由于后者具有更为显著的光物理活性，所以主要是有着近平面结构的后者负责发射红移荧光。计算预测的吸收和发射光谱与实验观测基本一致。

3. 我们对 4-二氰亚甲基-2-甲基-6- (对位-二甲基氨基苯乙烯基)

-4 氢-吡喃 (DCM) 的低能电子态的结构和性质进行了理论研究。计算表明, DCM 分子第一激发态 ( $S_1$ ) 势能面上的二甲基氨以及二甲基苯胺扭转构型都有着相对高的稳定性以及显著的分子内电荷转移特征。这两个结构都有可能是极性溶剂下发射红移荧光的荧光态结构。尤其是二甲基苯胺扭转的 ICT 态, 我们的 CASSCF 计算预测其相对基态有一个约 20D 的偶极矩增量, 与实验预测值吻合的很好。优化所得的  $S_1$  态结构的中心碳碳双键显著增长, 键长为 1.458Å, 使 DCM 分子的反-顺式异构化过程可以通过在  $S_1$  态势能面上绕中心碳碳双键的转动而发生。 $S_1$  态是 ICT 荧光态以及光诱导的反-顺式异构化过程的前驱态。反-顺式异构化过程得以进行依赖于  $S_0$  和  $S_1$  态势能面在极性溶剂中的交叉或者在气相和非极性溶剂中的避免交叉。在强极性的溶剂中,  $S_1/S_0$  交叉提前, 通过前交叉区域, 激发态分子可以返回到反式的最低能态, 从而导致异构化效率降低。

**关键词:** 激发态; 分子内电荷转移; 双荧光

## Abstract

Organic conjugated molecules consisting of electron-donor and electron-acceptor groups have potential applications in nonlinear optical materials and molecular devices due to their remarkable photophysical and electro-optical properties. The photoinduced intramolecular charge transfer (ICT) as a fundamental process is involved in photophysics of the excited state. The detailed understanding of excited-state properties and ICT mechanisms of such donor-acceptor systems is important to facilitate design of molecular materials. In this dissertation, plausible photoinduced ICT mechanisms of selected aromatic conjugated systems have been investigated systemically by density functional theory and sophisticated *ab initio* methodologies.

The dissertation is composed of three parts: The first part is the first chapter, where the theoretical basis of electron transfer, the status of research, the controversy about ICT have been introduced; in the second part, we focused on introduction of quantum-chemistry methodologies for the excited state relative to our work; the third part is the most important part of this dissertation, where we have explored photoinduced ICT mechanisms and corresponding photophysics and photochemistry of some representative aromatic conjugated molecules on the basis of their excited-states and photophysical properties.

Target systems and concluding remarks in the present study can be summarized as follows:

1. **DMABN.** Low-lying singlet and triplet states of 4-dimethylamino-

benzonitrile (DMABN) and its derivatives have been studied by the density functional theory and *ab initio* methodologies. Calculations reveal that the existence of the methyl groups in the phenyl ring and the amino twisting significantly modify properties of their excited states. A twisted singlet intramolecular charge transfer state ( $^1\text{TICT}$ ) can be accessed through decay of the second planar singlet excited state with charge transfer character along the amino twisting coordinate or by an intramolecular charge transfer (ICT) reaction involved with a locally first excited singlet state ( $^1\text{LE}$ ). On the basis of calculations, the ICT reaction and dual fluorescence mechanisms of DMABN have been elucidated with the state-crossing model. Plausible charge transfer triplet states and intersystem crossing (ISC) processes among singlet and triplet states have been explored by spin-orbit coupling calculations. Calculations show that the twisted intramolecular charge transfer triplet state ( $^3\text{TICT}$ ), close to the  $^1\text{TICT}$  in energy, can be in an equilibrium with the lowest twisted triplet state ( $^3\text{TT}_1$ ) via the internal conversion process, and consequently it is probably involved in the ISC process. However, its transient presence makes experimental detection difficult. The intersystem crossing process was predicted to be the dominant deactivation channel of the photoexcited 4-dimethylaminobenzonitrile.

**2. PP and FPP.** Low-lying states and intramolecular charge transfers in *N*-phenylpyrrole (PP) and its planar-rigidized derivative fluorazene (FPP) have been investigated by *ab initio* methodologies. The effect of polar solvent on properties of the electronic states and the photophysics processes has been estimated by CASSCF calculations in connection of the polarized continuum model (PCM). On the basis of calculations, properties of the excited states and

plausible dual-fluorescence mechanisms have been elucidated. Present results show that the polar solvent plays a crucial role in the dual fluorescence mechanism, and the second singlet excited state ( $S_2$ ) as a key state is involved in the consecutive photophysical processes. The  $S_2$  state is easily populated under excitation. In the polar MeCN solution,  $S_2$  can evolve to either a lower-energy locally excited state or a lower-energy solvated intramolecular charge transfer state (S-ICT). The former emits a normal fluorescence back to the ground state, and the latter is exclusively responsible for the red-shifted fluorescence band. Calculations reveal that the emissive ICT states in both FPP and PP have similar geometrical and  $\pi$ -bonding features, an elongated *N*-phenyl bond, a pyramidal carbon atom linking the pyrrole ring, and a quinonoid phenyl ring. The twisting of molecule around the *N*-phenyl bond is not necessary for ICT. Although the twisting form with a twisted angle of  $\sim 90^\circ$  of the ICT state of PP, where the carbon connecting the pyrrole ring experiences a pyramidal deformation, is slightly more stable than its planar counterpart, the latter with near planar conformation will be basically responsible for the red-shifted fluorescence emission due to its significant photophysical activity. Predicted absorption and emission spectra are in reasonable agreement with the experimental observations.

**3. DCM.** Structures and properties of low-lying states in 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran (DCM) have been investigated theoretically. Calculations show that the dimethylamino and dimethylanilino twisted conformations of DCM on the potential energy surface of the first excited state ( $S_1$ ) have relatively high stabilities and remarkably intramolecular charge transfers. Both structures can



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