Study on the prediction of visible absorption maxima
of azobenzene compounds

LIU Jun-na (刘军娜)[†], CHEN Zhi-rong (陈志荣), YUAN Shen-feng (袁慎峰)

(*School of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, China*)

[†]E-mail: liujunna@zju.edu.cn

Abstract: The geometries of azobenzene compounds are optimized with B3LYP/6-311G* method, and analyzed with nature bond orbital, then their visible absorption maxima are calculated with TD-DFT method and ZINDO/S method respectively. The results agree well with the observed values. It was found that for the calculation of visible absorption using ZINDO/S method could rapidly yield better results by adjusting $OWF_{\pi\text{-}\pi}$ (the relationship between $\pi\text{-}\pi$ overlap weighting factor) value than by the TD-DFT method. The method of regression showing the linear relationship between $OWF_{\pi\text{-}\pi}$ and $BL_{N\text{-}N}$ (nitrogen-nitrogen bond lengths) as $OWF_{\pi\text{-}\pi}=-8.1537+6.5638BL_{N\text{-}N}$, can be explained in terms of quantum theory, and also be used for prediction of visible absorption maxima of other azobenzne dyes in the same series. This study on molecules' orbital geometry indicates that their visible absorption maxima correspond to the electron transition from HOMO (the highest occupied molecular orbital) to LUMO (the lowest unoccupied molecular orbital).

Key words: Azobenzene compound, Nature bond orbital (NBO), Visible absorption maxima

doi:10.1631/jzus.2005.B0584   **Document code:** A   **CLC number:** O641

INTRODUCTION

As one of the most important properties of dyes, the visible absorption maxima have been predicted by quantum theory (Kogo, 1985; Griffiths, 1982; Cheng *et al.*, 1986; Türker, 2002; Machado *et al.*, 2003). Time-dependent density functional theory is popularly used to deal with excited state and to calculate electron spectrum (Liao *et al.*, 2003; Song *et al.*, 2003; Carlo *et al.*, 1999). Azobenzene compound is an important and valuable multi-functional dye with pure chromophoric properties, high molar extinction coefficient, and fine staining qualities. In this study, the visible absorption spectra of azobenzene compounds with the general structure shown in Fig.1 are discussed based on TD-DFT method and ZINDO/S

method to obtain applicable results.

CALCULATION METHOD

All computation in this study was carried out with the Gaussian 98 package. The molecular geometries are optimized by B3LYP method with the 6-311G* basis, and then are analyzed by nature bond orbital (NBO) theory. Finally, the visible absorption maxima are calculated with TD-DFT/6-311G* method and ZINDO/S method respectively. In the process of computation based on ZINDO/S method, the relationship between $\pi\text{-}\pi$ overlap weighting factor ($OWF_{\pi\text{-}\pi}$) and relevant geometry parameters reveal the change tendency of $OWF_{\pi\text{-}\pi}$.

RESULTS AND DISCUSSION

Geometry optimization

The optimized configurations with B3LYP/6-311G* are shown in Fig.2, and partial data on the
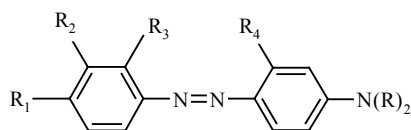

Fig.1 The general structure of azobenzene dyes

optimized parameters are listed in Table 1. The initial geometries are obtained with PM3 method based on Hyperchem 7 package.

Table 1 shows that nitrogen-nitrogen bond lengths (BL_{N-N}) are all shorter than those of common nitrogen-nitrogen single-bond (about 1.4 Å) but longer than those of double-bond (about 1.2 Å), which is attributed to the conjugation of the system. The average net charges on nitrogen of the diethyl-amine are negative.

Nature bond orbital analysis

Nature bond orbital analysis provides an efficient method for studying intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge-transfer or conjugative interaction in molecular systems (Alan *et al.*, 1988; Carpenter and Weinhold, 1988; Yi, *et al.*, 1994). Some electron donor orbitals, acceptor orbitals and the interacting stabilization energy resulted from the second-order micro-disturbance theory are listed in
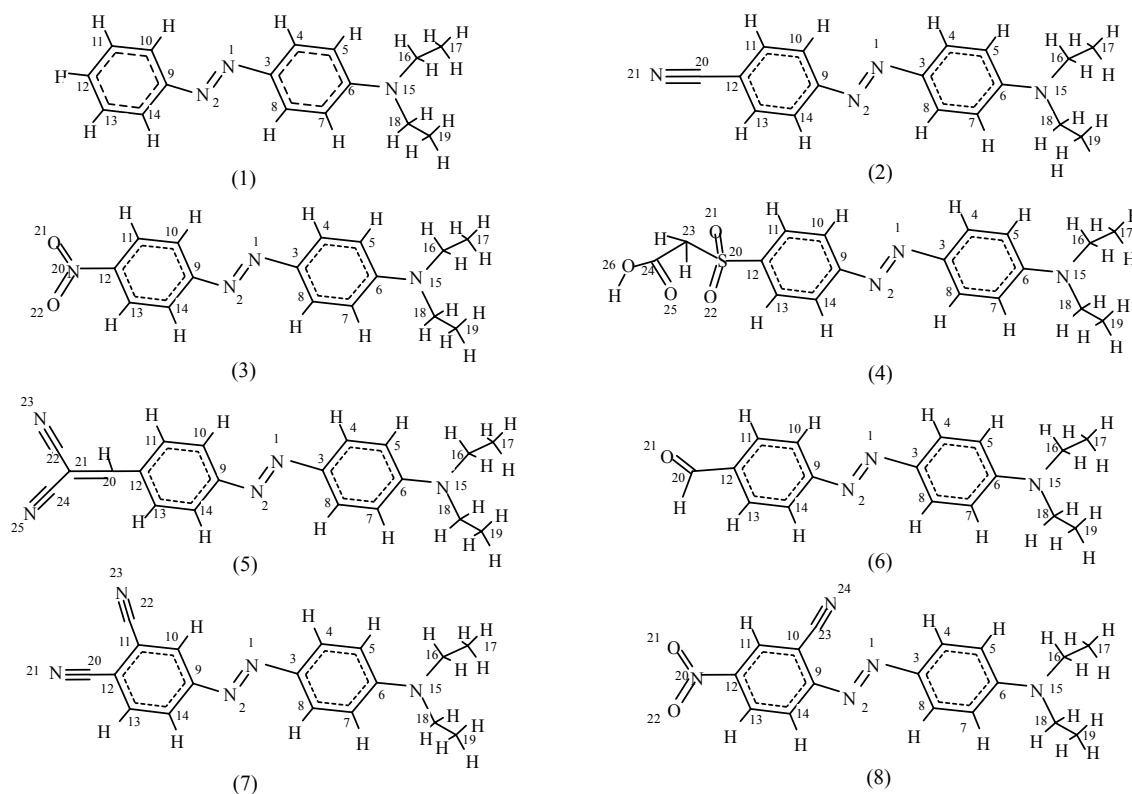
Fig.2 The optimized geometries based on B3LYP/6-311G* method
The compounds 1−8 are accordance with Tables 1, 2 and 3

Table 1 Partial data on optimized geometry parameters

Compound	Substituent					BL_{N-N} (Å)[a]	C_{N15}[b]
	R_1	R_2	R_3	R_4	R		
1	H	H	H	H	CH_2CH_3	1.3092	−0.7085
2	CN	H	H	H	CH_2CH_3	1.3019	−0.7076
3	NO_2	H	H	H	CH_2CH_3	1.3036	−0.7071
4	SO_2CH_2COOH	H	H	H	CH_2CH_3	1.2971	−0.6226
5	$CH=C(CN)_2$	H	H	H	CH_2CH_3	1.3033	−0.6662
6	CHO	H	H	H	CH_2CH_3	1.3008	−0.7078
7	CN	CN	H	H	CH_2CH_3	1.2983	−0.6727
8	NO_2	H	CN	H	CH_2CH_3	1.3027	−0.6817

[a]: The length of nitrogen-nitrogen bond; [b]: The net charge on N15

Table 2. The larger the *E* value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. The analysis results of stronger electron donor diehyl-amine and its adjacent bonds whose *E* values are the largest among them are shown in Table 2. The serial number of atoms is the same as those shown in Fig.2.

As shown in Table 2, when there are electron accepting groups on the benzene ring (compounds 2−8), the stabilizing energy *E* between the lone pair electron N15 and carbon-carbon bond of the adjacent benzene ring is larger than those of without electron acceptors (compound 1). Furthermore, the greater electron accepting ability the acceptor has, the larger the *E* value is, i.e. the more intensive is the system delocalization, the greater is the extent of the system conjugation.

Visible absorption maxima

On the basis of the optimized geometries above,

Table 2　Part of calculated results by NBO analysis

Compound	Donor	Acceptor	E (kJ/mol)
1	LP[a] N15	BD[*b] C6-C7	179.23
2	LP N15	BD[*] C5-C6	210.28
3	LP N15	BD[*] C6-C7	229.71
4	LP N15	BD[*] C6-C7	224.82
5	LP N15	BD[*] C6-C7	250.05
6	LP N15	BD[*] C5-C6	217.23
7	LP N15	BD[*] C6-C7	232.64
8	LP N15	BD[*] C6-C7	258.40

[a]: The lone pair electron; [b]: 2-center antibond

their visible absorptions are calculated by ZINDO/S method and B3LYP/6-311G* of TD-DFT method, respectively. Yuan *et al.*(2003) found that satisfactory results could not be obtained with fixed $OWF_{\pi\text{-}\pi}$ value in the course of predicting visible absorption maxima of phthalocyanine compounds by ZINDO/S method. Whereas, the results agree well with experiment results if appropriate $OWF_{\pi\text{-}\pi}$ value is selected. The observed and calculated visible absorption maxima of these compounds (Lü *et al.*, 1993; Pan and Wang, 1994; Cheng *et al.*, 1989) in this study are given in Table 3. Showing by comparison that although the obtained visible absorption maxima with TD-DFT method and ZINDO/S method are both consistent with observed values, the results with ZINDO/S method are closer to experimental data. Therefore, for computation of visible absorption maxima, the results by semi-empirical ZINDO/S method could be more precise in much shorter time by adjusting appropriate $OWF_{\pi\text{-}\pi}$ value than those of TD-DFT method.

The relationship between $OWF_{\pi\text{-}\pi}$ and configuration parameters

To determine the relationship between $OWF_{\pi\text{-}\pi}$ and configuration parameters, the method of stepwise regression was used for correlating $OWF_{\pi\text{-}\pi}$ value with $BL_{N\text{-}N}$, C_{N15} etc. showing that $BL_{N\text{-}N}$ has the best linear relationship with $OWF_{\pi\text{-}\pi}$ just as in Eq.(1) and Fig.3 show, and that the coefficient *R* is 0.9939.

$$OWF_{\pi\text{-}\pi} = -8.1537 + 6.5638 BL_{N\text{-}N} \qquad (1)$$

Fig.3 shows that the relationship between $OWF_{\pi\text{-}\pi}$ and $BL_{N\text{-}N}$ is excellent. It is indicated in Eq.(1)

Table 3　Observed visible absorption maxima and corresponding calculated results

Compound	λ_{obs} (nm)[a]	λ_{cal} (nm)[b]	ZINDO/S	
			$OWF_{\pi\text{-}\pi}$	λ_{cal} (nm)[c]
1	415	419.12	0.443	415.41
2	468	475.43	0.391	468.21
3	486	493.62	0.402	485.37
4	487	495.07	0.363	487.57
5	535	541.85	0.398	532.54
6	473	479.32	0.387	472.86
7	500	509.77	0.368	500.10
8	536	544.91	0.393	534.95

[a]: The observed visible absorption maxima; [b]: Calculated visible absorption maxima based on TD-DFT method; [c]: Calculated visible absorption maxima based on ZINDO/S method with adjusted $OWF_{\pi\text{-}\pi}$ value

and Fig.3 that the $OWF_{\pi\text{-}\pi}$ value rises with the increase of $BL_{N\text{-}N}$. In terms of quantum theory, the more single bond and less double bond properties the nitrogen-nitrogen bond has, i.e. the longer the $BL_{N\text{-}N}$ is, the greater is the conjugation of the molecular system, and the greater is the $OWF_{\pi\text{-}\pi}$ value.

Electron transition

The absorption spectra of organic compounds stem from the ground-excited state vibrational tran-
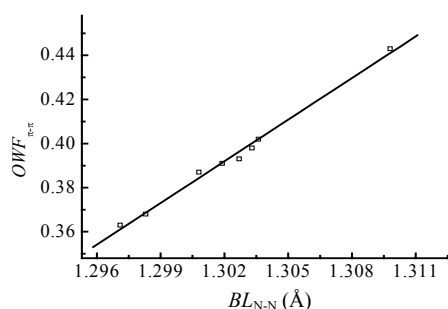

Fig.3 The relationship between $OWF_{\pi\text{-}\pi}$ and $BL_{N\text{-}N}$

sition of electrons. Calculations of molecular orbital geometry show that the visible absorption maxima of this kind of azobenzene dye correspond to the electron transition from HOMO to LUMO. The composition of HOMO and HUMO calculated by ZINDO/S method for the eight compounds mentioned above are listed in Table 4 on the percentage of the contribution of component atoms (values less than 1.5 have been excluded for the sake of simplicity). The serial numbers of atoms are consistent with those shown in Fig.2.

Table 4 shows that the composition of HOMO and LUMO of compounds 1−8 is quite similar. HOMO is mainly composed of N15 and the atoms on the adjacent benzene ring, and LUMO generally consists of atoms on the other benzene ring and the electron accepting groups on it. From HOMO to LUMO, the contribution of atoms in the region around N15 and the adjacent benzene ring reduce obviously, while those around the other benzene ring and the substituent groups on it increase. Therefore, it

Table 4 The %contribution of component atoms to HOMO and LUMO

Compd.	1		2		3		4		5		6		7		8	
Orbital	HO[a]	LU[b]	HO	LU	HO	LU	HO	LU	HO	LU	HO	LU	HO	LU	HO	LU
N1		18.1		16.1		10.4		15.7		6.1		15.8		13.2		13.6
N2	4.6	17.1	4.5	11.2	4.2	7.6	4.3	10.5	4.5	3.2	4.5	11.3	4.5	7.3	4.4	5.8
C3	16.6	6.2	16.7	2.6	16.9	1.6	16.9	2.3	16.7		16.7	2.8	16.8		16.9	
C4	1.9	6.5	1.7	4.2	1.2	2.7	1.4	3.9	1.6		1.7	4.3		2.9		2.5
C5	9.7		10.1		10.8		10.5		10.1		9.9		10.4		10.6	
C6	8.4	10.4	7.9	5.7	7.2	3.6	7.6	5.2	7.7		8.1	5.8	7.4	3.5	7.0	2.8
C7	8.9		9.3		10.2		9.8		9.5		9.3		9.8		10.1	
C8	2.1	6.1	1.7	3.9		2.5	1.5	3.8	1.7			3.9	1.5	2.8		2.5
C9		7.7		13.6		19.3		16.1		9.8		13.1		15.3		21.1
C10		5.9		5.87		3.9		5.5		2.1		5.0		2.1		3.8
C11				4.25		8.4		5.9		5.5		4.4		8.4		10.3
C12	1.6	9.9		14.85		15.8		14.9		7.9		12.9		19.6		15.8
C13				3.85		8.4		5.6		5.3		3.9				3.9
C14		6.4		6.34		3.9		5.3		2.6		6.3		10.3		7.3
N15	35.7	1.5	37.4		40.5		39.2		33.7		37.0		38.6		39.8	
C20/N20/S20				3.25		14.9		11.0		2.3		14.0				31.6
C21/O21/N21				14.21		2.7		5.7		17.1		14.1		12.2		2.1
C22/O22								5.3		1.5						1.9
N23/C23														15.2		
C24/N24																11.6
N25										4.8						

[a]: HOMO, the highest occupied molecular orbital; [b]: LUMO, the lowest unoccupied orbital

can be concluded that visible absorption maxima of azobenzene dyes correspond to electron transition from regions around N15 and the adjacent benzene ring to those around another benzene ring and its substituent groups.

This kind of azobenzene dyes is a typical chromophoric system of electron donors and acceptors, with the main electron donor being, the N15 on the amine group and the main electron acceptor being comprised of the electron-accepting groups on another benzene ring. If there are electron-accepting groups on the azobenzene system with electron donors, the chain of system conjugation is extended, and the asymmetry of the whole dye molecular system is strengthened, so the excited energy is decreased, and the electron transition from HOMO to LUMO is facilitated and consequently leads to a bathochromic shift. This result is consistent with the results from NBO analysis. This is why the

compounds without electron accepting groups on the benzene ring of the diazo group have shorter maximum absorption wavelength than others.

Prediction of visible absorption maxima

To illustrate the validity of the results obtained above, visible absorption maxima of some other azobenzene dyes in the same series are calculated. With B3LYP/6-311G* method, the geometries are optimized and the values of BL_{N-N} are obtained. Then the values of $OWF_{\pi-\pi}$ are obtained according to Eq.(1). Subsequently, the visible absorption maxima are calculated with ZINDO/S method. The results are shown in Table 5, together with directly calculated results by TD-DFT method and observed values (Lü *et al.*, 1993; Pan and Wang, 1994; Cheng *et al.*, 1989). Table 5 showing that the calculated results with ZINDO/S method is consistent with those observed, implies the good applicability of Eq.(1).

Table 5 The observed visible absorption maxima and corresponding predicted results

Substituent					λ_{obs}[a] (nm)	λ_{cal}[b] (nm)	ZINDO/S method		
R_1	R_2	R_3	R_4	R			BL_{N-N} (Å)[c]	$OWF_{\pi-\pi}$[d]	λ_{cal} (nm)
CN	H	CN	H	CH_2CH_3	515	526.36	1.2981	0.367	512.07
SO_2CH_2COOH	H	H	$NHCOCH_3$	CH_2CH_3	495	503.21	1.2982	0.368	502.10
OCH_3	H	H	$C_3H_6OCH_3$	CH_2CH_2CN	480	488.52	1.3044	0.408	487.76

[a]: The observed visible absorption maxima; [b]: Calculated visible absorption maxima based on TD-DFT method; [c]: The length of nitrogen-nitrogen bond; [d]: $OWF_{\pi-\pi}$ value calculated by Eq.(1)

CONCLUSION

Gaussian 98 package was used to optimize the structures of some azobenzene compounds by B3LYP/6-311G* method. It was found that the stabilizing energy *E* is larger when there are electron donors on one benzene ring and electron acceptor on another ring, i.e. the extent of system conjugation is more intensive. The visible absorption maxima can be precisely calculated by both TD-DFT method and ZINDO/S method, but better results can be obtained by ZINDO/S method in much shorter time by selecting appropriate $OWF_{\pi-\pi}$ value. The regression method revealed that there is excellent linear relationship between $OWF_{\pi-\pi}$ and BL_{N-N}. The prediction of the visible absorption spectra of some other compounds in the same series successfully proved the calculating method and the relationship obtained above. At the same time, the research on molecular orbital geometry shows that the visible absorption maxima of

azobenzene compound correspond to the electron transition from HOMO to LUMO. These are helpful for improving the accuracy of predicting visible absorption maxima of dyes and for revealing the relationship between the visible absorption spectrum and molecular structure.

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