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Research on the prediction of absorption half-band width of some azobenzene compounds

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Abstract

In order to predict the absorption half-band width, the ground state and the first singlet-excited state configurations of some azobenzene compounds are calculated by B3LYP/6-311G* and CIS methods, respectively. Based on the configurations obtained above, the absorption maximum and emission maximum are calculated by TD-DFT method, the results are in good agreement with observed values. Further study shows a linear relationship between $\Delta\lambda_{1/2}$ (the observed absorption half-band width) and S (the difference between the emission maximum and absorption maximum). According to the relationship obtained, the absorption half-band width of other azobenzene derivatives in the same series could be predicted successfully.

Keywords: Azobenzene compounds; TD-DFT; Absorption maximum; Emission maximum; Half-band width

1. Introduction

The absorption bandwidth has a great influence on the color and brightness of dyestuffs. For functional dyes, such as laser dyes, fluorescent dyes and organic non-linear optical materials and so on, strict demands on absorption band have to be satisfied. Therefore, the research on absorption bandwidth of dyes is of great importance. However, owing to the complexity of the formation of absorption bandwidth and the variety of its influencing factors, such as molecular configuration, steric hindrance effect, solvent effect and so on, the prediction of absorption bandwidth is a difficult work. Usually, half-band width ($\Delta\lambda_{1/2}$, the width at the half height of the absorption band) is used to characterize the width of the absorption band.

As pointed out in Ref. [1], the absorption bandwidth is dependent on the overall equilibrium geometry difference between the ground state and the first singlet-excited state, and great geometry differences would lead to broad absorption bands. For example, the bandwidth of cyanine dyes is narrower than that of polyene compounds because the geometry change from the ground state to the first singlet-excited state of cyanine dyes is less than that of polyene compounds.

Since both the bandwidth and Stoke's shift (the frequency difference between the absorption maximum and fluorescence maximum) are dependent on the equilibrium geometry difference between the ground state and the first singlet-excited state, perhaps it is not surprising that there exists a simple relationship between them. In literature, M. Pestemer etc. [2] illustrated that for a wide range of fluorescent brighteners there existed a simple relationship between the width of the absorption band and the Stoke's shift, and L. B. Cheng etc. [3] found a relationship between the half-band width and the Stoke's shift obtained by PPP-MO method for 31 dyes.

In recent years, DFT method has been developed for optimizing molecular geometry and calculating electronic spectrum, and generally speaking, better results could be obtained than semi-empirical methods. In this article, the absorption maximum and emission maximum of 10 azobenzene compounds (Fig. 1) are calculated by DFT method, and their absorption half-band width is studied on the basis of the results of predecessors [2,3].

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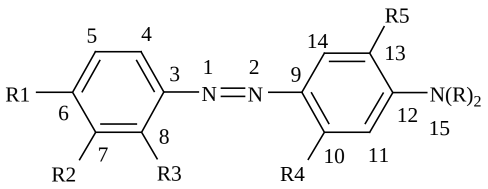

Fig. 1. The general structure of azobenzene compounds.

2. Calculation method

Based on Gaussian 98 package, the ground state configuration is optimized with B3LYP/ 6-311G* method, and the absorption maximum $\lambda_{\max}$ is calculated with time-dependent density functional theory (TD-DFT) at the level 6-311G*. The CIS method, which has been used popularly in recent years in the research of the electron excited states [4–6], is used to optimize the first singlet-excited state configuration at the level 6-311G*, and then the emission maximum $\lambda^*_{\max}$ is also calculated by TD-DFT method at the level 6-311G*. For the convenience of comparison of calculated results with observed ones in ethanol, all calculations are performed with ethanol as solvent (with key words scrf in Gaussian package).

3. Results and discussion

3.1. Geometry optimization

Partial data of the optimized ground state and first singlet-excited state geometries are shown in Tables 1 and 2, respectively. For the convenience of comparison, the differences between them are also listed in Table 2.

Viewed from the data in Table 1, the length of nitrogen–nitrogen bond (L_{N-N}) is longer than that of common nitrogen–nitrogen double-bonds (about

Table 1
Partial data of the optimized ground state geometry

No.	substituent[a]				$L_{N\text{-}N}$[b] (10^{-10} m)	Q_{N15}[c] (1.6×10^{-19} C)
	R1	R2	R3	R4		
1	NO_2	H	H	H	1.3036	−0.7071
2	CN	H	H	H	1.3019	−0.7076
3	CHO	H	H	H	1.3001	−0.7078
4	SO_2CH_2COOH	H	H	$NHCOCH_3$	1.2994	−0.7135
5	SO_2CH_2COOH	CH_3	H	$NHCOCH_3$	1.2985	−0.7134
6	SO_2CH_2COOH	OCH_3	H	$NHCOCH_3$	1.2983	−0.7133
7	SO_2CH_2COOH	H	OCH_3	$NHCOCH_3$	1.2965	−0.7126
8	OCH_3	SO_2CH_2COOH	H	$NHCOCH_3$	1.2973	−0.7127
9	SO_2CH_2COOH	H	H	H	1.2971	−0.7006
10	NO_2	H	CN	H	1.3031	−0.7053

[a] R=CH_2CH_3, R5=H.
[b] The length of nitrogen–nitrogen bond.
[c] The net charge on atom N15.

Table 2
Partial data of the optimized first singlet-excited state geometry

No.	L_{N-N}[a] (10^{-10}m)	ΔL[b] (10^{-10} m)	Q_{N15}[c] (1.6×10^{-19} C)	ΔQ[d] (1.6×10^{-19} C)
1	1.3174	0.0138	−0.7083	−0.0012
2	1.3089	0.0070	−0.7095	−0.0019
3	1.3087	0.0086	−0.7085	−0.0007
4	1.3123	0.0129	−0.7146	−0.0011
5	1.3080	0.0095	−0.7145	−0.0011
6	1.3085	0.0102	−0.7139	−0.0006
7	1.3177	0.0212	−0.7133	−0.0007
8	1.3032	0.0059	−0.7138	−0.0011
9	1.3028	0.0057	−0.7012	−0.0006
10	1.3184	0.0153	−0.7059	−0.0006

[a] The length of nitrogen–nitrogen bond.
[b] The difference of L_{N-N} between the ground state and the first singlet-excited state.
[c] The net charge on atom N15.
[d] The difference of Q_{N15} between the ground state and the first singlet-excited state.