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Study on the prediction of maximum absorption wavelength for conjugated alkenes

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Abstract

The optimized geometry and maximum absorption wavelength of conjugated alkenes were calculated by semi-empirical PM3 and ZINDO/S method in HyperChem, the results showed that based on the optimized geometry obtained from PM3 method, the maximum absorption wavelength of conjugated alkenes could be predicted precisely by setting $OWF_{\pi-\pi}$ (one of the adjustable parameters in ZINDO/S method) at an appropriate value. It was found that there existed an excellent linear relationship between $OWF_{\pi-\pi}$ and n (the number of conjugated double-bonds in the conjugated chain), the value of $OWF_{\pi-\pi}$ decreased as n increased. The relationship could be extrapolated to the calculation of maximum absorption wavelength for β-carotene and lycopene, and the agreement with experiment was excellent. At the same time, the research on molecular orbital showed that the maximum absorption wavelength of conjugated alkenes originated from electron transition from HOMO to LUMO — a transition weakened the bonding of double-bonds while enhanced the bonding of single-bonds.

Keywords: Conjugated alkenes; PM3; ZINDO/S; Maximum absorption wavelength; $OWF_{\pi-\pi}$; Molecular orbital

1. Introduction

Conjugated alkenes belong to the chromogen of polyene type, in terms of molecular structure, they were chain compounds that had the same number of π-electrons and carbon-atoms in the conjugated chain, and they could be expressed by the typical structure of single-bonds and double-bonds alternation. Fig. 1 shows the typical structure of conjugated alkenes studied in this article.

It had been the research interests in recent years to predict the maximum absorption wavelength of chromogens by quantum theory [1–10]; the maximum absorption wavelength of conjugated alkenes had also been studied by CNDO/2 method and CNDO/S method [11,12], but the agreement with experiment was not satisfactory. In order to improve the prediction accuracy, ZINDO/S method was used in this paper to investigate the maximum absorption wavelength of conjugated alkenes.

Developed by the research group of Michael C. Zerner of the Quantum Theory Project at the University of Florida, the so-called ZINDO/S is a modified Intermediate Neglect of Differential Overlap (INDO) method parameterized to reproduce UV–visible spectroscopic transition. A new pair of adjustable parameters was introduced to ZINDO/S by its developers, i.e. σ–σ overlap weighting factor (simplified as $OWF_{\sigma-\sigma}$) and π–π overlap weighting factor (simplified as $OWF_{\pi-\pi}$), to modify the resonance integrals for the off-diagonal elements of the Fock matrix. Adjusting the parameters

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$R\!-\!(HC{=}CH)_n\!-\!R$ R=hydrogen, methyl, phenyl

Fig. 1. Typical structure of conjugated alkenes.

provides a mechanism to adjust the relative contributions of σ versus π bonding. Consequently, the value of $OWF_{\pi-\pi}$ could be considered as a measurement of the extent of π-electron delocalization in a molecule.

Since almost all UV–visible absorption originates from electron transition involved π-electron or π-orbital, the extent of π-electron delocalization in a molecule has great influence upon its UV–visible absorption spectroscopy, that is to say, different UV–visible absorption spectroscopy would be obtained with different values of $OWF_{\pi-\pi}$. Therefore, the value of $OWF_{\pi-\pi}$ used in the calculation is of great importance.

In HyperChem 7 (the software used in the paper), the default value is 1.267 and 0.585 for $OWF_{\sigma-\sigma}$ and $OWF_{\pi-\pi}$, respectively, however, considering the variety of molecular structure and the complexity of molecular conformation, the extent of π-electron delocalization is different for different compounds. In other words, different values of $OWF_{\pi-\pi}$ should be used for different compounds. Although several different values for $OWF_{\pi-\pi}$ had been used in the literature [13], researches concerned how to evaluate $OWF_{\pi-\pi}$ and its influence on UV–visible absorption spectroscopy had not been seen.

In our research group, the visible absorption maxima of phthalocyanine compounds had been calculated with ZINDO/S method by comparison with observed values, a relationship between $OWF_{\pi-\pi}$ and molecular structural parameters was obtained, and using the relationship obtained, the prediction accuracy could be improved greatly for compounds of the same series [14]. In this article, in order to investigate the feasibility of adjusting $OWF_{\pi-\pi}$ according to molecular structural parameters for other chromogens, the maximum absorption wavelength of conjugated alkenes was studied.

2. Calculation method

2.1. Geometry optimization

Semi-empirical PM3 method in HyperChem 7 was used for the geometry optimization of conjugated alkenes, 'Model Build' all-*trans*-conformation was used as the initial one. In PM3 method, RHF was used and in SCF controls, the accelerate convergence was selected and the convergence limit was set as 0.01; in optimization calculation, the algorithm of Polak–Ribiere (conjugate gradient) was adopted and as termination condition, RMS gradient was set as 0.01.

2.2. Electronic spectrum

Using the optimized geometry, the maximum absorption wavelength was calculated by semi-empirical ZINDO/S method in HyperChem 7. $OWF_{\sigma-\sigma}$ was set as 1.267 (default value) and $OWF_{\pi-\pi}$ was so determined that calculated maximum absorption wavelength could coincide with that of observed; RHF was used and in SCF controls, the accelerate convergence was selected and the convergence limit was set as 0.01; in order to save computing time, the maximum excitation energy of singlet excited configuration interaction was set as 10 eV. All calculations were performed on a Pentium 4 computer.

3. Results and discussion

3.1. Geometry optimization

For optimized geometry, the coplanarity of the conjugated molecular backbone was still kept, partial structural parameters are shown in Table 1. As shown, ABL_1 (average bond length for double-bonds in the conjugated chain) was a little longer than the bond length for pure double-bond (1.33 Å), while ABL_2 (average bond length for single-bonds in the conjugated chain) was a little shorter than the bond length for pure single-bond (1.54 Å), in other words, single-bonds were shortened whereas double-bonds were lengthened (rather than the typical structure of single-bonds and double-bonds alternation as shown in Fig. 1) owing to the delocalization of π-electrons.

3.2. Maximum absorption wavelength

Table 2 shows the maximum absorption wavelength and the corresponding oscillator strength calculated by

Table 1
Partial molecular structural parameters for optimized geometry

R	*n*	ABL_1[a]/Å	ABL_2[b]/Å	ABL[c]/Å	$(ABL_2 - ABL_1)$/Å
Hydrogen	5	1.33881	1.45153	1.38891	0.11272
	6	1.33972	1.45102	1.39031	0.11130
	8	1.34086	1.45042	1.39199	0.10956
Methyl	5	1.34190	1.45008	1.38998	0.10818
	6	1.34230	1.44986	1.39119	0.10756
	8	1.34279	1.44958	1.39263	0.10679
Phenyl	4	1.34365	1.44847	1.39606	0.10482
	5	1.34379	1.44860	1.39620	0.10481
	6	1.34387	1.44866	1.39627	0.10479

[a] Average bond length for double-bonds in the conjugated chain.
[b] Average bond length for single-bonds in the conjugated chain.
[c] Average bond length in the conjugated chain.

Table 2
The observed and calculated results for conjugated alkenes

R	n	$\lambda_{obs}{}^{a}$/nm	$\lambda_{cal}{}^{b}$/nm	$\lambda_{cal}{}^{c}$/nm	ZINDO/S method	
					$\text{OWF}_{\pi-\pi}$	λ_{cal}/nm (f^{d})
Hydrogen	5	334	331	331	0.512	333.96 (1.962)
	6	364	367.7	353	0.492	363.86 (2.168)
	8	410	406	395	0.460	410.02 (2.610)
Methyl	5	326	335	335	0.578	326.02 (2.226)
	6	352	342	342	0.560	352.04 (2.474)
	8	396	383	383	0.521	396.14 (2.949)
Phenyl	4	384	–	–	0.514	383.89 (2.247)
	5	403	–	–	0.498	402.95 (2.518)
	6	420	–	–	0.483	420.11 (2.793)

[a] Observed values of maximum absorption wavelength.
[b] Calculated results with CNDO/2 method.
[c] Calculated results with CNDO/S method.
[d] Calculated oscillator strength.

ZINDO/S method and the value of $\text{OWF}_{\pi-\pi}$ used, for the convenience of comparison, the observed maximum absorption wavelength was also listed in Table 2 [12,15], and the results calculated by CNDO/2 method and CNDO/S method as well [11,12]. Seen from Table 2, the maximum absorption wavelength calculated by CNDO/2 method and CNDO/S method were almost the same, but the agreement with the observed one was not satisfactory, whereas the maximum absorption wavelength calculated by ZINDO/S method coincided with the observed one well by setting $\text{OWF}_{\pi-\pi}$ at an appropriate value.

In order to reveal the relationship between $\text{OWF}_{\pi-\pi}$ and molecular structural parameters, ABL_1, ABL_2, ABL, $\text{ABL}_2 - \text{ABL}_1$ and n (the structural parameters in Table 1) were selected to correlate with the value of $\text{OWF}_{\pi-\pi}$ in Table 2. Using the method of linear regression, the results showed that n (the number of conjugated double-bonds in the conjugated chain) correlated best with the value of $\text{OWF}_{\pi-\pi}$ (Fig. 2). As shown in Fig. 2, there existed an excellent linear relationship between $\text{OWF}_{\pi-\pi}$ and n, the value of $\text{OWF}_{\pi-\pi}$ decreased as n increased. For different substituent R, Eqs. (1)–(3) were obtained:

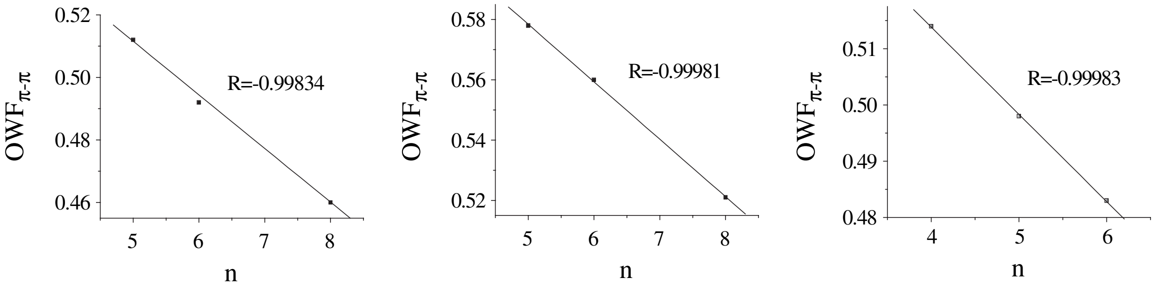
$$R = \text{hydrogen} : \text{OWF}\pi-\pi = 0.59657 - 0.01714n \tag{1}$$

$$R = \text{methyl} : \text{OWF}\pi-\pi = 0.67379 - 0.01907n \tag{2}$$

$$R = \text{phenyl} : \text{OWF}\pi-\pi = 0.57583 - 0.01550n \tag{3}$$

As Eqs. (1)–(3) show, the value of intercept and slope was different for different substituent R. From Eq. (1) (R is hydrogen) to Eq. (2) (R is methyl), the value of intercept and slope increased, the increase in intercept meant the increase of molecular conjugation, the increase in slope meant the effect of methyl decreased as n increased. In terms of quantum chemistry, owing to the σ–π hyperconjugation between methyl and the conjugated chain, it was obvious that the molecular conjugation increased and it was understandable that the effect of methyl decreased as n increased. However, from Eq. (1) (R is hydrogen) to Eq. (3) (R is phenyl), the value of intercept and slope decreased, the decrease in intercept meant the decrease of molecular conjugation, the decrease in slope meant the effect of phenyl decreased as n increased. In terms of quantum chemistry, owing to the conjugation between phenyl and the conjugated chain, the conjugated chain was lengthened (equivalent to the increase of n), according to Eq. (1), the molecular conjugation decreased and it was understandable that the effect of phenyl decreased as n increased.

In order to test the validity of Eqs. (1)–(3), the maximum absorption wavelength of three compounds was calculated, the results are shown in Table 3, for the convenience of comparison, the observed maximum absorption wavelength and the results calculated by CNDO/2 method and CNDO/S method are also listed in Table 3 [11,12,15]. As shown, using the $\text{OWF}_{\pi-\pi}$ calculated from Eqs. (1)–(3), the maximum absorption wavelength could be predicted successfully with ZINDO/S method.



R=hydrogen R=methyl R=phenyl

Fig. 2. The relationship between $\text{OWF}_{\pi-\pi}$ and n.

Table 3
The observed and calculated results for conjugated alkenes

R	n	λ_{obs}[a]/nm	λ_{cal}[b]/nm	λ_{cal}[c]/nm	ZINDO/S method	
					$OWF_{\pi-\pi}$	λ_{cal}/nm
Hydrogen	7	390	404	404	0.477[d]	388.80
Methyl	9	413	–	–	0.502[e]	413.24
Phenyl	7	435	–	–	0.467[f]	435.21

[a] Observed values of maximum absorption wavelength.
[b] Calculated results with CNDO/2 method.
[c] Calculated results with CNDO/S method.
[d] Calculated from Eq. (1).
[e] Calculated from Eq. (2).
[f] Calculated from Eq. (3).

3.3. Electron transition

The research on molecular orbital showed that the maximum absorption wavelength of conjugated alkenes originated from electron transition from HOMO to LUMO. As an example, for conjugated alkenes of $n = 6$, the shape of HOMO and LUMO is shown in Figs. 3–5.

As Figs. 3–5 show, for HOMO, it was bonding on double-bonds of typical structure, whereas it was anti-bonding on single-bonds of typical structure; for LUMO, it was in the opposite situation. Consequently, the electron transition that resulted in the maximum absorption wavelength, i.e., the electron transition from HOMO to LUMO, weakened the bonding of double-bonds while enhanced the bonding of single-bonds.

3.4. Applications

To further illustrate the applicability of Eqs. (1)–(3) in complicated systems, the maximum absorption wavelength of β-carotene and lycopene was studied. Figs. 6 and 7 show the optimized geometries of β-carotene and lycopene, respectively. Using the optimized geometry, ZINDO/S method was used in the maximum absorption wavelength calculation, $OWF_{\pi-\pi}$ was determined as 0.408 according to Eq. (1) ($OWF_{\pi-\pi} = 0.59657 - 0.01714 \times 11 = 0.408$) and the results are shown in Table 4, for the convenience of comparison, the observed values are also given [15]. As Table 4 shows, the agreement of calculated results with observed values was excellent.

For β-carotene and lycopene, there are substituents both in and at the end of the conjugated chain, the substituents at the end of the conjugated chain increased the molecular conjugation (as seen from Eqs. (1) and (2)), while the substituents in the conjugated chain decreased the molecular conjugation owing to steric hindrance (as seen from Figs. 6 and 7, the coplanarity of the conjugated chain was destroyed slightly). As a result, the effects of the substituents could be neglected approximately. Therefore, using the $OWF_{\pi-\pi}$ calculated from Eq. (1), the maximum absorption wavelength of β-carotene and lycopene could be predicted successfully.

4. Conclusions

Based on the optimized geometry obtained from PM3 method, the maximum absorption wavelength of conjugated alkenes could be predicted precisely with ZINDO/S method by setting $OWF_{\pi-\pi}$ at an appropriate value. It was found that there existed an excellent linear relationship between $OWF_{\pi-\pi}$ and n, the value of $OWF_{\pi-\pi}$ decreased as n increased. The relationship could be

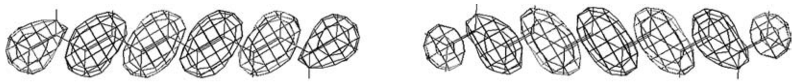

HOMO LUMO

Fig. 3. The shape of HOMO and LUMO for conjugated alkenes (R = hydrogen, $n = 6$).


HOMO LUMO

Fig. 4. The shape of HOMO and LUMO for conjugated alkenes (R = methyl, $n = 6$).

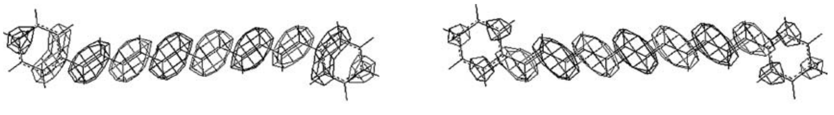

HOMO LUMO

Fig. 5. The shape of HOMO and LUMO for conjugated alkenes (R = phenyl, $n = 6$).

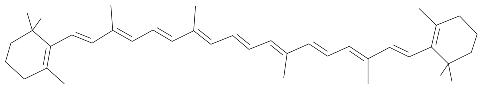


Fig. 6. The optimized geometry of β-carotene.

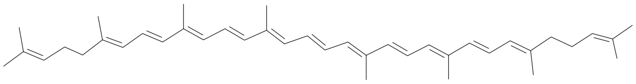


Fig. 7. The optimized geometry of lycopene.

Table 4
Observed and calculated values of maximum absorption wavelength for β-carotene and lycopene

Compound	$\lambda_{obs}{}^{a}$/nm (log ε)	$\lambda_{cal}{}^{b}$/nm (f)
β-Carotene	453 (5.14)	453.69 (2.581)
Lycopene	470 (5.27)	470.29 (3.110)

[a] Observed values in hydrocarbon, the value in parenthesis is the denary logarithm of the molar extinction coefficient.

[b] Calculated results with ZINDO/S method, the value in parenthesis is the calculated oscillator strength.

extrapolated to the calculation of maximum absorption wavelength for β-carotene and lycopene, and the agreement with experiment was excellent. At the same time, the research on molecular orbital showed that the maximum absorption wavelength of conjugated alkenes originated from electron transition from HOMO to LUMO — a transition weakened the bonding of double-bonds while enhanced the bonding of single-bonds.

The significance of this study lay in that by adjusting the value of $\mathrm{OWF}_{\pi-\pi}$ according to molecular structural parameters, the maximum absorption wavelength of conjugated alkenes could be predicted successfully. This was important in improving the accuracy of electronic absorption spectroscopy prediction and revealing the relationship between electronic absorption spectroscopy and molecular structure, and in some sense, it also helped in molecular structure design of dyes.

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