



A substructure-based topological quantum chemistry approach for the estimation of the ultraviolet absorption energy of some substituted linear conjugated compounds



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ABSTRACT

The linear conjugated compounds are a class of important organic compounds with good ultraviolet (UV) absorption, which are usually employed as the parent molecules of a lot of optical materials. The traditional topological quantum chemistry approach can accurately predict the UV absorption energies of unsubstituted linear conjugated alkenes. However, for the alkyl-substituted conjugated alkenes, this approach seems unsatisfactory. It is known that the π conjugated chain is a good conductor for the electron mobility, while the alkyl substituent is a bad one. As a result, their influences on the π electron transition will be different from each other. In order to distinguish the contribution of these two different structural parts, a substructure approach was proposed, in which a substituted linear conjugated molecule was divided into two substructures: the π conjugated chain part and the substituent part. Different methods were employed to characterize their structures. The relative frontier orbital energy gap of the conjugated chain (ΔE_{HL}^0) and the polarization energy of the substituents (P_{RE}) were calculated by substructure-based topological quantum chemistry method. A good linear regression model was built between the UV absorption wavenumbers and two parameters ΔE_{HL}^0 and P_{RE} for 23 typical conjugated alkenes. Based on this model, the UV absorption wavenumbers of other 70 alkenes were also predicted with high accuracy. This substructure-based topological quantum chemistry method was also extended to the investigation of the UV absorption of 89 olefinic aldehydes and ketones, and good results were also obtained.

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1. Introduction

The topological quantum chemistry approach has been proposed in our previous studies [1–5], where the polarizability effect indexes (PEI) of alkyl groups were assigned as the principal diagonal elements of the bond adjacency matrices of C–C, C–H, C=C, C=O and N=O bonds. Investigations have indicated that the eigenvalues of such bond adjacency matrices have good correlation with the bond dissociation energy [1], thermochemical properties [2,3], infrared spectroscopy stretching vibration frequency of C=O and N=O [4], and the nucleophilic addition reaction rate on the C=O [4]. The wide applications of the topological quantum chemistry method motivated us to extend it to the estimation of the ultraviolet (UV) absorption energies of linear conjugated compounds.

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The linear conjugated compounds are a class of important organic molecules, where the conjugated chain is a good one-dimensional conductor and possesses excellent properties in absorption spectroscopy. Thus, these compounds are usually employed as the target molecules for chemical theoretical investigation and the parent compounds of a lot of optical materials [6–8]. Recently, Zeeshan et al. [9] has synthesized the longest polyene so far recorded containing 27 conjugated double bonds with the ultimate λ_{max} . Rademacher [10] has studied the correlation between the first UV–Vis absorption of polyenes with three to thirteen conjugated C=C double bonds and the HOMO–LUMO energy gap calculated by PM3. Martínez [11,12] also proposed that the length of conjugated chain of the linear conjugated polyenes had effect on their antiradical, antioxidant, and antireductant properties, which are closely related to the wavelengths of UV absorption maximum. Therefore, the UV absorption of linear conjugated compounds are usually focused on by theoretical and experimental chemists.

Our previous work has observed that the UV absorption energies of the unsubstituted linear conjugated alkenes can be accurately estimated by the topological quantum chemistry method [4,5]. However, for the substituted conjugated alkenes, we found that the UV absorption energies cannot be predicted with satisfying accuracy. Similarly, Joantéguy et al. [13] also pointed out even if one function can accurately estimate the ionization potentials of unsaturated compounds such as C_2H_4 through quantum mechanical calculations, any substitutions to the $C=C$ bond would deteriorate the performances of the function. As we know, the ionization and the UV absorption are both the results of π electron transition. It means that it is also difficult to accurately predict the UV absorption energies for substituted unsaturated compounds. What is responsible for such differences between the substituted and unsubstituted conjugated alkenes in the estimation of UV absorption energies?

It is known that the structural characteristics between the conjugated chain and the alkyl substituents on the chain are quite different. As for the electron mobility, the conjugated chain is a good conductor, while the alkyl substituent is a bad conductor, which results in the different influences on the π electron transition from each other. It is necessary to characterize the structural information of the conjugated chain and the alkyl substituent from distinct perspectives. Therefore, we proposed a substructure approach to deal with the substituted conjugated molecules, where the molecule is divided into two substructures, i.e., the π conjugated chain part and the substituents part. The former influences the UV absorption energy through the frontier orbital energy gap of π molecular orbital, the latter exerts influences by the polarization energy of the substituent. In this paper, we tried to apply the substructure method to estimate the UV absorption energy of the substituted linear conjugated alkenes, olefinic aldehydes and ketones with the topological quantum chemistry approach.

2. Computational methods

2.1. The traditional topological quantum chemistry approach

In order to compare the performance of the substructure-based topological quantum chemistry approach to that of the traditional topological quantum chemistry approach in the next section, the traditional topological quantum chemistry method is briefly illustrated here. Take the linear conjugated alkenes for example.

Firstly, the bond adjacency matrix of the π molecular orbital is constructed, where the sum of the polarizability effect index ($\sum PEI$) [14,15] of the substituted groups or atoms attached to each carbon atom in the conjugated chain is assigned as the principal diagonal elements.

Then, we solve the $2m \times 2m$ -order bond adjacency matrix of the π conjugated chain (m is the number of π bond), and get $2m$ eigenvalues. These eigenvalues are ordered from small to large, and represented as $\chi_{(O_m)}, \dots, \chi_{(O_i)}, \dots, \chi_{(O_1)}, \chi_{(U_1)}, \dots, \chi_{(U_i)}, \dots, \chi_{(U_m)}$ in sequence. According to the conception of orbital energy in molecular orbital theory, we assign the first m eigenvalues, $\chi_{(O_m)}, \dots, \chi_{(O_i)}, \dots,$ and $\chi_{(O_1)}$ as the corresponding relative orbital energies of the occupied π molecular orbitals (RE_{OMO}), and the last m eigenvalues, $\chi_{(U_1)}, \dots, \chi_{(U_i)}, \dots,$ and $\chi_{(U_m)}$ as the corresponding relative orbital energies of the unoccupied π molecular orbitals (RE_{UMO}). Therefore, the $\chi_{(O_1)}$ is considered as the relative orbital energy of the HOMO (RE_{HOMO}), and the $\chi_{(U_1)}$ is corresponding to the relative orbital energy of the LUMO (RE_{LUMO}). The relative frontier orbital energy gap ΔRE_{HL} can be calculated as $\Delta RE_{HL} = RE_{LUMO} - RE_{HOMO}$.

As we know, the UV absorption energy is related to the frontier orbital energy gap, so the wavenumbers of UV absorption maximum ($\nu_{max} \times 10^4 \text{ cm}^{-1}$) of the linear conjugated alkenes can be

correlated to the relative frontier orbital energy gap ΔRE_{HL} of π molecular orbital. It is expressed by Eq. (1).

$$\nu_{max} (\times 10^4 \text{ cm}^{-1}) = a + b\Delta RE_{HL} \quad (1)$$

Take 2,4,4-trimethyl 1,3-butadiene as an example (see Fig. 1) to illustrate the computation of the relative frontier orbital energy gap ΔRE_{HL} .

According to the PEI values of alkyls [14,15] and hydrogen atom [16], the $\sum PEI$ of the substituted groups and atoms attached to each carbon atom (C^1-C^4) in the conjugated chain are calculated as follows:

$$\begin{aligned} \sum PEI(C^1) &= 1.0000 + 1.0000 = 2.0000 \\ \sum PEI(C^2) &= 0.6243 \\ \sum PEI(C^3) &= 1.0000 \\ \sum PEI(C^4) &= 0.6243 \times 2 = 1.2486 \end{aligned}$$

With the $\sum PEI$ values as the principal diagonal elements, the adjacency matrix of π bond (CM_π) of 2,4,4-trimethyl 1,3-butadiene is constructed as Eq. (2).

$$CM_\pi = \begin{bmatrix} 2.0000 & 1 & 0 & 0 \\ 1 & 0.6243 & 1 & 0 \\ 0 & 1 & 1.0000 & 1 \\ 0 & 0 & 1 & 1.2486 \end{bmatrix} \quad (2)$$

By solving the matrix CM_π by computer, four eigenvalues are obtained as $-0.6469, 0.6475, 2.0886,$ and 2.7836 . Thus, the RE_{HOMO} and RE_{LUMO} of 2,4,4-trimethyl 1,3-butadiene are 0.6475 and 2.0886 , respectively. The relative frontier orbital energy gap ΔRE_{HL} can be calculated as $\Delta RE_{HL} = RE_{LUMO} - RE_{HOMO} = 2.0886 - 0.6475 = 1.4411$. Likewise, the ΔRE_{HL} of 23 linear conjugated alkenes were also calculated and listed in Table 1.

2.2. The substructure-based topological quantum chemistry approach

In the substructure approach, a substituted linear conjugated alkene $R_1-(CR_i=CR_j)_n-R_2$ is divided into the π conjugated chain part $-(C=C)_n-$ and the substituents part $R_1-(R_i \sim R_j)_n-R_2$.

For the π conjugated chain part, $-(C=C)_n-$ is a good one-dimensional conductor, and the delocalization of its π electrons can be well described by quantum mechanics. Hence, its contribution to the UV absorption energy can be scaled by the relative frontier orbital energy gap of the π conjugated chain, which is corresponding to the ΔRE_{HL} of the unsubstituted conjugated alkenes $H-(CH=CH)_n-H$. However, according to the traditional topological quantum chemistry method [1–5] introduced in Section 2.1, the substituents on the π conjugated chain are taken into consideration for the calculation of ΔRE_{HL} of the substituted linear conjugated alkene. Thus, the ΔRE_{HL} of the substituted linear conjugated alkene calculated by the traditional topological quantum chemistry method is different from that by the substructure-based topological quantum chemistry method. In order to make a distinction between these two ΔRE_{HL} , we introduced ΔRE_{HL} and ΔRE_{HL}^0 to represent the relative frontier orbital energy gap calculated by the traditional topological quantum chemistry method and the substructure-based topological quan-

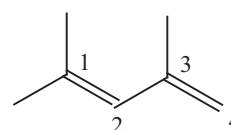


Fig. 1. Skeleton of 2,4,4-trimethyl butadiene. (The digits are the serial numbers of carbon atoms on the conjugated chain.)

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