

Diflavylene 的压色性的机理

陈凯, 朱小蕾, 姚杰, 周志华

(南京师范大学化学与环境科学学院 210097, 南京)

[摘要] 采用 Hartree-Fock(HF)量子化学方法研究了 Diflavylene 的压色性. 利用 HF/STO-3G 方法优化了体系的结构. 振动频率计算表明, 优化的结构是真实存在的结构. 根据计算的 Diflavylene 顺反异构体的总能量, 紫外可见光谱和偶极矩探讨了 Diflavylene 的压致变色机理, 并尝试设计新的压色性材料.

[关键词] 压色性, 顺反异构, 量子化学

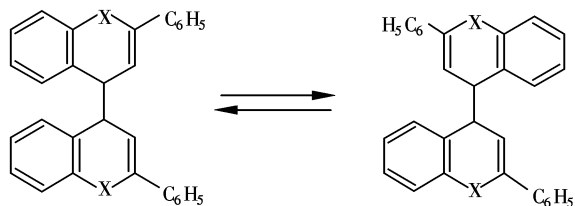
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温度、压力和光辐射是影响化学反应的主要外界因素. 许多研究者对温度和光辐射引起的热致变色和光致变色的机理作了广泛深入的研究. 热色性材料和光色性材料在许多科技领域及日常生活中已得到了广泛的应用. 由压力引起的化合物颜色的变化—压致变色的实验和理论已有一些报道^[1-29], 如美国的压敏涂料用于测定飞机飞行中机翼各部分的受压情况, 以及用于有效检查食品包装袋密封情况的压敏染料等. 目前, 国外的压色性材料的实验研究涉及到下列物质结构的变化: (1)顺反异构^[3] (2)物相变化^[2] (3)酮烯醇异构^[5] (4)闭环异构 (5)几何异构^[5-8] (6)单聚-多聚异构^[11, 16] (7)自旋异构^[17-20] (8)价态异构. 尽管有些学者已开始研究压色性与化合物分子结构的关系, 但目前国内外对压色性的系统的理论研究^[30, 31]极少. 设计低压下的(或压敏的)压色性材料具有重要的理论意义和应用价值.

Alexander Schnberg^[3]早在 1958 年报导了 Diflavylene 具有压色性. 这种物质在室温下呈橙黄色, 经研磨可转变为红色. 放置数小时或数天将恢复到原来的颜色. Kortum 等认为 Diflavylene 存在可逆的顺反异构引起了它的压色性. 本工作通过 Hartree-Fock(HF)量子化学方法计算了 Diflavylene 的顺反异构体的总能量, 紫外可见光谱, 电荷分布, 偶极矩等, 探讨 Diflavylene 的压致变色机理, 并尝试设计新的压色性材料.

1 Diflavylene 的压色机理

我们用“Hyperchem”软件构造了体系 1(Diflavylene)见图 1, X 为 O)顺式和反式的起始结构. 考虑到研究的 Diflavylene 体系较大, 在初步的研究工作中, 我们选择了 HF/STO-3G 方法. 为了得到体系的真实的结构, 我们用 HF/STO-3G 方法对体系 1 进行了全结构优化(没有任何对称性约束), 并计算了优化结构的振动频率和红外强度. 在此基础上, 用 HF/STO-3G 方法计算了这些体系的总能量, 电荷分布, 偶极矩等. ZINDO/S 方法是预测化合物紫外可见光谱的有效方法^[32]. 由表 1 的紫外光谱数据可以看出, 用 ZINDO/S 方法计算的间-二硝基苯和间-胺基苯酚的紫外可见光谱数据与实验值吻合较好. 因而, 我们采用 ZINDO/S 方法计算了体系 1(Diflavylene)的紫外可见光谱.



(1) X=O; (2) X=C=O; (3) X=N-H; (4) X=C=S

图 1 化合物的结构

表 1 间-二硝基苯和间-胺基苯酚的实验和计算的紫外吸收峰峰值

体系	实验值/nm	计算值/nm
间-二硝基苯	244*	233
间-胺基苯酚	279, 239**	287, 225

* Sadtler Standard Ultra-Violet Spectra 33 UV, Sadtler research Laboratories Inc. 1973.

** Sadtler Standard Ultra-Violet Spectra 3509, Sadtler research Laboratories Inc. 1973.

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作者简介 陈凯, 1980-, 南京师范大学化学与环境科学学院硕士研究生, 主要从事分子模拟研究, E-mail: zhenjiangchenkai@126.com

通讯联系人 朱小蕾, 女, 1958-, 南京师范大学化学与环境科学学院副教授, 主要从事分子模拟研究, E-mail: zhuxiaolei@njnu.edu.cn

万方数据

由 HF/STO-3G 方法计算得到的体系 1 的频率中没有发现虚频,说明优化的结构是真实存在的. 由于篇幅有限,优化的结构的几何参数和振动频率数据将不列入本文中.表 2、表 3 和表 4 分别给出了研究体系的总能量,紫外可见光谱的峰位和偶极矩.我们对体系的总能量进行了零点振动能校正.

表 2 化合物的总能量*和零点能

体系	HF/STO-3G(Hartree)		零点能(Hartree)	
	顺式	反式	顺式	反式
1	- 1 280.949 02	- 1 280.944 99	0.474 55	0.474 72
2	- 1 355.698 97	- 1 355.694 96	0.487 11	0.487 31
3	- 1 241.869 87	- 1 241.863 61	0.504 69	0.504 44
4	- 1 994.335 91	- 1 994.334 27	0.482 28	0.482 55

* 已作零点能校正.

基于表 2 的能量数据和表 3 的紫外可见光谱数据,我们可以对 Diflavylene 的压致变色作如下解释: Diflavylene 的顺反异构体的能差很小,而且顺式异构体的能量较低,即常温下, Diflavylene 应该是顺式结构并显橙色.如果研磨 Diflavylene 体系,相当于对体系做功,体系得到了足够的能量,就可以由橙色($\lambda_{max} \approx 484\text{ nm}$)的顺式异构体转变为红色($\lambda_{max} \approx 493\text{ nm}$)的反式异构体.当放置数小时或数天后, Diflavylene 将会自发地转变为能量较低的橙色的顺式异构体.理论计算表明, Diflavylene 是一种压敏的且颜色变化明显的压色性材料.杂原子环,共轭体系的大小及可逆的顺反异构是决定 Diflavylene 具有压色性的重要因素.我们对 Diflavylene 的理论计算证实了 Kortum 对 Diflavylene 压色性机理的推测.

表 3 化合物的紫外可见吸收峰峰值

体系	顺式	反式
1	484 314	493 315
2	502 369	520 358
3	483 317	486 371
4	551 361 294	576 293

表 4 化合物的偶极矩

体系	顺式(Debye)	反式(Debye)
1	0.461	0.669
2	0.378	2.272
3	1.256	0.462
4	0.196	1.662

2 压色性材料的分子设计

从上述 Diflavylene 的理论计算和分析可以看出,用 HF/STO-3G 和 ZINDO/S 方法研究和探讨物质的压色性是可行的.因此,我们设计和构造了图 1 中的化合物 α (X 为 C=O) β (X 为 N-H) γ (X 为 C=S).我们用 HF/STO-3G 方法优化了体系 2-4 的起始结构,通过振动频率的分析证实优化的结构是稳定的.计算结果表明,化合物 1-4 的顺反异构体都具有 C_2 点群.由表 4 可以看出,化合物 1-4 的顺反异构体都有偶极矩.这是由于杂原子环的存在使得共轭体系不完全共面.尽管如此,杂原子环对这些体系的压色性起了重要的作用.

表 2 和表 3 给出了体系 2-4 的总能量和紫外可见光谱数据.表 2 和表 3 的计算结果表明,这些化合物的顺反异构体的能量相近,而且在可见光区都有明显的吸收峰.在低压下,就可能实现顺反异构互变,进而发生颜色的变化,即体系 2-4 都可能是压敏的压色性材料.这些预测对合成新的压色性材料有一定的指导意义.

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Electrocatalytic Activity of Pt/C Catalystprepared with Solid Phase Reaction Method for Formic Oxidation

Yuan Qingyun¹ ,Tang Yawen¹ ,Zhou Yiming¹ ,Xing Wei² ,Lu Tianhong^{1,2}

(1 .School of Chemistry and Environmental Science , Nanjing Normal University , 210097 , Nanjing , PRC)
(2 .Changchun Institute of Applied Chemistry , Chinese Academy of Sciences , 130022 , Changchun , PRC)

Abstract In this paper , the electrocatalytic activity of the Pt/C catalyst prepared with solid phase reaction method(Pt/ (C s)) was investigated for the oxidation of formic acid. XRD and TEM measurements indicated that the average diameter and the crystalline extent of Pt particles in Pt/ (C s) catalyst are much lower than that of the Pt/C catalyst prepared with the traditional liquid phase reaction method(Pt/ (C l)). Therefore , the electrocatalytic activity of Pt/ (C s) catalyst for the oxidation of formic acid is much better than that of Pt/ (C l) catalyst.

Key words Solid phase reaction , Formic acid , Direct methanol Fuel cell , Pt/C catalyst

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Piezochromic Mechanism of Diflavylene

Chen Kai , Zhu Xiaolei , Yao Jie , Zhou Zhihua

(School of Chemistry and Environmental Science , Nanjing Normal University , 210097 , Nanjing , PRC)

Abstract A Hartree-Fock quantum chemical calculation has been performed to study the piezochromism of Diflavylene. The structure of Diflavylene is optimized at the HF/STO-3G level. Vibrational frequency calculation shows that the optimized geometry is stable at the HF/STO-3G potential surface. The piezochromic mechanism of Diflavylene is discussed in terms of total energies ,UV-vis spectra , and dipole moments of compounds. New piezochromic materials are designed.

Key words piezochromism cis-trans isomers quantum chemistry

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