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Covalent Excited States of Polyenes $C_{2n}H_{2n+2}$ ($n = 2-8$) and Polyenyl Radicals $C_{2n-1}H_{2n+1}$ ($n = 2-8$): An Ab Initio Valence Bond Study

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Abstract: The ab initio valence bond (VB) methods, VBSCF and VBCI, are applied to the ground states and the covalent excited states of polyenes $C_{2n}H_{2n+2}$ ($n = 2-8$) and polyenyl radicals $C_{2n-1}H_{2n+1}$ ($n = 2-8$). The excitation energy gap was computed at the ab initio VB level, which is in good agreement with the semiempirical VB method, VBDFT(s), and the experimental values as well as with the molecular orbital theory based methods, CASPT3 and MRCI. The ab initio VB wave functions of systems are also in very good agreement with those of the VBDFT(s) method, even though the former is based on the ab initio VB scheme while the latter is a semiempirical Hückel type method, in which no orbital optimization procedure is performed. The computational results show that the ab initio VB method is capable now of providing numerical accuracy not only for bond forming and breaking processes, as shown in the past, but also for excitation energies, as shown here. In addition, the computational results validate the efficiency of the VBDFT(s) method, which is a simple VB model with less computational effort but which provides intuitive insights into the excited states of conjugated molecules.

Introduction

Polyenes are versatile molecules with great appeal for the chemical, biochemical, and physical communities. The excited states of these molecules are especially important in several processes in nature, such as vision and light harvesting. It is no surprise therefore that this molecular family has attracted much interest both experimentally and theoretically. There is special interest in the properties of the longer chain members of the polyene series because of their potential use in nanodevices. As such, the present paper uses the modern valence bond (VB) theory to calculate the excitation energies and elucidate the properties of the covalent states of the even-

and odd-membered polyene series and their asymptotic behavior as the polyene grows.

The ground-state of polyenes with an even number of carbon atoms is 1^1A_g. One of the key excited states is the so-called dark state 2^1A_g, which has drawn much attention since the discovery by Hudson and Kohler.[1,2] The pioneering study of Karplus and Schulten[3] has shown that 2^1A_g is the first adiabatic excited-state for small polyenes. After their study, more sophisticated calculations established the same trend for larger members, up to $C_{10}H_{12}$.[4−12]

The odd carbon series, the so-called polyenyl radicals, share an unpaired electron. The smallest polyenyl radical is allyl, which is of particular interest due to its doublet instability observed in molecular orbital (MO)-based calculations.[13−18] Higher polyenyl radicals have also been subjects of interest as models for electron transport in polyacetylene, in terms of migrations of neutral solitons.[19−21] The covalent

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excited states in this series have state symmetries A_2 and B_1 that alternate along the series, starting from the smallest member.

VB theory provides a powerfully intuitive tool for understanding the electronic structures and reactivity patterns of excited states. Indeed, quite a few VB approaches have been designed and utilized for theoretical studies of the covalent excited states of polyenes.[11–14,22–31] Recently, we have developed a semiempirical VB method,[32–35] called VBDFT(s), which is scaled with a single parameter to give the energy of the density functional theory (DFT). We used the method to discuss the electronic structures of covalent excited states in terms of the chemical VB structures, called also the Rumer structures. In the previous studies, we derived the ground rules needed to understand the results and used these rules to discuss the asymptotic behavior of these molecules as the number of carbon atoms goes to infinity. Furthermore, the spin density distribution was discussed for radical series. These studies showed that the VB theory provides a coherent and lucid understanding of the properties of the covalent excited state, such as the makeup of the various states, their energies and geometries, the opposite bond alternation properties of the ground and covalent excited state, isomerization patterns, soliton characteristics, and so on.

Although the VBDFT(s) excitation energies were in good accord with sophisticated MO-based methods, such as CASPT2 and MRCI, there is still a challenging question; whether ab initio VB approaches are also capable of reproducing quantitatively correct results and offering at the same time lucid insight native to the VB method. Ab initio VB applications to chemical problems are still lagging behind the MO theory, due to their heavier computational cost, associated with the use of nonorthogonal atomic orbitals in VB theory. However, thanks to the rapid development in computational science, VB theory has been enjoying some revival for the last two-three decades.[36–38] Very recently, we have developed a VB method,[39] called VBCI, which incorporates configuration interaction into the VB method, while still keeping the minimal set of VB structures used in the simple VBSCF method. Several applications[40] show that the computational results of the VBCI method are in good agreement with those of MO-based sophisticated methods. We have therefore decided to apply in this paper two VB methods, VBSCF and VBCI, to explore the ground and covalent excited states of polyenes and polyenyl radicals and to compare the results with CASPT3 and MRCI calculations.

Computational Methods

A Brief Summary of VB Methods. A many-electron VB wave function is expressed in terms of VB structures Φ_K

$$\Psi = \sum_K C_K \Phi_K \tag{1}$$

where Φ_K may be a spin-coupled VB function or a spin-free form of a VB function.[41–43] The coefficients C_K in eq 1 are subsequently determined by solving the usual secular equation. Since VB structures are not mutually orthogonal, normalized structure weights are defined as[44]

$$W_K = \sum_L C_K M_{KL} C_L \tag{2}$$

where M_{KL} is the overlap matrix element between structures K and L.

One of the significant features of modern VB methods is that the VB orbitals are optimized during the calculation. In the VBSCF method,[45] both the VB orbitals and structural coefficients C_K are optimized simultaneously to minimize the total energy. The VBSCF method takes care of the static electron correlation but lacks dynamic correlation,[46] which is an absolutely essential ingredient for the goal of quantitative accuracy. Recently, an improved VB method, called VBCI,[39,40] was introduced, which uses a configuration interaction technique to describe electron correlation, both static and dynamic ones. Taking optimized VB orbitals from the VBSCF calculation, a subsequent VBCI calculation includes, in addition to the entire set of the VBSCF space, also those excited VB structures, which are generated by replacing occupied orbitals with virtual orbitals. In order to keep the one-to-one correspondence of VB functions to classical VB structures, the virtual orbitals in the VBCI method are strictly localized, and during the CI procedure the occupied orbitals are replaced only by those virtual orbitals that are localized on the same atoms. In this manner the VBCI wave function can be written as a linear combination of the same set of VB structures as in the VBSCF method. Two levels of VBCI methods, VBCIS and VBCISD, are applied in this paper, where VBCIS involves only single excitations, while VBCISD involves also double excitations.

The Rumer Structure Set for Covalent States. For a system of electron number N and spin S, the total number of Rumer covalent structures is

$$d_{full} = \binom{N}{N/2 - S} - \binom{N}{N/2 - S - 1} \tag{3}$$

For polyenes ($N = 2n$), with one π electron per π atomic orbital, each VB structure contains n covalent π-spin pairs, while for polyenyl radicals ($N = 2n$-1), each structure possesses n-1 covalent π-pairs and one unpaired electron. For linear polyenes and polyenyl radicals, there are spin-pairs over adjacent carbon atoms, which are actual π-bond and there are spin-pairs over longer distances; the longest being the one that links the two terminal carbon atoms. In this paper, a π-bond of two neighboring atoms is called a short bond, and any more distant spin-pair is called a long π-bond. Although the energies of Rumer structures are computed at the ab inito level in this paper, the spectrum of the Rumer structures may be discussed qualitatively by counting the number of short π-bonds.[32–35]

Scheme 1 shows the spectrums in terms of blocks that differ in the number of short-bonds, where parts a and b of Scheme 1 are for polyenes and polyenyl radicals, respectively. For polyenes ($N = 2n$), the lowest energy structure is the fundamental Rumer structure which involves n short π-bonds, denoted as R(0). The uppermost Rumer structure possesses only a single π-bond in the center of the molecule, while the rest of the electrons are paired into n-1 long bonds. A Rumer structure belonging to a general block is indicated by R(k), where k is the excitation rank and is simply the

Scheme 1. (a) Spectrum of the Rumer Basis Set for Polyenes and (b) Spectrum of the Rumer Basis Set for Polyenyl Radicals
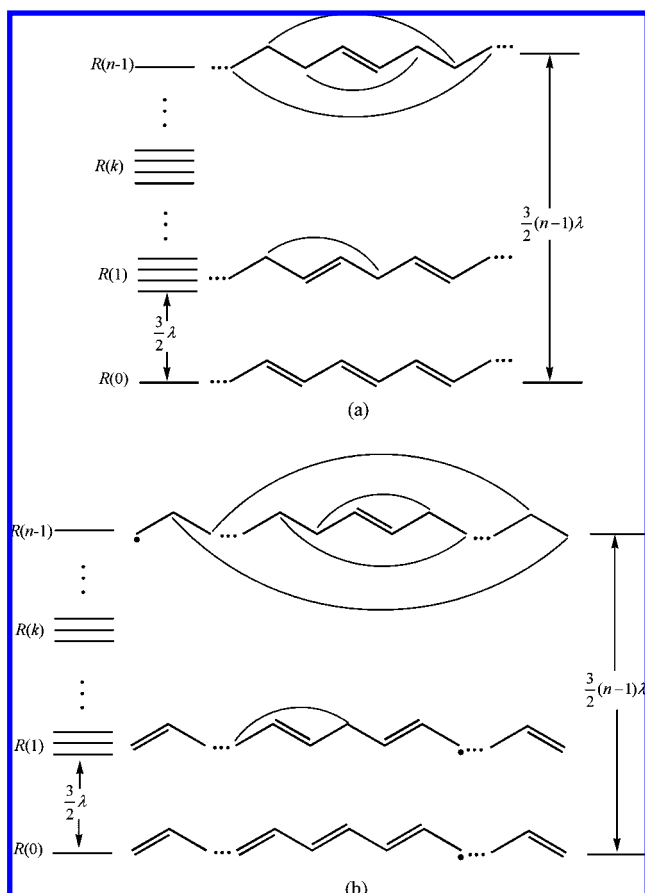
number of long bonds possessed by all the Rumer structures of the k block.

For polyenyl radicals ($N = 2n\text{-}1$), the lowest energy block contains n fundamental Rumer structures, which involve $n\text{-}1$ short bonds and an unpaired electron located on an odd-numbered carbon atom. The uppermost block consists of only one pair of twin Rumer structures, each of which possesses only one short π-bond near the center. In the VBDFT(s) method,[32–35] for uniform C–C bond lengths, all Rumer structures in the same block share the same energy, and the energy difference between the two neighboring blocks is 1.5λ, where λ is a parameter for the energy of a short π-bond. This is because the excitation breaks one π-bond and adds an additional nonbonded repulsion, which costs 0.5λ.

It can be seen from eq 3 that the number of total Rumer structures increases exponentially with the number of carbon atoms. In practice, it is impossible to include the full set of Rumer structures in the calculations of long polyenes, especially for ab initio VB treatments. The VBDFT(s) studies[33–35] showed that the ground-state properties were well reproduced by using only the fundamental, the singly and doubly excited Rumer structure blocks, while the excited states naturally require to include also the triply excited Rumer structures. In this paper, this truncation technique is applied for the long polyenes for which the full Rumer set is much too extensive. Therefore, two types of truncations are employed in this paper and are symbolized as VB-

SCF(S,D), VBCIS(SD), etc. One type reduces the VBSCF space by including only parts of the Rumer structures. This information is designated with "S" or "S, D" in parentheses, for example, VBSCF(S,D) means that one utilizes only those Rumer structures belonging to the fundamental, singly excited and doubly excited blocks of Scheme 1 for the VBSCF structure space. The other type of truncation information is for VBCI space. This is denoted as VBCIS and VBCISD, where the S and SD refer now to the excitation levels from occupied to virtual orbitals. Thus, for example, using a label such as VBCIS(S,D) would mean that the VBSCF space is (S,D), and the CI space of the VBCI involves only singles.

State Symmetries. In our previous papers,[33,35] the symmetries of states have been didactically and intuitively illustrated by means of the VB theory. In short, for polyenes, both of the ground-state and the dark state are A_g symmetry, designated as 1^1A_g and 2^1A_g, respectively. For polyenyl radicals, the ground-state is A_2 symmetry for even-membered n and B_1 symmetry for odd-membered n, respectively. Conversely, the symmetry for the first covalent excited-state is $B_1(A_2)$ for even(odd)-membered n.

Software. All VBSCF and VBCI calculations were carried out using the Xiamen Valence Bond (XMVB) package.[47] CASPT3 and MRCI calculations were performed using the MOLPRO package,[48] in which all π-electrons are included and N orbitals are taken as active space for C_NH_{N+2} molecule ($N = 2n$ for polyenes or $2n\text{-}1$ for polyenyl radicals). The MRCI(SD) level is used for MRCI calculations.

Basis Sets and Geometries. In order to produce good accuracy for the studies of excited states, a large basis set is usually required. However, our goal in this paper is to reach the chains of polyenes and polyenyl radicals as long as possible, and therefore large basis sets are prohibitive. Instead we use a D95V basis set, which is of a double-ζ quality and is used for all calculations, including VB-based VBSCF and VBCI methods and the MO-based CASPT3 and MRCI methods. The 6–31G(d) is applied for $C_{11}H_{13}$ and $C_{12}H_{14}$ to test basis set dependence. Optimized geometries for the ground states of polyenes and polyenyl radicals, C_3H_5–$C_{16}H_{18}$, were determined using B3LYP/D95V calculations implemented in the Gaussian 03 package.[49] The calculations were carried out in C_{2v} symmetry for polyenes and C_{2h} symmetry for polyenyl radicals. The B3LYP/D95V geometries are in good agreement with those obtained[17e] using the CASSCF method.

Results and Discussion

The Effect of Truncating the Rumer Basis. To check the errors that arise from the truncation of Rumer structures, the polyenyl radical $C_{11}H_{13}$ and the polyene $C_{12}H_{14}$ were tested at different truncation levels. Table 1 shows the effect of truncating the Rumer basis on the excitation energies with various VB methods. It can be seen that for $C_{11}H_{13}$ the excitation energies with (S) and (S,D) structure truncation are in good agreement with their corresponding values for all three methods, VBSCF, VBCIS, and VBCISD, in which the full Rumer set is used in the VBSCF calculation. The

Table 1. Effect of Truncation of the Rumer Space on the Vertical Excitation Energy (eV) for $C_{11}H_{13}$ and $C_{12}H_{14}$ Computed with the D95V Basis Set

molecule	space of VB structures[a]	no. of Rumer structures	VBSCF	VBCIS	VBCISD
$C_{11}H_{13}$	full	132	1.534	1.527	1.586
	(S)	46	1.541	1.534	1.563
	(S,D)	106	1.535	1.528	1.551
$C_{12}H_{14}$	full	132	3.562	3.548	3.497
	(S)	16	4.966	4.955	5.085
	(S,D)	66	3.564	3.551	3.602

[a] The space of the structure set which is used for the VB calculation, where "full" denotes the full Rumer set, while (S) means that those Rumer structures belonging to the fundamental and singly excited blocks are used, and (S, D) adds also for doubly excitations.

maximal deviation is 0.035 eV for VBCISD calculation. For $C_{12}H_{14}$, the difference in excitation energy of singly truncation (S) from the full Rumer set is pretty large, ca. 1.5 eV, while the deviation of doubly excitation truncation (S,D) is quite small, 0.002, 0.003, and 0.105 eV for VBSCF, VBCIS, and VBCISD, respectively. Therefore, these tests show that for polyenyl radicals, reliable results can be obtained when the Rumer set is truncated at the single excitation, while doubly excitation should be included in calculations for the polyene series.

VB Excitation Energies and the Convergence of the Excitation Gap. Table 2 shows the VB vertical excitation energies of polyenes, alongside the results of the semiempirical VB method, VBDFT(s), and sophisticated ab initio methods such as CASPT3 and MRCI. Full Rumer set calculations were performed for $C_4H_6-C_{12}H_{14}$ except for the VBCISD of $C_{12}H_{14}$, which is calculated at the VBCISD(S,D) level. For $C_{14}H_{16}$, there are 429 Rumer structures, which are too many to perform a VBSCF calculation with complete orbital optimization. A more effective way is to use only the singly excited structures (S) during the orbital optimization procedure, followed by VBSCF(full) and VBCIS(S) calculations with the so obtained optimized orbitals. For $C_{16}H_{18}$, only the fundamental and eight singly excited Rumer structures were included in orbital optimization, and then VBSCF(S,D) was performed. As can be seen from Table 2, the excitation energies of the all three levels of ab initio VB methods match one another very well. The deviation among the different methods is within only 0.09 eV. This indicates that VBCI accounts well and on equal footing for the dynamic correlation energies for both the ground-state and the covalent excited states. The excitation energies of ab initio VB methods are slightly higher than their corresponding values of VBDFT(s) by 0.3−0.4 eV. The results of the two sophisticated MO-based method, CASPT3 and MRCI, are slightly different, where the excited energies of the MRCI method are a little lower than those of CASPT3 by 0.2−0.4 eV. Note that the results of the ab initio VB methods are in good agreement with those of the MRCI method; especially good is the VBCISD method. The deviation of VBCISD from the MRCI method is in a range of 0.03−0.08 eV. Compared to experimental values, both of the ab initio VB and MO-based methods predict higher excitation energies, while VBDFT(s) values are in better agreement with experiments. It should be noted that the theoretical vertical

excitation energy is generally higher than experimental values, and thus the agreement between VBDFT(s) and experimental values does not show that the VBDFT results are better than those of ab initio VB and MRCI results.

Table 3 shows the VB vertical excitation energies for polyenyl radicals. Similar to the polyene series, a full Rumer set results are tabulated for $C_3H_5-C_{11}H_{13}$, while for $C_{13}H_{15}$ only singles (S) are involved in orbital optimization procedure, followed by VBSCF(full), VBCIS(S), and VBCISD(S) calculations, with no further orbital optimization. Similarly, for $C_{15}H_{17}$, only eight fundamental Rumer structures of the lowest energy were included in the orbital optimization procedure, followed by VBSCF(S) and VBCIS(S) calculations. As can be seen from Table 3, all the results of the three ab initio VB levels, VBSCF, VBCIS, and VBCISD, are in very good agreement mutually. The maximum of deviation is 0.06 eV. At the same time, all three ab initio VB results are seen to be in very good agreement with the corresponding semiempirical VBDFT(s) data. This latter match is very gratifying considering the fact that VBDFT(s) is just a Hückel-type VB method. Different from the polyene series, here the MO-based methods, CASPT3 and MRCI, match each other very well. The match between ab initio VB results with those of CASPT3 and MRCI is also good; the difference between VBCISD and MRCI methods are in a range of 0.03−0.06 eV.

In order to check the basis set dependence, Tables 4 and 5 collect the excitation energies for polyenes and polyenyl radicals with the 6−31G(d) basis set, respectively. It can be seen from Tables 2 and 4 that the VBSCF values of 6−31G(d) are higher than those obtained by using D95V by 0.12−0.30 eV for the polyene series, while for the VBCI levels, the values of 6−31G(d) are lower than those of D95V. Different from polyenes, for polyenyl radicals the excitation energies of ab initio VB methods are almost identical and are in very good agreement with those of 6−31G(d). Furthermore, the excitation energies of ab initio VBSCF methods for 6−31G(d) are in very good agreement with those of MRCI and CASPT3.

Figure 1 shows the excitation energies of various methods plotted against the number of carbons in the polyene chain, while Figure 2 exhibits the same information for the radical series. For the sake of economy, only VBSCF and VBDFT(s) as well as MRCI curves are shown in the same plot. As can be seen from the figures, all the three curves match very well. The VBSCF curve is close to that of MRCI, compared to that of semiempirical VBDFT(s) curve. The plots show the falloff of the excitation energy as the chain gets longer for both polyene and radical series. In a similar fashion to the VBDFT(s) studies,[33,35] an exponential fit to the VBSCF curve in Figure 1 leads to eq 4

$$\Delta E = 2.63 + 7.848e^{-0.179(2n)}, R^2 = 0.99987; n = 2, 3, 4, \ldots \quad (4)$$

The intercept value of 2.63 eV at $n \rightarrow \infty$ is larger than that of VBDFT(s), 2.05 eV. This means that long polyenes will have a residual energy gap, presumably due to bond alternation.

Table 2. VB Vertical Excitation Energies (eV) for Polyenes $C_{2n}H_{2n+2}$ ($n = 2-8$) Computed with the D95V Basis Set

n	no. of Rumer structures	VBSCF	VBCIS	VBCISD	VBDFT(s)[a]	CASPT3	MRCI	exp.
2	2	6.47	6.47	6.56	6.28	6.75	6.53	
3	5	5.29	5.28	5.36	5.02	5.57	5.42	5.21[b]
4	14	4.49	4.49	4.55	4.19	4.79	4.60	4.41[c]
5	42	3.95	3.94	4.00	3.63	4.48	4.07	3.48[d]
6	132	3.56	3.55	3.60[e]	3.32	3.90	3.68	>2.68[f]
7	429	3.27	3.26[e]		2.93			>2.34[f]
8	225[e]	3.06[e]			2.70			

[a] The semiempirical method of ref 33. [b] Reference 8. [c] References 9 and 50. [d] Reference 51. [e] VB(S, D) type. [f] Reference 52.

Table 3. VB Vertical Excitation Energies (eV) for Polyenyl Radicals $C_{2n-1}H_{2n+1}$ ($n = 2-8$) Computed with the D95V Basis Set

n	no. of Rumer structures	VBSCF	VBCIS	VBCISD	VBDFT(s)[a]	CASPT3	MRCI
2	2	3.21	3.21	3.26	3.26	3.29	3.29
3	5	2.54	2.53	2.57	2.49	2.63	2.62
4	14	2.07	2.07	2.10	2.01	2.16	2.16
5	42	1.76	1.75	1.78	1.68	1.85	1.84
6	132	1.53	1.53	1.59	1.45	1.63	1.61
7	429	1.40	1.41[b]	1.44[b]	1.29		
8	120[c]	1.27[b]	1.19[b]		1.16		

[a] Reference 35. [b] VB(S) type.

***Table 4.*** VB Vertical Excitation Energies (eV) for Polyenes $C_{2n}H_{2n+2}$ ($n = 2-5$) Computed with 6-31G(d)

n	structure	VBSCF	VBCIS	VBCISD	CASPT3	MRCI
2	2	6.59	6.30	6.36	6.67	6.65
3	5	5.49	5.19	5.24	5.57	5.42
4	14	4.75	4.45	4.49	4.72	4.70
5	42	4.25	3.94	3.85	4.17	4.15

Table 5. VB Vertical Excitation Energies (eV) for Polyenyl Radicals $C_{2n-1}H_{2n+1}$ ($n = 2-5$) Computed with 6-31G(d)

n	structure	VBSCF	VBCIS	VBCISD	CASPT3	MRCI
2	2	3.13	3.08	3.11	3.33	3.33
3	5	2.53	2.45	2.47	2.66	2.66
4	14	2.09	2.01	2.03	2.19	2.19
5	42	1.80	1.72	1.73	1.87	1.86

For radical series, fitting the VBSCF curve in Figure 2 as a cosine function leads to eq 5

$$\Delta E = 5.037 \cos \frac{n-1}{2n}\pi, R^2 = 0.86629; n = 2, 3, 4, ... \quad (5)$$
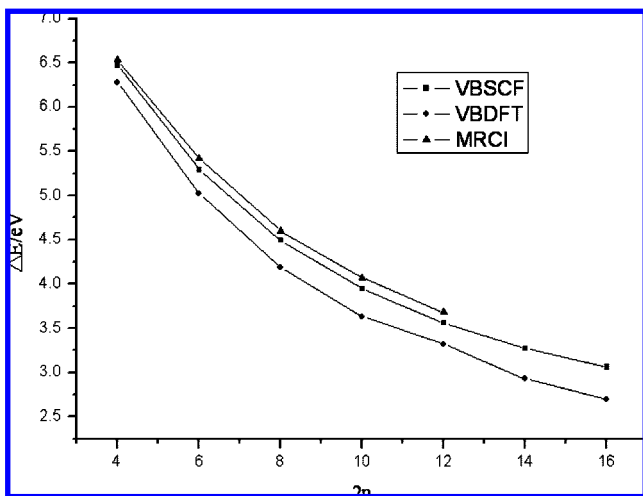
Figure 1. Dependence of the $1^1A_g \rightarrow 2^1A_g$ vertical excitation energy on the polyene length for $C_{2n}H_{2n+2}$.
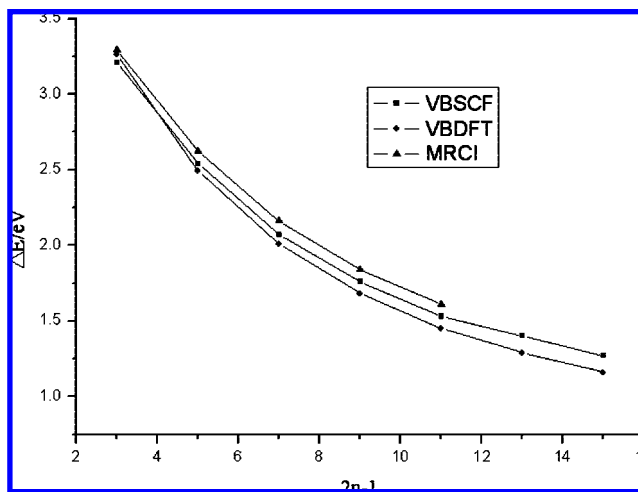
Figure 2. Dependence of the vertical excitation energy on the polyenyl radical chain length for $C_{2n-1}H_{2n+1}$.

The value of amplitude 5.04 eV in eq 4 is virtually identical to that of VBDFT(s), 4.96 eV. As discussed in the previous paper,[35] since the plot of radicals is done for ground-state geometries, this residual gap results from the nonuniform C−C bond-length of the chain and represents thereby the "soliton binding energy" *(stabilization of the radical by geometric distortion)*. For *an infinite chain* with uniform C−C bond length, the state symmetry is independent of the parity of *n*. As such, the symmetries of ground and covalent excited states, A_2 and/or B_1, collapse into a degenerate state of E symmetry. Therefore, the gap between the ground and covalent excited states for uniform C−C bond length should converge to zero.

Conclusion

This paper utilizes the ab initio VB methods, VBSCF and VBCI, to compute the relative energies and electronic structures of the ground and covalent excited states of

polyenes $C_{2n}H_{2n+2}$ ($n = 2-8$) and polyenyl radicals $C_{2n-1}H_{2n+1}$ ($n = 2-8$). The ab initio VB excitation energies are in good agreement with MRCI and CASPT3, with available experimental data, and with the formerly developed semiempirical VB method, VBDFT(s). VBDFT(s) performs extremely well compared with all the ab initio methods. Although not shown in the paper, the match is apparent also for the VB wave functions, for which VBDFT(s) and VBSCF have very similar results, despite the fact that VBSCF performs orbital optimization, while VBDFT(s) does not. As such, the computational results validate the efficiency of VBDFT(s) method, which is a simple nonexpensive VB model. Accordingly, VBDFT(s) can be used to obtain intuitive insight into the covalent excited states of conjugated molecules, as demonstrated in the previous publications.[32-35]

From the perspective of method development, the computational results show that the ab initio VB theory is able to provide numerical accuracy for the physical properties of excited states. We believe that this ability to deal with excited states is one more step in the revival of the VB theory.

Finally, while the present paper focuses on covalent excited states, the ab initio VB method is also capable of exploring the ionic excited states of polyenes, which are important in excited-state chemistry and photophysics. For the ionic excited states, there are many more Rumer structures than those of covalent excited states. We are currently studying the levels of truncation of the Rumer set that will provide good accuracy and compact wave functions.

Supporting Information Available: Two tables and the full reference for ref 49. This material is available free of charge via the Internet at http://pubs.acs.org.

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