# 吡啶酮系偶氮类化合物可见吸收光谱的预测

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**摘要** 利用密度泛函的 B3LYP 方法,在 6-311G\* 基组水平对吡啶酮系偶氮类化合物进行构型优化,并进 行了自然键轨道(NBO)分析,然后用 TDDFT 方法和 ZINDO/S 方法分别计算了它们的可见吸收光谱,结果均 与实验值十分吻合.通过对比发现,对于最高吸收波长的计算,ZINDO/S 能以较快的速度得到较好的结果. 在用 ZINDO/S 计算的过程中,回归分析发现 *π-π* 重叠加权因子(OWF<sub>*n-n*</sub>)与染料分子吡啶环上两个羰基氧原 子平均电荷 Z<sub>0</sub> 有较好的线性关系:OWF<sub>*n-π*</sub>=0.11425-1.04178Z<sub>0</sub>,这一关系不仅可从量子化学的角度进行解 释,而且可用于同类染料可见吸收光谱的预测.分子轨道的研究表明,这些化合物的最高可见吸收波长主要 对应着共轭体系中给电子体到受电子体的电子跃迁.

关键词: 吡啶酮系偶氮类化合物, 自然键轨道, TDDFT, ZINDO/S 中图分类号: O641

吡啶酮系化合物从六十年代开始作为偶合组 分与苯胺衍生物作用合成偶氮染料<sup>1-3]</sup>.此类染料不 仅色泽鲜艳,而且染色性能优异,它们存在着如图 1所示的偶氮体和腙体之间的互变异构. Cheng 等<sup>[3]</sup> 通过实验和理论计算证明了吡啶酮染料主要以腙 体形式存在, Cee 等<sup>[4]</sup>也得出过相同结论. 从理论 上分析, 腙体结构中亚胺基上的氢原子易与羰基 氧原子形成分子内氢键, 形成六元环, 这样既有利 于分子的稳定,又能与吡啶酮环形成共轭发色系 统. 因此本文仅对腙体构型进行了研究.

可见吸收光谱是染料的重要性质之一,运用 量子化学方法对其进行预测已成为近来研究的热 点.陈兴等<sup>[5-6]</sup>曾采用 PPP-MO(Pariser-Parr-Pople-Molecular-Orbital)法对吡啶酮系偶氮类染料的最高 可见吸收波长进行了计算,但结果与实测值有一 定差距.近年来用含时的密度泛函理论(TDDFT)处 理激发态计算电子光谱成为非常活跃的领域<sup>[7-8]</sup>.本 文分别用 TDDFT 方法和 ZINDO/S 方法对结构通 式如图 1 所示的吡啶酮系偶氮类化合物的可见吸 收光谱进行研究,得到了具有一定普遍适用性的 结论. 密度泛函理论(DFT)将复杂的 N 电子波函数 及其对应的薛定谔方程转化为简单的电子密度函 数及其对应的计算体系.在核处于静态的假设下, 可以计算原子、分子等体系的能量和结构等各种性 质,由于泛函理论考虑了电子自旋相关效应,故精 度较好.B3LYP 是密度泛函理论的一种,在使用梯 度校正泛函的基础上加入了三参数杂化泛函.含 时的密度泛函(TDDFT)方法以新的方式定义了有 效势和时间交换关联势<sup>(9)</sup>,在处理分子激发态方面 比其它量子化学方法有较大的优势.计算表明, TDDFT 方法能够较准确地计算分子激发态和电子 光谱.

ZINDO/S 法是基于 INDO 法建立起来的一种 半经验量子化学方法. Yuan 等<sup>[10]</sup>在用 ZINDO/S 法 预测金属酞菁类化合物的可见吸收光谱的过程中 发现, π-π 重叠加权因子(OWF<sub>ππ</sub>)对计算结果起着 决定性作用. OWF<sub>ππ</sub> 主要是调节 π-π 键对共振积



## 1 理论方法

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图 2 B3LYP/6-311G\*优化构型 Fig.2 The optimized geometry based on B3LYP/6-311G\* method

分贡献的大小,分子共轭程度越大, π-π 键对共振 积分的贡献也越大.因此,OWF<sub>ππ</sub>可看作分子共 轭程度的一个量度,不同的分子应该有不同的值. 计算中发现,将OWF<sub>ππ</sub>设为定值无法得到对大多 数分子都满意的结果.为提高计算的准确度,本文 首先根据实测值确定OWF<sub>ππ</sub>值,而后通过回归方 法揭示OWF<sub>ππ</sub>与分子构型参数的关系,然后用此 关系对其它同类化合物的最高可见吸收波长进行

#### 表 1 部分优化构型参数

Та	bl	e 1		Partial	data	of	optimized	geometry	parameters
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Compd.	$l_{N-N}^{a}/nm$	Zo <sup>b</sup>
1	0.1294	-0.392
2	0.1304	-0.373
3	0.1300	-0.363
4	0.1303	-0.386
5	0.1299	-0.383
6	0.1292	-0.391
7	0.1294	-0.403
8	0.1309	-0.352
9	0.1312	-0.367
10	0 1325	-0.334

a) $l_{N-N}$ : the length of nitrogen-nitrogen bond; b) $Z_0$ : the average net charge on oxygen of carbonyls in pyridone

预测.

本文先采用 Hyperchem 7.0 程序包中的 PM3 方法对染料分子构型进行预优化,为了获得精确的 结果,在此基础上利用 Gaussian 03 程序包<sup>[11]</sup>,用密 度泛函的 B3LYP 方法在 6-311G\* 基组水平下再优 化,并进行了自然键轨道(NBO)分析,然后分别用 TDDFT 方法和 ZINDO/S 法对分子的最高吸收波 长进行计算.

由于上述化合物中最高吸收波长的实测值都 是在甲苯中得到的,所有的计算都是模拟在甲苯 溶液中进行的.

# 2 结果与讨论

# 2.1 构型优化

B3LYP/6-311G\* 方法优化的分子构型如图 2 所示,优化构型的部分参数在表 1 中列出.由表 1 可见,这些化合物的氮氮键长大于一般的氮氮双 键(约 0.12 nm)而小于一般的氮氮单键(约 0.144 nm),这是体系共轭的结果;吡啶环上羰基氧原子 的平均电荷值较小,从量子化学角度分析,羰基是 吸电子基团,可使其它部分的电子通过分子骨架 转移过来,导致羰基氧原子电子密度较大,即电荷 值较小.

表 2 部分自然键轨道分析值

Table 2	Part of calculated	results by	NBO analysis
Compd.	Donor	Acceptor	$E/kJ \cdot mol^{-1}$
1	LP <sup>a</sup> N <sub>7</sub>	BD*b N8=C9	239.40
1	BD <sup>c</sup> N <sub>8</sub> =N <sub>9</sub>	$BD^* C_{10} = C_{11}$	73.10
0	LP N <sub>7</sub>	BD* N <sub>8</sub> =C <sub>9</sub>	212.20
2	BD N <sub>8</sub> =N <sub>9</sub>	$BD^* C_{10}=C_{11}$	68.20
9	LP N <sub>7</sub>	$BD^* N_8 = C_9$	222.60
3	BD N <sub>8</sub> =N <sub>9</sub>	$BD^* C_{10}=C_{11}$	70.52
4	LP N <sub>7</sub>	BD* N <sub>8</sub> =C <sub>9</sub>	217.24
4	BD N <sub>8</sub> =N <sub>9</sub>	$BD^* C_{10}=C_{11}$	69.12
-	LP N <sub>7</sub>	BD* N <sub>8</sub> =C <sub>9</sub>	225.60
Э	BD N <sub>8</sub> =N <sub>9</sub>	$BD^* C_{10}=C_{11}$	70.93
(	LP N <sub>7</sub>	BD* N <sub>8</sub> =C <sub>9</sub>	450.36
0	BD N <sub>8</sub> =N <sub>9</sub>	$BD^{*}C_{10}=C_{11}$	96.56
7	LP N <sub>7</sub>	BD* N <sub>8</sub> =C <sub>9</sub>	291.36
1	BD N <sub>8</sub> =N <sub>9</sub>	$BD^* C_{10}=C_{11}$	79.76
0	LP N <sub>7</sub>	BD* N <sub>8</sub> =C <sub>9</sub>	325.24
0	BD N <sub>8</sub> =N <sub>9</sub>	$BD^* C_{10}=C_{11}$	73.12
0	LP N <sub>7</sub>	BD* N <sub>8</sub> =C <sub>9</sub>	254.68
9	BD N <sub>8</sub> =N <sub>9</sub>	$BD^* C_{10}=C_{11}$	71.04
10	LP N <sub>7</sub>	BD* N <sub>8</sub> =C <sub>9</sub>	186.18
10	BD N <sub>8</sub> =N <sub>9</sub>	BD * C <sub>10</sub> =C <sub>11</sub>	61.96

a) LP:the lone pair electron; b) BD\*:2-center antibond;

c) BD:2-center bond; The number of compd. same as

Fig.2

表 3

可见吸收光谱实测值和计算值

	Table 3 Ob	served visible	absorption	maxima and corresponding	calculated results			
C 1	) 3/		) b/	TDDFT	ZIN	DO/S		
Compa.	$\Lambda_{\rm obs}/{\rm n}$	m	$\Lambda_{\rm cal}/\rm{nm}$	$\lambda_{cal}/nm$	$OWF_{\pi\cdot\pi}^{c}$	$\lambda_{cal}/nm$		
1	433		460	439.12	0.525	433.83		
2	435		433	440.43	0.504	435.54		
3	423	i	431	426.62	0.498	423.25		
4	429	1	431	431.07	0.515	429.38		
5	423	i	429	426.85	0.513	423.81		
6	457		449	462.32	0.521	456.76		
7	442		437	448.77	0.533	442.35		
8	455		466	460.25	0.485	455.59		
9	431		435	436.16	0.492	431.48		
10	435		462	442 91	0.461	435.73		

a) $\lambda_{cbs}$ : the observed visible absorption maxima; b) $\lambda_{cal}$ : calculated visible absorption maxima based on PPP method<sup>[5-6]</sup>; c)OWF<sub> $\pi$ - $\pi$ </sub> :  $\pi$ - $\pi$  overlap weighting factor

#### 2.2 自然键轨道分析

自然键轨道(nature bond orbital)能较好地对分子的成键情况和键键相互作用进行分析<sup>[12-14]</sup>.表2中列出了部分电子供体(donor)轨道和电子受体(acceptor)轨道以及由二阶微扰理论得到的它们之间的相互作用稳定化能 *E*, *E* 越大表明供电子体和受电子体的相互作用越强,即供电子体向受电子体提供电子的倾向越大.计算中发现,上述吡啶酮类化合物主要是 N<sub>7</sub>与吡啶酮环上一些化学键的共轭,所以表 2 中仅列出了这些键的计算结果,化合物及各原子序号如图 2 所示.

由表 2 可看到, 当苯环上有供电子基团 (化合物 6、7), N<sub>7</sub>上的孤对电子与 N<sub>8</sub>=C<sub>9</sub> 双键的  $\sigma$  反键轨道、N<sub>8</sub>=C<sub>9</sub> 双键的  $\sigma$  成键轨道与 C<sub>10</sub>=C<sub>11</sub> 的  $\sigma$ 反键轨道的稳定化能 *E* 值较大; 当苯环上有吸电子基团 (化合物 2、3、4、5)时, *E* 较小. 当供电性较强的OCH<sub>3</sub> 存在(化合物 6、7)时, *E* 值最大, 即供电体的供电倾向更大, 电子离域化程度越大, 共轭链越长.

#### 2.3 可见吸收光谱

得到优化构型后,分别在 B3LYP/6-311G\* 水 平上用 TDDFT 方法和用 ZINDO/S 法对上述化合 物的可见吸收光谱进行计算.表 3 中列出了这些化 合物最高吸收波长的实测值、PPP 法的计算值<sup>[5-0]</sup>和 本文的计算结果.通过比较可以看到,用 TDDFT 法和 ZINDO/S 法计算最高可见吸收波长,都能得 到与实验值较吻合的结果.但是,通过调节 OWF<sub>ππ</sub> 值,半经验的 ZINDO/S 法可以用较少的计算时间 得到更为精确的结果.

# 2.4 OWF<sub>#-#</sub>与分子构型参数的关系

在用 ZINDO/S 法计算过程中,为找到 OWF<sub>ππ</sub> 与分子构型参数之间的关系,利用 ORIGIN 软件

将 OWF<sub>#</sub>,分别对 *l*<sub>N-N</sub>,*Z*<sub>0</sub>进行回归,发现以 *Z*<sub>0</sub>回 归的结果最好,相关系数 *R* 为 0.99136,回归结果 如图 3 所示,并得到了 OWF<sub>#</sub>,与 *Z*<sub>0</sub>的关系式(1):

 $OWF_{\pi-\pi}=0.11425-1.04178 Z_0$  (1)

由图 3 可见, OWF<sub>#-</sub>与吡啶环上羰基氧原子 平均电荷 Z<sub>0</sub>存在较好的线性关系, 随着 Z<sub>0</sub> 的减 小, OWF<sub>#-</sub>增大. 从量子化学角度来看, 羰基是吸 电子基团, 若分子中的电子能够有效地通过分子 骨架转移到羰基上, 使羰基的电子密度较大, 即 Z<sub>0</sub> 较小, 则分子的共轭程度较大, OWF<sub>#-</sub> 也越大.

#### 2.5 电子跃迁

有机分子的吸收光谱是分子吸收能量之后,电子由基态到激发态的跃迁产生的,分子轨道的计算表明,这些化合物的最高可见吸收波长对应的均是从最高占有轨道(HOMO)到最低空轨道(LUMO)的电子跃迁.表4中列出了它们 HOMO 和 LUMO 的组成.表中的数据是各原子对轨道贡献的百分率,(为便于比较,小于1.5的数值忽略不计),化合物及各原子编号如图2所示.



表 4 HOMO 和 LUMO 中各组成原子的贡献百分率

CompolIIIPII <th></th> <th>Tab</th> <th>ole 4 T</th> <th>he contr</th> <th>ibutive p</th> <th>ercentage</th> <th>of compon</th> <th>ent atoms</th> <th>to HOMO</th> <th>and LUM</th> <th>0</th> <th></th>		Tab	ole 4 T	he contr	ibutive p	ercentage	of compon	ent atoms	to HOMO	and LUM	0	
orbialPLMMO <t< td=""><td>Compd.</td><td></td><td>1</td><td></td><td></td><td>2</td><td></td><td>3</td><td>_</td><td>4</td><td></td><td>5</td></t<>	Compd.		1			2		3	_	4		5
C1         3.20         1.52         2.53         3.50         3.76           C2         7.02         7.02         8.68         6.65         6.35           C3         15.30         16.77         13.38         16.02         15.34           C5         8.27         8.96         6.69         8.05         9.22           C6         15.28         10.64         12.29         13.51         9.125         9.20           N8         30.12         2.44         2.745         2.77         9.037         9.052         10.09         10.99           C0         9.57         11.25         9.25         12.35         8.55         12.66         8.029         10.09         11.97           C10         15.21         10.62         1.38         13.15         10.69         10.09         11.97           C11         6.58         10.52         6.67         9.21         8.38         13.15         11.63         13.23           C14         5.512         4.49         5.26         5.65         5.19         5.19           C16         -         5.12         2.449         3.44         1.13         2.429         4.31 <tr< td=""><td>orbital</td><td>1</td><td>HOMO</td><td>LUMO</td><td>HOMO</td><td>LUMC</td><td>HOMO</td><td>LUMO</td><td>HOMO</td><td>LUMO</td><td>HOMO</td><td>LUMO</td></tr<>	orbital	1	HOMO	LUMO	HOMO	LUMC	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
C2         7.42         7.92         8.68         6.45         6.36           C3         15.30         16.77         7.833         16.82         15.3           C4         2.21         2.43         2.26         5         3.51         12.90           C5         8.27         8.98         6.49         8.05         9.25         12.9         1.51         12.90         5.89           N7         2.268         7.89         2.450         3.82         2.256         5.33         17.0         6.75         2.19         30.08           C9         9.57         11.25         9.25         12.32         8.55         12.66         8.23         10.09         11.37           C11         0.59         10.62         6.67         9.21         8.01         10.02         5.06         10.68         1.33           C13         5.12         4.49         5.26         5.56         1.63         1.33         1.35         1.43         1.48         1.48         1.48         1.49         3.44         1.18         2.62         2.90         1.52         2.90         1.52         2.91         2.91         2.91         2.91         2.91         2.91         <	C1		3.20		1.52		2.53		3.50		3.76	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	C2		7.02		7.92		8.68		6.45		6.36	
C42.212.232.539.229.24C53.237.9924.503.8222.505.3319.716.7520.895.90N830.122.4427.452.7730.8730.3220.0910.0911.07C1015.212.2427.452.7730.8710.5210.0911.07C1015.2110.626.679.218.0110.925.0610.087.8110.03C126.446.679.218.0110.925.0610.087.8110.03C136.446.679.218.0110.925.0610.087.8110.03C145.124.495.265.265.555.192.993.992.993.99 <td< td=""><td>C3</td><td></td><td>15.36</td><td></td><td>16.77</td><td></td><td>13.83</td><td></td><td>16.82</td><td></td><td>15.84</td><td></td></td<>	C3		15.36		16.77		13.83		16.82		15.84	
CS         B.27         B.064         I2.23         B.305         9.22           N7         22.68         7.90         24.50         3.82         22.56         5.33         19.71         6.75         20.09         5.59           N8         30.12         2.44         27.45         22.77         30.87         10.52         2.19         30.09         11.97           C10         15.21         10.62         1.38         13.15         11.67         13.32           C11         6.98         10.62         6.76         9.21         8.01         10.92         5.65         5.59           N13         -         -         6.78         9.26         5.55         5.19           C14         -         5.12         4.49         2.06         4.51         1.62         4.08         2.44         4.58           C15         -         -         5.2         6.06         1.82         6.01         1.61         5.76           C20         -         5.52         2.06         1.82         6.01         1.61         5.76           C21         2.11         2.87         2.32         2.29         5.76         2.29         0.16	C4		2.21				2.43		2.56			
C615.2810.6412.2313.3112.94N722.687.9922.565.3319.750.5221.930.08N830.122.4427.452.7730.8730.3221.930.08C16.9810.526.679.218.0110.925.8.2330.2310.0911.97C116.986.526.679.218.0110.925.9610.087.8110.33C126.446.676.787.087.085.905.955.955.95N135.124.495.826.655.655.655.825.655.952.29C155.122.322.505.651.622.892.814.58O181.854.431.943.942.585.441.832.022.89O191.975.635.525.655.125.125.125.125.12O22N22/C225.535.525.615.615.615.615.615.61C16.045.522.295.125.145.615.615.61C205.535.525.515.615.615.615.615.615.61C215.645.745.745.745.745.615.745.615.745.61C215.925.124.845.745.745.615.745.615.745.61 <td>C5</td> <td></td> <td>8.27</td> <td></td> <td>8.98</td> <td></td> <td>6.89</td> <td></td> <td>8.05</td> <td></td> <td>9.22</td> <td></td>	C5		8.27		8.98		6.89		8.05		9.22	
N7       22.60       7.89       24.40       27.45       27.77       30.87       30.52       21.99       30.08         C9       9.57       11.25       9.25       12.32       8.55       12.05       8.23       10.92       10.09       11.97         C10       15.21       10.62       1.33       13.15       11.07       13.32         C11       6.98       10.52       6.67       9.21       8.01       10.92       5.26       10.08       7.81       10.03         C12       6.44       6.67       9.21       8.01       10.92       5.26       5.65       5.19         C14       5.12       4.43       1.94       3.94       2.06       4.31       1.43       2.62       2.29         O13       1.21       2.87       2.32       2.36       2.58       3.44       1.43       2.64       2.83       4.38         O19       1.97       5.63       5.52       6.06       1.32       6.01       1.61       5.76         C16       .211       2.87       2.32       2.99       .226       .229       .229       .229       .229       .229       .229       .229       .210       .229	C6		15.28		10.64		12.23		13.51		12.98	
N8       30.12       2.44       27.45       2.77       30.87       30.25       2.19       90.08         C0       9.57       11.25       925       12.23       8.55       12.65       8.23       10.92       10.09       11.97         C10       6.98       10.52       6.67       9.21       8.01       10.92       5.96       10.08       7.81       10.03         C14       6.44       6.37       6.78       7.68       5.56       5.51       5.19         C15       -	N7		22.68	7.89	24.50	3.82	22.56	5.33	19.71	6.75	20.89	5.89
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	N8			30.12	2.44	27.45	2.77	30.87		30.52	2.19	30.08
C10         15.21         10.62         1.38         1.31         1.67         13.39           C11         6.58         10.52         6.67         9.21         8.01         10.92         5.96         10.08         5.59           N13         -         -         -         -         -         -         5.26         5.65         5.19           C14         -         5.12         -         4.49         5.26         5.65         5.19           C16         -         -         -         -         -         -         -         2.29           C18         1.62         2.43         3.94         2.06         4.51         1.62         4.03         2.44         4.58           C19         1.65         -         3.35         -         6.16         1.62         4.04         5.36           C20         -         1.52         2.29         -         -         6.18         -         1.51         -         6.18         -         1.52           C21         6.44         -         1.52         2.29         -         6.18         -         1.51         -         6.18         -         1.52	C9		9.57	11.25	9.25	12.32	8.55	12.65	8.23	10.92	10.09	11.97
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C10			15.21		10.62	1.38	13.15		11.67		13.32
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C11		6.98	10.52	6.67	9.21	8.01	10.92	5.96	10.08	7.81	10.03
N13	C12			6.44		6.87		6.78		7.68		5.59
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	N13											
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C14			5.12		4.49		5.26		5.65		5.19
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	C15											
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C16											
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	N17		2.11	2.87	2.32	2.36	2.58	3.44	1.83	2.62		2.29
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O18		1.85	4.43	1.94	3.94	2.06	4.51	1.62	4.08	2.84	4.58
C20         N21//C21       S.35         023       1.52       2.29         023         Compd.       C       S.35         Compd.       C       S.35         Compd.       C       S.35         Compd.       C       S.35         Compd.       C       S       9       II         Compd.       G       T       S       S         Compd.       G       HOMO       LUMO       HOMO       LUMO       HOMO       LUMO         Compd.       G       S       S         Compd.       G       J         Compd.       G       S       S         Compd.       G       S       S         G       S <th< td=""><td>O19</td><td></td><td>1.97</td><td>5.63</td><td></td><td>5.52</td><td></td><td>6.06</td><td>1.82</td><td>6.01</td><td>1.61</td><td>5.76</td></th<>	O19		1.97	5.63		5.52		6.06	1.82	6.01	1.61	5.76
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	C20											
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	N21/C21					3.35						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O22/N22/C	22			1.52	2.29				6.18		
O24 O25         9         10           Compd.         6         7         8         9         10           Orbital         HOMO         LUMO         HOMO         LUMO         HOMO         LUMO           C1         6.04         5.35         14.04         13.37         12.79           C3         19.28         19.04         14.35         15.74         16.56           C4         5.02         3.58         5.12         4.84         3.64           C5         9.23         8.43         2.85         5.01         5.98           C6         18.28         16.84         12.77         2.03         12.75         12.37         2.82           N7         15.86         7.69         17.52         8.54         20.28         4.42         21.02         4.65         20.87         1.96           N8         30.64         30.49         2.13         22.57         2.35         27.07         3.29         20.76           C9         7.96         11.25         10.07         9.22         8.08         10.42         8.50         12.02         6.83         12.88           C10         12.93         14.08         9.69 <td>O23</td> <td></td> <td></td> <td></td> <td>1.52</td> <td>2.29</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	O23				1.52	2.29						
O25           Compd.         6         7         8         9         10           orbital         HOMO         LUMO         HOMO         HOMO         LUMO	024											
$ \begin{array}{ c c c c c c c c c c } \hline \begin{tabular}{ c c c c c c c } \hline \hline \begin{tabuarray}{ c c c c c c c } \hline \hline \begin{tabuarray}{ c c c c c c c c c c c c c c c c c c c$	025											
orbital OrbitalHOMOLOMOHOMOLONOHOMOLONOHOMOLONOHOMOLONOHOMOLONOHOMOLONOHOMO <th< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></th<>												
C10.045.53C25.836.8714.0413.3712.79C319.2819.0414.3515.7416.56C45.023.585.124.843.64C59.238.432.855.015.98C618.2816.8412.772.0312.7512.37N715.867.6917.528.5420.284.4221.024.6520.87N830.6430.6412.772.0312.026.6312.82C97.9611.2510.079.228.0810.428.5012.026.8312.88C1012.9314.089.6911.181.878.57C115.0310.025.549.605.147.597.399.566.578.68C126.956.845.456.925.878.685.678.683.50C145.675.323.944.683.505.673.59C161171.981.772.472.052.362.322.492.332.14O184.361.684.661.673.971.654.283.29O195.025.665.835.674.833.29O21/C211.786.572.469.333.29O22/N22/C224.751.786.053.55O23/N2313.554.811.776.17<	Compd.		6		7		8	LUNIO	9		1	0
C23.630.6414.0415.3712.19C319.2819.0414.3515.7416.56C45.023.585.124.843.64C59.238.432.855.015.98C618.2816.8412.772.0312.7512.372.82N715.867.6917.528.5420.284.4221.024.6520.871.96N830.6430.492.1322.572.3527.073.2920.76C97.9611.2510.079.228.0810.428.5012.026.8312.88C1012.9314.089.6911.181.878.57C115.0310.025.549.605.147.599.566.578.68C126.956.685.456.925.878.683.50C145.675.323.944.683.502.322.492.332.14O184.361.684.661.673.971.654.283.29O21/C215.025.665.835.674.835.674.83O22/N22/C224.751.786.050.336.050.33O22/N235.655.551.786.050.673.55O21/C215.555.665.675.665.676.67O21/C215.556.576.655.665.67	Compd. orbital	HOMO	6 LUMC	D HC	7 0MO 1	LUMO	8 HOMO	LUMO	9 HOMO	LUMO	HOMO	0 LUMO
C319.2319.0414.3313416.36C4 $5.02$ $3.58$ $5.12$ $4.84$ $3.64$ C5 $9.23$ $8.43$ $2.85$ $5.01$ $5.98$ C6 $18.28$ $16.84$ $21.77$ $2.03$ $12.75$ $12.37$ $2.82$ N7 $15.86$ $7.69$ $17.52$ $8.54$ $20.28$ $4.42$ $21.02$ $4.65$ $20.87$ $1.96$ N8 $30.64$ $30.49$ $2.13$ $22.57$ $2.35$ $27.07$ $3.29$ $20.76$ C9 $7.96$ $11.25$ $10.07$ $9.22$ $8.08$ $10.42$ $8.50$ $12.02$ $6.83$ $12.88$ C10 $12.93$ $14.08$ $9.69$ $11.18$ $1.87$ $8.57$ C11 $5.03$ $10.02$ $5.54$ $9.60$ $5.14$ $7.59$ $7.39$ $9.56$ $6.57$ $8.68$ C12 $6.95$ $6.57$ $5.32$ $3.94$ $4.68$ $3.50$ $5.67$ $8.68$ C14 $5.67$ $5.32$ $3.94$ $4.68$ $3.50$ $2.33$ $2.14$ O18 $4.36$ $1.68$ $4.66$ $1.67$ $3.97$ $1.65$ $4.28$ $3.29$ O19 $5.02$ $5.66$ $5.83$ $5.67$ $4.83$ $3.29$ O21/C21 $4.77$ $2.47$ $2.05$ $2.36$ $2.32$ $2.49$ $2.33$ $2.14$ O21/C21 $4.75$ $1.78$ $6.05$ $3.57$ $4.81$ $1.77$ $6.17$ O21/C24 $5.5$ $5.67$ <td< td=""><td>Compd. orbital C1</td><td>HOMO 6.04</td><td>6 LUMC</td><td>D HC</td><td>7 DMO 1 .35</td><td>LUMO</td><td>8 HOMO</td><td>LUMO</td><td>9 HOMO</td><td>LUMO</td><td>HOMO</td><td>0 LUMO</td></td<>	Compd. orbital C1	HOMO 6.04	6 LUMC	D HC	7 DMO 1 .35	LUMO	8 HOMO	LUMO	9 HOMO	LUMO	HOMO	0 LUMO
C4 $5.02$ $3.38$ $5.12$ $4.84$ $3.64$ C5 $9.23$ $8.43$ $2.85$ $5.01$ $5.98$ C6 $18.28$ $16.84$ $12.77$ $2.03$ $12.75$ $12.37$ $2.82$ N7 $15.86$ $7.69$ $17.52$ $8.54$ $20.28$ $4.42$ $21.02$ $4.65$ $20.87$ $1.96$ N8 $30.64$ $30.49$ $2.13$ $22.57$ $2.35$ $27.07$ $3.29$ $20.76$ C9 $7.96$ $11.25$ $10.07$ $9.22$ $8.08$ $10.42$ $8.50$ $12.02$ $6.83$ $12.88$ C10 $12.93$ $14.08$ $9.69$ $11.18$ $1.87$ $8.57$ C11 $5.03$ $10.02$ $5.54$ $9.60$ $5.14$ $7.59$ $7.39$ $9.56$ $6.57$ $8.68$ C12 $6.95$ $6.84$ $5.45$ $6.92$ $5.87$ $8.68$ C13 $5.67$ $5.32$ $3.94$ $4.68$ $3.50$ C14 $5.67$ $5.32$ $3.94$ $4.68$ $3.50$ C15 $1.77$ $2.47$ $2.05$ $2.36$ $2.32$ $2.49$ $2.33$ $2.14$ O18 $4.36$ $1.68$ $4.66$ $1.67$ $3.97$ $1.65$ $4.28$ $3.29$ O19 $5.02$ $5.66$ $5.83$ $5.67$ $4.83$ $6.05$ O21/C21 $4.77$ $2.47$ $2.05$ $2.36$ $2.32$ $2.46$ $9.33$ O21/C24 $5.66$ $5.83$ $5.67$ $4.63$ $9.33$ $6.05$	Compd. orbital C1 C2 C2	HOMO 6.04 5.83	6 LUMC	D HC	7 DMO 1 0.35 0.87	LUMO	8 HOMO 14.04	LUMO	9 HOMO 13.37	LUMO	10 HOMO	0 LUMO
C5 $9.23$ $8.43$ $2.28$ $5.01$ $5.98$ C6 $18.28$ $16.84$ $12.77$ $2.03$ $12.75$ $12.37$ $2.82$ N7 $15.86$ $7.69$ $17.52$ $8.54$ $20.28$ $4.42$ $21.02$ $4.65$ $20.87$ $1.96$ N8 $30.64$ $30.49$ $2.13$ $22.57$ $2.35$ $27.07$ $3.29$ $20.76$ C9 $7.96$ $11.25$ $10.07$ $9.22$ $8.08$ $10.42$ $8.50$ $12.02$ $6.83$ $12.88$ C10 $12.93$ $14.08$ $9.69$ $11.18$ $1.87$ $8.57$ C11 $5.03$ $10.02$ $5.54$ $9.60$ $5.14$ $7.59$ $7.39$ $9.56$ $6.57$ $8.68$ C12 $6.95$ $6.84$ $5.45$ $6.92$ $5.87$ $8.68$ $5.67$ $8.68$ C14 $5.67$ $5.32$ $3.94$ $4.68$ $3.50$ $5.67$ $8.68$ C15 $1.98$ $1.77$ $2.47$ $2.05$ $2.36$ $2.32$ $2.49$ $2.33$ $2.14$ O18 $4.36$ $1.68$ $4.66$ $1.67$ $3.97$ $1.65$ $4.28$ $3.29$ O19 $5.02$ $5.66$ $5.83$ $5.67$ $4.83$ $2.20$ O21/C21 $4.75$ $1.78$ $6.05$ $0.37$ $0.65$ O23/N23 $4.81$ $1.77$ $6.17$ $0.55$ O24/C24 $5.55$ $5.55$ $5.55$ $5.67$ $5.67$	Compd. orbital C1 C2 C3 C3	HOMO 6.04 5.83 19.28	6 LUMC	D HC 5 6 19	7 DMO 1 5.35 5.87 0.04	LUMO	8 HOMO 14.04 14.35	LUMO	9 HOMO 13.37 15.74	LUMO	14 HOMO 12.79 16.56	0 LUMO
C618.2816.8412.772.0312.7512.372.32N715.867.6917.528.5420.284.4221.024.6520.871.96N830.6430.492.1322.572.3527.073.2920.76C97.9611.2510.079.228.0810.428.5012.026.8312.88C1012.9314.089.6911.181.878.57C115.0310.025.549.605.147.597.399.566.578.68C126.956.845.456.925.878.683.506.925.87N1315.675.323.944.683.503.50C1611.981.772.472.052.362.322.492.332.14O184.361.684.661.673.971.654.283.29O195.025.665.835.674.833.29O21/C21115.665.835.674.836.05O23/N2314.811.776.170.470.176.17O24/C243.5513.551.786.05	Compd. orbital C1 C2 C3 C4	HOMO 6.04 5.83 19.28 5.02	6 LUMC	D HC	7 0MO 1 0.35 0.87 0.04 0.58	LUMO	8 HOMO 14.04 14.35 5.12	LUMO	9 HOMO 13.37 15.74 4.84	LUMO	10 HOMO 12.79 16.56 3.64	0 LUMO
N715.867.6917.528.5420.284.4221.024.6520.871.96N8 $30.64$ $30.49$ 2.1322.572.3527.073.2920.76C97.9611.2510.079.228.0810.428.5012.026.8312.88C1012.9314.089.6911.181.878.57C115.0310.025.549.605.147.597.399.566.578.68C126.956.845.456.925.878.68C145.675.323.944.683.50C151.673.971.654.283.29O184.361.684.661.673.971.654.283.29O195.025.665.835.674.833.29O21/C216.572.469.336.059.33O22/N22/C223.554.811.776.17O24/C243.55 $3.55$ $3.57$ $3.57$	Compd. orbital C1 C2 C3 C4 C5	HOMO 6.04 5.83 19.28 5.02 9.23	6 LUMC	D HC	7 0MO 1 0.35 0.87 0.04 0.58 0.43 0.04	LUMO	8 HOMO 14.04 14.35 5.12 2.85	LUMO	9 HOMO 13.37 15.74 4.84 5.01	LUMO	12.79 16.56 3.64 5.98	
N8 $30.64$ $30.49$ $2.13$ $22.57$ $2.35$ $27.07$ $3.29$ $20.76$ C9 $7.96$ $11.25$ $10.07$ $9.22$ $8.08$ $10.42$ $8.50$ $12.02$ $6.83$ $12.88$ C10 $12.93$ $14.08$ $9.69$ $11.18$ $1.87$ $8.57$ C11 $5.03$ $10.02$ $5.54$ $9.60$ $5.14$ $7.59$ $7.39$ $9.56$ $6.57$ $8.68$ C12 $6.95$ $6.84$ $5.45$ $6.92$ $5.87$ N13	Compd. orbital C1 C2 C3 C4 C5 C6	HOMO 6.04 5.83 19.28 5.02 9.23 18.28	6 LUMC		7 0MO 1 .35 .87 0.04 .58 .43 .684	LUMO	8 HOMO 14.04 14.35 5.12 2.85 12.77 12.77	2.03	9 HOMO 13.37 15.74 4.84 5.01 12.75	LUMO	10.000 12.79 16.56 3.64 5.98 12.37	0 LUMO 2.82
C97.9611.2510.079.228.0810.428.5012.026.8312.88C1012.9314.089.6911.181.878.57C115.0310.025.549.605.147.597.399.566.578.68C126.956.845.456.925.87N13 $$	Compd. orbital C1 C2 C3 C4 C5 C6 N7	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86	6 LUMC 7.69		7 0MO 1 .35 .87 0.04 .58 .43 .684 7.52	LUMO 8.54	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28	LUMO 2.03 4.42	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02	LUMO 4.65	10.000 12.79 16.56 3.64 5.98 12.37 20.87	0 LUMO 2.82 1.96
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86	6 LUMC 7.69 30.64		7 0MO 1 .35 .87 0.04 .58 .43 .684 7.52	8.54 30.49	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13	2.03 4.42 22.57	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35	4.65 27.07	10.000 12.79 16.56 3.64 5.98 12.37 20.87 3.29	0 LUMO 2.82 1.96 20.76
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96	6 LUMC 7.69 30.64 11.25	D HC 5 6 19 3 8 16 10 10	7 0MO 1 0.35 0.87 0.04 0.58 0.43 0.84 7.52 0.07	8.54 30.49 9.22	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08	2.03 4.42 22.57 10.42	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50	4.65 27.07 12.02	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83	0 LUMO 2.82 1.96 20.76 12.88
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96	6 LUMC 7.69 30.64 11.25 12.93	D HC 5 6 19 3 8 16 10	7 0MO 1 0.35 0.04 0.58 0.43 0.84 7.52 0.07	8.54 30.49 9.22 14.08	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08	2.03 4.42 22.57 10.42 9.69	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50	4.65 27.07 12.02 11.18	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87	0 LUMO 2.82 1.96 20.76 12.88 8.57
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02	D HC 5 6 19 3 8 8 16 1' 10 5	7 0MO 1 .35 .87 0.04 .58 .43 .84 7.52 0.07 .54	8.54 30.49 9.22 14.08 9.60	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14	2.03 4.42 22.57 10.42 9.69 7.59	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39	4.65 27.07 12.02 11.18 9.56	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95	HC           5           6           19           3           8           16           1           1           5	7 0MO 1 .35 .87 0.04 .58 .43 5.84 7.52 0.07 .54	8.54 30.49 9.22 14.08 9.60 6.84	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14	2.03 4.42 22.57 10.42 9.69 7.59 5.45	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39	4.65 27.07 12.02 11.18 9.56 6.92	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95	D HC 5 6 19 3 8 16 1' 10 5	7           0MO         1           3.35	8.54 30.49 9.22 14.08 9.60 6.84	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14	2.03 4.42 22.57 10.42 9.69 7.59 5.45	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39	4.65 27.07 12.02 11.18 9.56 6.92	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67	D HC 5 6 19 3 8 16 1' 10 5	7 0MO 1 0.35 0.87 0.04 0.58 0.43 0.84 7.52 0.07 54	8.54 30.49 9.22 14.08 9.60 6.84 5.32	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39	4.65 27.07 12.02 11.18 9.56 6.92 4.68	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50
N17       1.98       1.77       2.47       2.05       2.36       2.32       2.49       2.33       2.14         O18       4.36       1.68       4.66       1.67       3.97       1.65       4.28       3.29         O19       5.02       5.66       5.83       5.67       4.83         C20	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67	D HC 5 6 19 3 8 16 17 10 5	7 MO 1 .35 .87 0.04 .58 .43 .84 7.52 0.07 .54	8.54 30.49 9.22 14.08 9.60 6.84 5.32	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39	4.65 27.07 12.02 11.18 9.56 6.92 4.68	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50
018       4.36       1.68       4.66       1.67       3.97       1.65       4.28       3.29         019       5.02       5.66       5.83       5.67       4.83         C20       -       -       -       -       -       -       -       -       4.83         C20       -       -       -       -       -       -       -       -       -       4.83         O21/C21       -       -       6.57       2.46       9.33       -	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15 C16	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67	D HC 5 6 19 3 8 16 1 1 5	7 0MO 1 0.35 0.04 0.58 0.43 0.84 7.52 0.07 54	8.54 30.49 9.22 14.08 9.60 6.84 5.32	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39	4.65 27.07 12.02 11.18 9.56 6.92 4.68	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50
019       5.02       5.66       5.83       5.67       4.83         C20       . <td>Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15 C16 N17</td> <td>HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03</td> <td>6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67 1.98</td> <td></td> <td>7 0MO 1 .35 .87 0.04 .58 .43 .58 .43 .684 7.52 0.07 .54</td> <td>8.54 30.49 9.22 14.08 9.60 6.84 5.32 2.47</td> <td>8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14</td> <td>2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94 2.36</td> <td>9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39 2.32</td> <td>4.65 27.07 12.02 11.18 9.56 6.92 4.68 2.49</td> <td>12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57</td> <td>0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50 2.14</td>	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15 C16 N17	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67 1.98		7 0MO 1 .35 .87 0.04 .58 .43 .58 .43 .684 7.52 0.07 .54	8.54 30.49 9.22 14.08 9.60 6.84 5.32 2.47	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94 2.36	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39 2.32	4.65 27.07 12.02 11.18 9.56 6.92 4.68 2.49	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50 2.14
C20       6.57       2.46       9.33         O221/C21       6.57       1.78       6.05         O22/N22/C22       4.75       1.78       6.05         O23/N23       4.81       1.77       6.17         O24/C24       3.55       50	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15 C16 N17 O18	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67 1.98 4.36		7 0MO 1 .35 .87 0.04 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .58 .43 .58 .58 .58 .58 .58 .58 .58 .58	8.54 30.49 9.22 14.08 9.60 6.84 5.32 2.47 4.66	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14 2.05 1.67	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94 2.36 3.97	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39 2.32 1.65	4.65 27.07 12.02 11.18 9.56 6.92 4.68 2.49 4.28	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50 2.14 3.29
O21/C21       6.57       2.46       9.33         O22/N22/C22       4.75       1.78       6.05         O23/N23       4.81       1.77       6.17         O24/C24       3.55       50	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15 C16 N17 O18 O19	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67 1.98 4.36 5.02	D         HC           5         6           19         3           8         16           1         1           5         5	7 0MO 1 .35 .87 0.04 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .52 .007 .54 .54 .54 .54 .54 .55 .55 .67 .68 .58 .68 .58 .68 .58 .68 .58 .68 .58 .68 .58 .68 .58 .68 .58 .58 .68 .58 .58 .58 .68 .58 .58 .684 .55 .55 .67 .56 .57 .56 .684 .55 .56 .57 .57 .56 .57 .57 .57 .58 .58 .58 .58 .684 .55 .67 .56 .57 .57 .56 .57 .57 .56 .56 .57 .57 .57 .56 .57 .57 .57 .57 .58 .58 .58 .58 .58 .58 .58 .58	8.54 30.49 9.22 14.08 9.60 6.84 5.32 2.47 4.66 5.66	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14 2.05 1.67	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94 2.36 3.97 5.83	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39 2.32 1.65	LUMO 4.65 27.07 12.02 11.18 9.56 6.92 4.68 2.49 4.28 5.67	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50 2.14 3.29 4.83
O22/N22/C22     4.75     1.78     6.05       O23/N23     4.81     1.77     6.17       O24/C24     3.55     5.00	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15 C16 N17 O18 O19 C20	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67 1.98 4.36 5.02	HC           5           6           19           3           10           11           10           5	7 0MO 1 .35 .87 0.04 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .52 .007 .54 .77 .68	8.54 30.49 9.22 14.08 9.60 6.84 5.32 2.47 4.66 5.66	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14 2.05 1.67	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94 2.36 3.97 5.83	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39 2.32 1.65	LUMO 4.65 27.07 12.02 11.18 9.56 6.92 4.68 2.49 4.28 5.67	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50 2.14 3.29 4.83
O23/N23     4.81     1.77     6.17       O24/C24     3.55     7.00	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15 C16 N17 O18 O19 C20 O21/C21	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67 1.98 4.36 5.02	D         HC           5         6           19         3           8         16           1         1           5         5	7 0MO 1 .35 .87 0.04 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .58 .43 .58 .58 .58 .43 .58 .58 .58 .58 .58 .58 .58 .58	8.54 30.49 9.22 14.08 9.60 6.84 5.32 2.47 4.66 5.66	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14 2.05 1.67	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94 2.36 3.97 5.83 6.57	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39 2.32 1.65	LUMO 4.65 27.07 12.02 11.18 9.56 6.92 4.68 2.49 4.28 5.67 2.46	10.000 12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57 2.33	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50 2.14 3.29 4.83 9.33
024/C24 3.55	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15 C16 N17 O18 O19 C20 O21/C21 O22/N22/C22	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67 1.98 4.36 5.02	HC           5           6           19           3           8           16           1           10           5	7 0MO 1 .35 .87 0.04 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .43 .58 .58 .43 .58 .58 .58 .58 .58 .58 .58 .58	8.54 30.49 9.22 14.08 9.60 6.84 5.32 2.47 4.66 5.66	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14 2.05 1.67	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94 2.36 3.97 5.83 6.57 4.75	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39 2.32 1.65	LUMO 4.65 27.07 12.02 11.18 9.56 6.92 4.68 2.49 4.28 5.67 2.46 1.78	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50 2.14 3.29 4.83 9.33 6.05
	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15 C16 N17 O18 O19 C20 O21/C21 O22/N23	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67 1.98 4.36 5.02	HC           5           6           19           3           8           10           1           10           5	7 0MO 1 .35 .87 0.04 .58 .43 .84 7.52 0.07 .54 .77 .68	8.54 30.49 9.22 14.08 9.60 6.84 5.32 2.47 4.66 5.66	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14 2.05 1.67	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94 2.36 3.94 2.36 3.97 5.83 6.57 4.75 4.81	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39 2.32 1.65	LUMO 4.65 27.07 12.02 11.18 9.56 6.92 4.68 2.49 4.28 5.67 2.46 1.78 1.77	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50 2.14 3.29 4.83 9.33 6.05 6.17
020	Compd. orbital C1 C2 C3 C4 C5 C6 N7 N8 C9 C10 C11 C12 N13 C14 C15 C16 N17 O18 O19 C20 O21/C21 O22/N22/C22 O23/N23 O24/C24	HOMO 6.04 5.83 19.28 5.02 9.23 18.28 15.86 7.96 5.03	6 LUMC 7.69 30.64 11.25 12.93 10.02 6.95 5.67 1.98 4.36 5.02	HC           5           6           19           3           8           16           1           10           5	7 0MO 1 .35 .87 0.04 .58 .43 .84 7.52 0.07 .54 .77 .68	8.54 30.49 9.22 14.08 9.60 6.84 5.32 2.47 4.66 5.66	8 HOMO 14.04 14.35 5.12 2.85 12.77 20.28 2.13 8.08 5.14 2.05 1.67	2.03 4.42 22.57 10.42 9.69 7.59 5.45 3.94 2.36 3.94 2.36 3.97 5.83 6.57 4.75 4.81	9 HOMO 13.37 15.74 4.84 5.01 12.75 21.02 2.35 8.50 7.39 2.32 1.65	LUMO 4.65 27.07 12.02 11.18 9.56 6.92 4.68 2.49 4.28 5.67 2.46 1.78 1.77	12.79 16.56 3.64 5.98 12.37 20.87 3.29 6.83 1.87 6.57	0 LUMO 2.82 1.96 20.76 12.88 8.57 8.68 5.87 3.50 2.14 3.29 4.83 9.33 6.05 6.17

# 的组成是极为相似的. HOMO 主要由 N7 和苯环附 近的原子组成, 而 LUMO 则主要由 N8 和吡啶酮环 附近的原子组成. 从 HOMO 到 LUMO, N7 和苯环

附近的原子对轨道的贡献明显减少, N8 和吡啶环 及吡啶环上吸电子基对轨道的贡献明显增加, 且当 苯环上有给电子基时, 吡啶酮环及环上吸电子基的

#### 表 5 其它吡啶酮系偶氮类化合物吸收光谱实测值和预测值

Table 5 The observed visible absorption maxima and corresponding predicted results of other

pjildone uzo compoundo	pyridone	azo	compounds
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Cupatituant	) 3/10.000	) blana	ZINDO/S		
Substituent	Aobs / IIIII	$\Lambda_{cal}$ / IIIII	$Z_0^{c}$	$\mathrm{OWF}_{\pi \cdot \pi^{\mathrm{d}}}$	$\lambda_{cal}/nm$
$R_1=H$ $R_2=H$ $R_3=CN$ $R_4=CH_3$	425	450	-0.386	0.516	430.36
$R_1$ =OCH <sub>3</sub> $R_2$ =H $R_3$ =H $R_4$ =C <sub>4</sub> H <sub>9</sub>	454	-	-0.402	0.533	451.29
$R_1$ =OCH <sub>3</sub> $R_2$ =H $R_3$ =H $R_4$ =C <sub>3</sub> H <sub>6</sub> OCH <sub>3</sub>	456	_	-0.413	0.544	452.47

a) $\lambda_{ds}$ : the observed visible absorption maxima; b) $\lambda_{cal}$ : calculated visible absorption maxima based on PPP method; c) $Z_0$ : the average net charge on oxygen on carbonyls; d)OWF<sub> $\pi-\pi$ </sub>:  $\pi-\pi$  overlap weighting factor calculated by equation (1)

贡献增加更加显著. N7 是亚氨基上氮原子, 具有很强的给电子性, 可以认为它们吸收能量之后, 电子产生了一系列跃迁, 而由共轭体系中给电子体向受电子体的跃迁, 对应着最高可见吸收波长. 吡啶酮系偶氮类化合物分子是典型的给电子-受电子共轭发色体. 其中给电子基主要是亚氨基, 受电子体主要是吡啶环上的羰基、氰基等. 若在苯环上引入给电子取代基, 则延长了体系的共轭链, 增强了染料分子两端的不对称性, 从而降低了体系的激发能, 就引起深色效应. 反之, 则导致浅色效应, 这与NBO分析的结果一致. 表 3 中苯环上有甲氧基和甲基取代的化合物波长大于其它同类化合物的原因即在于此.

# 2.6 可见吸收光谱的预测

为验证上述计算和结论的适用性,本文对其它 一些同类吡啶酮系偶氮类化合物的可见吸收光谱进 行了预测,分子的优化构型也是由 B3LYP/6-311G\* 方法优化得到的,将所得构型参数 Z<sub>0</sub>代入式(1)求 得 OWF<sub>π-π</sub>,而后用 ZINDO/S 方法计算它们的最高 可见吸收波长,计算结果如表 5 所示.为便于比较, 将 PPP 法的计算值和实测值<sup>[56,15]</sup>也一并列出.由表 5 可见,计算结果与实测值比较吻合,表明式 (1)有 较好的适用性.

## 3 结论

以 Gaussian03 程序包为工具,采用 B3LYP 密度 泛函方法优化构型, 通过 NBO 分析发现, 当苯环上 有供电基团存在时, 体系共轭程度增大.用 TDDFT 法和 ZINDO/S 法都可以较准确计算吡啶酮系偶氮 类化合物的可见吸收光谱, 通过比较发现选取合 适的 OWF<sub>#</sub>值, ZINDO/S 法可以较快地得到更精 确的结果.通过回归分析, 发现 OWF<sub>#</sub>与吡啶环 酮上羰基氧原子电荷 Z<sub>0</sub>存在较好的线性关系, 利 用这一关系,对其它同类染料的可见吸收光谱的 预测结果与实测值较吻合,证明了其具有一定的 普遍适用性.分子轨道研究表明,此类化合物最高 吸收波长是分子吸收光之后电子从 HOMO 向 LUMO 的跃迁,即电子从共轭体系中给电子体跃 迁到受电子体引起的.这对提高染料分子可见吸 收光谱预测的准确度,揭示分子结构与吸收光谱 之间的规律有较大的作用.

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# Prediction of Visible Absorption of Pyridone Azo Compounds

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**Abstract** Based on B3LYP method of DFT, the geometry of pyridone azo compounds was optimized at the level of 6-311G\* basis, and analyzed by NBO (nature bond orbital) method. Their visible absorption maxima were calculated with TDDFT method and ZINDO/S method, the results agreed with the observed values excellently. It was shown that the visible absorption maxima can be calculated more precisely in much shorter time with ZINDO/S method by adjusting that the value of  $\pi$ - $\pi$  overlap weighting factor (OWF<sub> $\pi$ - $\pi$ </sub>) than TDDFT method. In the process of calculation with ZINDO/S, in virtue of the method of regression it was found that the linear relationship between OWF<sub> $\pi$ - $\pi$ </sub> and Z<sub>0</sub> (the average net charge on oxygen of the two carbonyl-groups in pyridone) was excellent, OWF<sub> $\pi$ - $\pi$ </sub>=0.11425–1.04718Z<sub>0</sub>, that is, with the drop of Z<sub>0</sub>, OWF<sub> $\pi$ - $\pi$ </sub> increased. The relationship not only could be explained in terms of quantum theory, but also could be used to predict the visible absorption maxima of other pyridone azo compounds in the same series. What's more, the study on molecular orbital implied that the electron transition from the electron donators to electron acceptors of conjugate system resulted in their visible absorption maxima.

Keywords: Pyridone azo compound, NBO, TDDFT, ZINDO/S

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