14 March 1997

ELSEVIER

Chemical Physics Letters 267 (1997) 82–90

CHEMICAL
PHYSICS
LETTERS

Theoretical study of the $\pi \to \pi^*$ excited states of linear polyene radical cations and dications

Yukio Kawashima, Kenichi Nakayama, Haruyuki Nakano, Kimihiko Hirao [*]

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Tokyo 113, Japan

Received 9 December 1996; in final form 7 January 1997

Abstract

Multireference Møller–Plesset theory is applied to the study of the valence $\pi \to \pi^*$ excited states of radical cations and dications of butadiene, hexatriene, octatetraene and decapentaene. The present theory satisfactorily describes the low-lying excited states of cations within an error of 0.1 eV. Theory confirms the general tendency observed in carotenoids that the first transition of the dications of polyenes is at a higher energy than the intense transition of the radical cations and at a lower energy than the first allowed transition of the neutral species.

1. Introduction

There has been a long and rich history of experimental and theoretical investigations on the nature of linear polyene excited states. In a previous paper [1] we studied the valence $\pi \to \pi^*$ excited states of neutral linear polyenes using the multireference Møller–Plesset (MRMP) method [2]. The emphasis is put on determining the nature of the two lowest lying singlet excited states, $1^1B_u^+$ and $2^1A_g^-$, and their ordering. The $1^1B_u^+$ state is a singly excited state with an *ionic* nature originating from a HOMO → LUMO one-electron transition while the *covalent* $2^1A_g^-$ state is the doubly excited state which mainly comes from a $(\text{HOMO})^2 \to (\text{LUMO})^2$ transition. The MRMP theory satisfactorily describes the ordering of low-lying $\pi \to \pi^*$ excited states of neutral polyenes. Based on the MRMP results, the ordering of doubly excited $2^1A_g^-$ below $1^1B_u^+$ at the ground state geometry is confirmed to be a general feature of polyenes except in butadiene and hexatriene. For butadiene the $^1B_u^+$ state is calculated to be slightly lower than the doubly excited $2^1A_g^-$ state and for hexatriene the two states are predicted to be virtually degenerate.

This Letter describes the electronic structure of the cation radicals and dications of all-trans-polyenes. Recently, polyene radical cations have received considerable attention since the primary species obtained upon doping polyacetylene are radical cations or radical anions, called polarons. The high energy radical cations can be reached directly through photoionization of the neutral species [3,4] and the resulting spectra are usually assigned on the basis of Koopmans' theorem. However, it is known that Koopmans' theorem breaks down for all excited states of linear polyene radical cations [6]. The radical cations of the first few members of linear polyenes can be stabilized under suitable conditions and the absorption spectra have been measured [5–8]. The radical cations of tert-butyl-capped polyenes were

---

[*] Corresponding author.

PII S0009-2614(97)00084-5

generated and investigated by electronic absorption spectroscopy by Bally et al. [7]. These spectra show intense high energy and weak low energy transitions. Recently, Jeevarajan et al. [8] observed the optical absorption spectra of radical cations and dications of carotenoids. The first transition of the dications of carotenoids is always found to be at a higher energy than the intense transition of the radical cations and at a lower energy than the first allowed transition ($1^1B_u^+$) of the neutral species. These observed spectra were discussed within the framework of a simple semi-empirical MO model. However, a more reliable ab initio prediction of transition energies as well as oscillator strengths are desired.

The purpose of this Letter is to elucidate the electronic structure of the ground and low-lying $\pi \rightarrow \pi^*$ excited states of linear polyene radical cations and dications. The main features of the electronic structure of linear polyene radical cations and dications can be derived in a qualitative fashion just as in the case of the neutral parents. All qualitative conclusions come from the pairing theorem for alternant hydrocarbons, the topological property of the systems. It is interesting to examine the similarities and differences of the radical cations and dications compared to the neutral species. The question also remains whether the localization or delocalization of spin and charge changes upon excitation in radical cations and dications.

In Section 2 we summarize the computational details. Vertical π–π^* excitation energies of radical cations and dications of butadiene, hexatriene, octatetraene, and decapentaene are discussed in Section 3. The nature of the excited states as well as the ground state is analyzed in terms of the complete active space valence bond (CASVB) method [9]. A summary will be given in the final section.

2. Computational details

The molecules are taken to have C_{2h} symmetry and chosen to lie in the xz-plane; thus the y-axis is the C_2 axis. The equilibrium geometries of radical cations and dications are optimized at the CASSCF [10] level.

The basis set effect on the transition energy of neutral polyenes is found to be significant, particularly for singlet states [1]. The transition energies decrease on increasing the quality of a basis set, indicating that the description of excited states needs a more flexible basis set than that used for the ground state. We also examined the basis set effect on the radical cations and dication of butadiene and hexatriene. However, in the case of radical cations and dications, the double zeta plus polarization (DZp) basis appears to be sufficient for a quantitative accuracy of the transition energy due to the rather compact electron density. Thus, we used DZp, [3s2p1d/2s] and/or triple zeta plus double polarization (TZ2p), [4s3p2d/3s2p] quality basis sets for carbon and hydrogen [11]. The polarization functions of hydrogen have little effect on the valence $\pi \rightarrow \pi^*$ excitation energies and oscillator strengths. The f and g polarization and Rydberg functions are not included in the present treatment.

We first carry out state-averaged CASSCF calculations. All π electrons are treated as active electrons and distributed among all valence bonding π and antibonding π^* orbitals. The abbreviation (n, m) is used to define the active electrons and active orbitals. The n is the number of active π electrons and m the number of active π orbitals. The enlargement of the active space of the reference function has a significant effect on the transition to the *ionic* states although it has a minor effect on the *covalent* states of neutral species. However, in the case of radical cations and dications, the excitation energy is found to be insensitive to the effect of the enlargement of the active space.

The effect of the σ electrons is included through a perturbation treatment. Perturbation calculations are performed with MRMP. Oscillator strengths are calculated by using transition moments computed at the CASSCF level and the MRMP transition energies.

3. Results and discussions

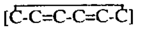
Polyenes are alternant hydrocarbons and the pairing properties are satisfied even at the CASSCF level [12]. Thus, the main features of the electronic structure of linear polyene radical cations and dications can be derived in a qualitative fashion just as in the case of the neutral parents. Let the occupied π

orbitals of neutral polyenes be designated by 1, 2, ..., from the highest one down and unoccupied ones by 1′, 2′, ..., from the lowest one up. The orbitals *i* and *i*′ are called a conjugated pair. In the case of all-trans-polyenes, the symmetry class of the conjugated pair of orbitals is (a_u, b_g) in C_{2h} symmetry. The 1 and 1′ of polyenes with odd number of double bonds (even number of double bonds) have symmetries of a_u (b_g) and b_g (a_u), respectively. For the neutral polyenes, the ground state is well described by a Hartree–Fock configuration. The dipole allowed *ionic* $^1B_u^+$ state comes predominantly from the 1 → 1′ excitation. Contrary to the $^1B_u^+$ state, the *covalent* $2^1A_g^-$ state is described mainly by a doubly excited configuration of $(1)^2 \rightarrow (1')^2$ but also includes a large fraction of singly excited configurations of 1 → 2′ and 2 → 1′.

Recently we have proposed a CASVB method [9]. A CASVB wavefunction can be obtained simply by transforming a canonical CASSCF function and readily interpreted in terms of the well known classical VB resonance structures. For example, the ground state of hexatriene is mainly comprised of the covalent Kekule-like structure,

$$[\mathrm{C{=}C{-}C{=}C{-}C{=}C}]$$

while the $2^1A_g^-$ state is expressed predominantly by the Dewar-like structure



$$[\overline{\mathrm{C{-}C{=}C{-}C{=}C{-}C}}]$$

The $1^1B_u^+$ state is expressed as a mixture of a large number of ionic structures where the leading terms are the singly polar structure of

$$[\mathrm{C{=}C{-}C^{-}{-}C^{+}{-}C{=}C}]{-}[\mathrm{C{=}C{-}C^{+}{-}C^{-}{-}C{=}C}]$$

and the doubly polar structure of

$$[\mathrm{C^{-}-C^{+}-C^{-}-C^{+}-C{=}C}]$$
$$-[\mathrm{C{=}C-C^{+}-C^{-}-C^{+}-C^{-}}]$$

Thus, the nature of the two lowest excited states of neutral polyenes can easily be understood from the CASVB description.

3.1. The $\pi \rightarrow \pi^*$ excited states of polyene radical cations

The ground equilibrium geometries of radical cations and dications are optimized at the CASSCF level with DZp. The molecular symmetry is assumed to be C_{2h} and therefore planar. The most interesting results on the structure are the values of the C–C bond lengths. The differences in bond angles and

Table 1
Calculated C–C bond lenghts (Å) for the neutral, cation radical and dication species of the polyenes [a]

	C_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–C_6
neutral [b]					
butadiene	1.335	1.463			
hexatriene	1.338	1.469	1.345		
octatetraene	1.345	1.457	1.351	1.451	
decapentaene	1.346	1.454	1.351	1.450	1.352
radical cation					
butadiene	1.390	1.400			
hexatriene	1.375	1.409	1.400		
octatetraene	1.365	1.423	1.394	1.395	
decapentaene	1.360	1.433	1.387	1.401	1.398
dication					
butadiene	1.452	1.382			
hexatriene	1.407	1.380	1.473		
octatetraene	1.387	1.387	1.451	1.368	
decapentaene	1.376	1.397	1.431	1.369	1.454

[a] Geometries are optimized at the CASSCF with the DZp basis set. The (*n*, *n*) active space is used for the neutral species, (*n* − 1, *n*) for radical cations and (*n* − 2, *n*) for dications.

[b] Taken from Ref. [1].

C–H bond lengths from the neutral species are quite small due to the small steric hindrance and we focus on the change in the C–C bond lengths. Table 1 summarizes the C–C bond lengths with the carbon chains.

The main feature of the electronic structure of radical cations were given by Bally et al. [6]. In the case of radical cations, the energy of the configuration obtained by exciting an electron from 2 (doubly occupied) to 1 (singly occupied) is nearly equal to that obtained by excitation from 1 (singly occupied) to 1′ (unoccupied). Both have B_g (A_u) symmetry for radical cations with an odd number (even number) of double bonds in C_{2h} symmetry. As the chains grow longer, the energies of the first two excited configurations decrease and the energy gap between them gets smaller. The linear combinations of two almost degenerate configurations generate so-called D_1 and D_2 states (the ground state is called D_0). The two configurations mix with a *plus* sign in the D_1 state and with a *minus* sign in the D_2 state. The electric dipole transition moment vectors for the 2 → 1 and 1 → 1′ transitions are similar in magnitude and antiparallel in their orientation. Thus, cancellation and addition of the dipole moments occur in the D_1 and D_2 states, respectively. For a series of radical cations with increasing chain length we expect a pair of absorption bands which move closer as their midpoint shifts to lower energies and their intensities become more disparate.

In order to study the nature of the excited D_1 and D_2 states, we obtained the CASVB description for these states of the radical cation of hexatriene. Results are shown in Fig. 1. For the ground state, the most important contribution comes from the following structure where the spin and charge are localized in the center of the chain

$$D_0\ [C{=}C{-}C^{\bullet}{-}C^{+}{-}C{=}C] + [C{=}C{-}C^{+}{-}C^{\bullet}{-}C{=}C]$$

However, as can be seen from Fig. 1 there are many other important resonance structures and the spin and charge are delocalized in the chain. This delocalization scheme can easily be understood from the classical VB resonance of the vinyl radical and vinyl cation

$$[C{=}C{-}C^{\bullet}] + [C^{\bullet}{-}C{=}C],$$
$$[C^{+}-C{=}C] + [C{=}C-C^{+}]$$

1^2A_u
$0.0914\{[C{=}C{-}C^{\bullet}{-}C^{+}{-}C{=}C] + [C{=}C{-}C^{+}{-}C^{\bullet}{-}C{=}C]\}$
$+0.0684\{[C^{\bullet}{-}C{=}C{-}C^{+}{-}C{=}C] + [C{=}C{-}C^{+}{-}C{=}C{-}C^{\bullet}]\}$
$+0.0587\{[C^{\bullet}{-}C^{+}{-}C{=}C{-}C{=}C] + [C{=}C{-}C{=}C{-}C^{+}{-}C^{\bullet}]\}$
$+0.0579\{[C^{\bullet}{-}C^{+}{-}C^{-}{-}C^{+}{-}C{=}C] + [C{=}C{-}C^{+}{-}C^{-}{-}C^{+}{-}C^{\bullet}]\}$
$+0.0509\{[C{=}C{-}C^{\bullet}{-}C^{+}{-}C^{-}{-}C^{+}] + [C^{+}{-}C^{-}{-}C^{+}{-}C^{\bullet}{-}C{=}C]\}$
$+\ldots$

1^2B_g
$0.1392\{[C^{\bullet}{-}C^{+}{-}C{=}C{-}C{=}C] - [C{=}C{-}C{=}C{-}C^{+}{-}C^{\bullet}]\}$
$+0.1216\{[C^{\bullet}{-}C{=}C{-}C^{+}{-}C{=}C] - [C{=}C{-}C^{+}{-}C{=}C{-}C^{\bullet}]\}$
$+0.1006\{[C^{\bullet}{-}C^{+}{-}C^{-}{-}C^{+}{-}C{=}C] - [C{=}C{-}C^{+}{-}C^{-}{-}C^{+}{-}C^{\bullet}]\}$
$+0.0638\{[C^{\bullet}{-}\overline{C{-}C^{+}{-}C}{-}C{=}C] - [C{=}C{-}\overline{C{-}C^{+}{-}C}{-}C^{\bullet}]\}$
$+0.0619\{[C^{+}{-}C^{\bullet}{-}C{=}C{-}C{=}C] - [C{=}C{-}C{=}C{-}C^{\bullet}{-}C^{+}]\}$
$+\ldots$

2^2B_g
$0.1073\{[C^{+}{-}C{=}C{-}C^{\bullet}{-}C{=}C] - [C{=}C{-}C^{\bullet}{-}C{=}C{-}C^{+}]\}$
$+0.0947\{[C^{+}{-}C{=}C{-}C{=}C{-}C^{\bullet}] - [C^{\bullet}{-}C{=}C{-}C{=}C{-}C^{+}]\}$
$+0.0785\{[C^{+}{-}C^{\bullet}{-}C{=}C{-}C{=}C] - [C{=}C{-}C{=}C{-}C^{\bullet}{-}C^{+}]\}$
$+0.0568\{[\overline{C{-}C^{+}{-}C}{-}C^{\bullet}{-}C{=}C] - [C{=}C{-}C^{\bullet}{-}\overline{C{-}C^{+}{-}C}]\}$
$+0.0533\{[\overline{C{-}C^{+}{-}C}{-}C{=}C{-}C^{\bullet}] - [C^{\bullet}{-}C{=}C{-}\overline{C{-}C^{+}{-}C}]\}$
$+\ldots$

2^2A_u
$0.2382\{[C{=}C{-}C^{\bullet}{-}C^{+}{-}C{=}C] + [C{=}C{-}C^{+}{-}C^{\bullet}{-}C{=}C]\}$
$+0.0746\{[C{=}C{-}C^{\bullet}{-}C^{+}{-}C^{-}{-}C^{+}] + [C^{+}{-}C^{-}{-}C^{+}{-}C^{\bullet}{-}C{=}C]\}$
$-0.0589\{[C^{\bullet}{-}C^{+}{-}C{=}C{-}C{=}C] + [C{=}C{-}C{=}C{-}C^{+}{-}C^{\bullet}]\}$
$+0.0540\{[C^{+}{-}C^{-}{-}C^{\bullet}{-}C^{+}{-}C{=}C] + [C{=}C{-}C^{+}{-}C^{\bullet}{-}C^{-}{-}C^{+}]\}$
$+\ldots$

Fig. 1. Description of the ground and excited state CASVB wavefunctions of the radical cation of trans-hexatriene. Values at the VB structures are occupation numbers. The occupation number n_I for the VB structure I is defined as

$$n_I = C_I \sum_J S_{IJ} C_J$$

where the sum goes over all possible VB structures. C_I and S_{IJ} are the coefficient of the VB structure I and the overlap integral between structures I and J, respectively. The n_I add to 1.

The CASVB descriptions for the excited D_1 and D_2 states are interesting. The main structures in the D_1 and D_2 states are

$$D_1\ [C^{\bullet}{-}C^{+}{-}C{=}C{-}C{=}C] + [C{=}C{-}C{=}C{-}C^{+}{-}C^{\bullet}]$$
$$D_2\ [C^{+}{-}C{=}C{-}C^{\bullet}{-}C{=}C] + [C{=}C{-}C^{\bullet}{-}C{=}C{-}C^{+}]$$

In the D_1 state the spin (the radical center) is localized on the terminal carbons while the charge (the cation center) is delocalized in the chain. On the other hand, in the D_2 state the charge is localized on the terminal carbons while the spin is delocalized in the chain. Thus, the two states are quite different in nature.

Let us now discuss the optimized equilibrium geometries of the radical cations. The calculated results in Table 1 show that the C–C bond lengths near the center of the chains approach around 1.4 Å, the mean value of the single and double bond lengths, i.e. the bond alternation disappears in the center of the chain. On the other hand, the terminal C–C bond becomes shorter on increasing the carbon chains and the second C–C bond from the terminal becomes more loose. This is consistent with the fact that the spin and charge of the radical cations are localized near the center of the chain in the ground state of radical cations.

The main configurations of the CASSCF wavefunction are given in Table 2 and vertical $\pi \rightarrow \pi^*$ excitation energies of radical cations are summarized in Table 3. The D_1 state is well described by singly excited configurations of $2 \rightarrow 1$ and $1 \rightarrow 1'$, which have nearly the same weight with the same sign while the D_2 state is represented by the same configurations, however, with a different sign. We observe in Table 3 that CASSCF tends to overestimate the excitation energies compared to the experimental values [5–9,13]. The largest error is found in the D_2 states. For the D_1 states, the CASSCF excitation energies are still too high compared to the experiment but the deviation is much smaller than that for the D_2 states. MRMP theory corrects the deficiency and represents a great improvement over CASSCF. MRMP transition energies to D_1 and D_2 states show an excellent agreement with the observed values. The errors are less than 0.1 eV for radical cations of butadiene, hexatriene and octatetraene. For decapentaene, no experimental data are available and we

Table 2
Main configurations in the CASSCF wavefunctions of the radical cation and dication of the polyenes [a]

State	Transitions	Butadiene	Hexatriene	Octatetraene	Decapentaene
radical cations					
$1^2B_g/1^2A_u$ (ground state)					
(D_0)	$\ldots(3)^2(2)^2(1)^1$	0.9531	0.9390	0.9159	0.8949
$1^2A_u/1^2B_g$					
(D_1)	$2 \rightarrow 1$	0.7689	0.7379	0.7104	0.6796
	$1 \rightarrow 1'$	0.5333	0.5472	0.5468	0.5322
$2^2A_u/2^2B_g$					
(D_2)	$2 \rightarrow 1$	0.5531	0.5212	0.5043	0.5047
	$1 \rightarrow 1'$	−0.7481	−0.6997	−0.6652	−0.6434
$2^2B_g/2^2A_u$					
	$3 \rightarrow 1$		0.7698	0.7028	0.6630
	$2 \rightarrow 1'$		−0.3747	−0.3711	−0.3952
	$1 \rightarrow 2'$		0.3521	0.3781	0.3760
dications					
1^1A_g (ground state)					
	$\ldots(3)^2(2)^2(1)^0$	0.9578	0.9249	0.9107	0.8915
1^1B_u					
	$2 \rightarrow 1$	0.8811	0.8753	0.8489	0.8212
	$3 \rightarrow 2$	–	−0.2649	−0.2325	−0.2103
2^1A_g					
	$(2)^2 \rightarrow (1)^2$	0.4948	0.5802	0.5806	0.5770
	$3 \rightarrow 1$		0.5313	0.4791	0.4482
	$2 \rightarrow 1'$	0.8092	−0.3433	−0.3855	−0.3962
	$(3)^2 \rightarrow (1)^2$		−0.3086	−0.1649	−0.1476

[a] CASSCF results with DZp. The $(n-1, n)$ active space is used for radical cations and $(n-2, n)$ for dications.

Table 3
Calculated vertical excitation energies (eV) of low-lying polyene radical cations

Radical cation	Method	CASSCF	MRMP	Oscillator strength	Exptl.
butadiene					
$1^2A_u(D_1)$	TZ2p/(3,4)	2.57	2.43	0.011	2.32 [a], 2.30 [b], 2.38 [c]
$2^2A_u(D_2)$	TZ2p/(3,4)	5.07	4.16	0.626	4.20 [a], 4.00 [b], 4.06 [c]
2^2B_g	TZ2p/(3,4)	6.79	6.27	forbidden	
hexatriene					
$1^2B_g(D_1)$	TZ2p/(5,6)	2.11	1.98	0.015	1.92 [a], 1.93 [h], 1.96 [d,e], 1.98 [f]
$2^2B_g(D_2)$	TZ2p/(5,6)	4.06	3.32	0.998	3.27 [a], 3.16 [h], 3.40 [d], 2.88 [f]
2^2A_u	TZ2p/(5,6)	3.57	3.36	forbidden	
octatetraene					
$1^2A_u(D_1)$	DZp/(7,12)	1.83	1.69	0.022	1.67 [a,g], 1.68 [f]
$2^2A_u(D_2)$	DZp/(7,12)	3.43	2.88	1.380	2.77 [a], 2.49 [f]
2^2B_g	DZp/(7,12)	3.22	3.01	forbidden	2.97 [a]
3^2A_u	DZp/(7,12)	4.16	3.93	0.008	~ 3.90 [i]
decapentaene					
$1^2B_g(D_1)$	DZp/(9,10)	1.61	1.43	0.022	1.44 [f]
$2^2B_g(D_2)$	DZp/(9,10)	2.89	2.46	1.706	2.17 [f]
2^2A_u	DZp/(9,10)	2.87	2.61	forbidden	
3^2B_g	DZp/(9,10)	3.83	3.53	0.004	

[a] From Ref. [6].
[b] From Ref. [13a].
[c] From Ref. [13b].
[d] From Ref. [13c].
[e] From Ref. [13d].
[f] Transition energies of tert-butyl-capped polyene radical cations; from Ref. [7].
[g] From Ref. [17].
[h] From Ref. [5c].
[i] From Ref. [4].

refer to the transition energies of tert-butyl capped polyene radical cations [7].

The dynamic σ–π polarization effects are introduced by perturbation theory. This means that the dynamic σ–π polarization effects are significant for the D_2 states. This may be related to the fact that the positive charge is localized on the terminal carbons in D_2 states while it is localized at the center of the chains in the ground state. The shift in charge from the center to the terminal may cause reorganization of the σ electrons upon excitation to the D_2 states.

Transition to the D_1 states is observed to be weak. The transition $D_0 \rightarrow D_1$ is pseudoparity forbidden due to cancellation of the dipole moment vectors as mentioned above. Contrary to the D_1 transition, the D_2 transition has a strong intensity. The two strong optically allowed transitions of $2 \rightarrow 1$ and $1 \rightarrow 1'$ make their addition in D_2 become more efficient with increasing chain.

MRMP predicts that the dipole forbidden state with the same symmetry as the ground state exists slightly above the D_2 state. This state is a mixture of singly excited configurations of $3 \rightarrow 1$ and singly excited configurations of $2 \rightarrow 1'$ and its conjugate $1 \rightarrow 2'$. Since the $3 \rightarrow 1$ transition is missing in butadiene, the third excited state of butadiene radical cation is quite different in character from that of the radical cation of longer polyenes.

3.2. The $\pi \rightarrow \pi^*$ excited states of polyene dications

In the case of dications, the single excitation from 2 (HOMO) to 1 (LUMO) gives rise to the dipole allowed ^1B_u states. The single excitation of $3 \rightarrow 1$ gives dipole forbidden ^1A_g states. A double excita-

Table 4
Calculated vertical excitation energies (eV) of low-lying polyene dications

Dication	Method	CASSCF	MRMP	Oscillator strength
butadiene				
1^1B_u	TZ2p/(2,4)	5.04	4.13	0.492
2^1A_g	TZ2p/(2,4)	7.17	5.96	forbidden
hexatriene				
1^1B_u	TZ2p/(4,6)	4.50	3.53	0.904
2^1A_g	TZ2p/(4,6)	3.91	3.75	forbidden
octatetraene				
1^1B_u	DZp/(6,12)	3.90	3.16	1.335
2^1A_g	DZp/(6,12)	3.59	3.32	forbidden
2^1B_u	DZp/(6,12)	4.71	4.34	0.015
decapentaene				
1^1B_u	DZp/(8,10)	3.51	2.69	1.650
2^1A_g	DZp/(8,10)	3.21	2.91	forbidden
2^1B_u	DZp/(8,10)	4.28	3.87	0.014

tion of $(2)^2 \rightarrow (1)^2$ also gives rise to a ${}^1A_g$ state, which is expected to lie in this energy range. If such a state exists, it interacts with the singly excited ${}^1A_g$ states.

The CASVB description for these states of the dication of hexatriene is given in Fig. 2. For the ground state, the most important contribution comes from the Kekule-type structure where two charge centers are located on the two terminal carbons to avoid the repulsion as much as possible,

$$1^1A_g\ [C^+{-}C{=}C{-}C{=}C{-}C^+]$$

The most important structure of the excited 1^1B_u state is

$$1^1B_u[C^+{-}C{=}C{-}C^+{-}C{=}C]{-}[C{=}C{-}C^+{-}C{=}C{-}C^+]$$

and that of the second excited 2^1A_g state comes from the Dewar-type structure of

$$2^1A_g\ [\overline{C{-}C^+{-}C{=}C{-}C^+{-}C}]$$

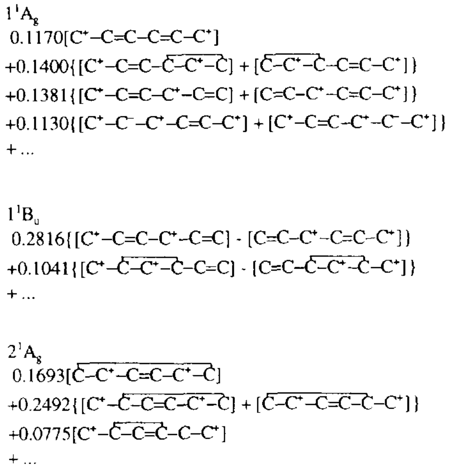
The calculated C–C bond lengths of dications given in Table 1 show clearly the inversion of bond alternation in the middle of the chains. This tendency becomes more apparent on increasing the chain length. This also suggests that the positive charges

Table 5
Calculated excitation energies (eV) and oscillator strengths of transitions for the neutral ($1^1B_u^+$), cation radical ($1^2A_u/1^2B_g$) and dication (1^1B_u) species of the polyenes using the MRMP method [a]

Molecule	Dication	Cation radical		Neutral [b]
State:	1^1B_u	$1^2A_u/1^2B_g$ (D_1)	$2^2A_u/2^2B_g$ (D_2)	$1^1B_u^+$
Transition:	$(2 \rightarrow 1)$	$(2 \rightarrow 1) + (1 \rightarrow 1')$	$(2 \rightarrow 1) - (1 \rightarrow 1')$	$(1 \rightarrow 1')$
butadiene	4.13 (0.492)	2.43 (0.011)	4.16 (0.626)	6.21 (0.803)
hexatriene	3.53 (0.904)	1.98 (0.015)	3.32 (0.998)	5.37 (1.082)
octatetraene	3.16 (1.334)	1.69 (0.022)	2.88 (1.380)	4.81 (1.382)
decapentaene	2.69 (1.650)	1.43 (0.022)	2.46 (1.706)	3.37 (1.396)

[a] Oscillator strengths are given in parentheses.

[b] Taken from Ref. [1].



1^1A_g

$0.1170[C^+{-}C{=}C{-}C{=}C{-}C^+]$

$+0.1400\{[C^+{-}C{=}C{-}\overline{C{-}C^+{-}C}] + [\overline{C{-}C^+{-}C}{-}C{=}C{-}C^+]\}$

$+0.1381\{[C^+{-}C{=}C{-}C^+{-}C{=}C] + [C{=}C{-}C^+{-}C{=}C{-}C^+]\}$

$+0.1130\{[C^+{-}C^-{-}C^+{-}C{=}C{-}C^+] + [C^+{-}C{=}C{-}C^+{-}C^-{-}C^+]\}$

$+\ldots$

1^1B_u

$0.2816\{[C^+{-}C{=}C{-}C^+{-}C{=}C] - [C{=}C{-}C^+{-}C{=}C{-}C^+]\}$

$+0.1041\{[C^+{-}\overline{C{-}C^+{-}C}{-}C{=}C] - [C{=}C{-}\overline{C{-}C^+{-}C}{-}C^+]\}$

$+\ldots$

2^1A_g

$0.1693[\overline{C{-}C^+{-}C{=}C{-}C^+{-}C}]$

$+0.2492\{[C^+{-}\overline{C{-}C{=}C{-}C^+{-}C}] + [\overline{C{-}C^+{-}C{=}C{-}C}{-}C^+]\}$

$+0.0775[C^+{-}\overline{C{-}C{=}C}{-}C{-}C^+]$

$+\ldots$

Fig. 2. Description of the ground and excited state CASVB wavefunctions of the dication of trans-hexatriene. Values at the VB structures are occupation numbers.

are localized in each terminal carbon as given in the above CASVB description.

Table 4 together with Table 2 shows that the first excited state of polyene dications is the 1^1B_u state which is well described by a singly excited configuration of 2 → 1. The transition to this state has a strong intensity. MRMP predicts that the dipole forbidden 2^1A_g state exists slightly above the 1^1B_u state. This state is a mixture of the doubly excited configuration of $(2)^2 \rightarrow (1)^2$ and the singly excited configurations of 3 → 1 and 2 → 1′. This situation is similar to the case of the neutral species. There are no experimental data available for these polyene dications.

4. Summary

Results are presented from MRMP calculations for low-lying $\pi \rightarrow \pi^*$ excited states of radical cation and dications of polyenes. The nature of the respective states is analyzed in terms of the CASVB description. The present approach has proved to provide a systematic quantitative understanding of electronic structure and spectroscopy of the linear neutral polyene, its radical cation and its dication.

Table 5 is a summary of dipole-allowed transitions of the neutral, radical cation and dication of polyenes. The neutral *ionic* $1^1B_u^+$ state originates from 1 → 1′ and the dication $1^1B_u^+$ state comes from 2 → 1. Both states are represented well by a single configuration. In the case of radical cations the configurations originating from the 1 → 1′ and 2 → 1 transitions become close in energy. The linear combinations of the two configurations generate so-called D_1 and D_2 states in radical cations. These correspond to weak low energy and intense high energy transitions in the absorption spectra. The spin is localized on the terminal carbons while the charge is delocalized in the chain in the D_1 state. On the other hand, the charge is localized on the terminal carbons while the spin is delocalized in the D_2 state. The present theory confirms the general tendency observed in carotenoids [8] that the first transition of the dications of polyenes is at a higher energy than the intense transition (D_2) of the radical cations and at a lower energy than the first allowed transition ($1^1B_u^+$) of the neutral species.

Acknowledgements

The present research is supported in part by a grant-in-aid from the Ministry of Education, Science and Culture and by a grant from the New Energy and Industrial Technology Development Organization (NEDO). One of the authors (KH) also thanks the grant from the Kawasaki Steel 21st Century Foundation. The computations were carried out on IBM SP2 workstations at IML. The CASSCF reference wavefunctions were obtained by MOLPRO [14] and HONDO96 [15]. The perturbation calculations were performed with the MR2D program [16].

References

[1] K. Nakayama, H. Nakano and K. Hirao, submitted for publication.

[2] K. Hirao, Chem. Phys. Lett. 190 (1992) 374; 196 (1992) 397; 201 (1993) 59; Int. J. Quantum Chem. S26 (1992) 517.

[3] T. Koenig, R. Wielesek, W. Snell and T. Balle, J. Am. Chem. Soc. 97 (1975) 3225; T. Koenig and S. Southworth, J. Am. Chem. Soc. 99 (1977) 2807.

[4] R.W. Bigelow, Int. J. Quantum Chem. 29 (1986) 35 and references therein.

[5] (a) T. Shida and S. Iwata, J. Am. Chem. Soc. 95 (1973) 3473; (b) R. Zahradnik and P. Carsky, Prog. Phys. Org.

Chem. 10 (1973) 327; (c) T. Shida, T. Kato and Y. Nosaka, J. Phys. Chem. 81 (1977) 1095; (d) R.W. Bigelow, Chem. Phys. Lett. 117 (1985) 22.

[6] T. Bally, S. Nitsche, K. Roth and E. Haselbach, J. Am. Chem. Soc. 106 (1984) 3927.

[7] T. Bally, K. Roth, W. Tang, R.R. Schrock, K. Knoll and L.Y. Park, J. Am. Chem. Soc. 114 (1992) 2440.

[8] J.A. Jeevarajan, C.C. Wei, A.S. Jeevarajan and L.D. Kispert, J. Phys. Chem. 100 (1996) 5637.

[9] K. Hirao, H. Nakano, K. Nakayama and M. Dupuis, J. Chem. Phys. 105 (1996) 9227.

[10] P.E. Siegbahn, A. Heiberg, B.O. Roos and B. Levy, Physica Scripta 21 (1980) 323; B.O. Roos, P.R. Taylor and P.E. Siegbahn, Chem. Phys. 48 (1980) 157; B.O. Roos, Int. J. Quantum Chem. S14 (1980) 175.

[11] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.

[12] T. Hashimoto, H. Nakano and K. Hirao, J. Chem. Phys. 104 (1996) 6244.

[13] (a) R.C. Dunbar, Chem. Phys. Lett. 32 (1975) 508; (b) R.C. Dunbar, Anal. Chem. 48 (1976) 723; (c) R.C. Dunbar and H.H.-I. Teng, J. Am. Chem. Soc. 100 (1978) 2279; (d) V.E. Bondybey, J.H. English and T.A. Miller, J. Mol. Spectrosc. 80 (1980) 200.

[14] MOLPRO is a package of ab initio programs written by H.-J. Werner and P.J. Knowles: H.-J. Werner and P.J. Knowles, J. Chem. Phys. 73 (1980) 2342; P.J. Knowles and H.-J. Werner, Chem. Phys. Lett. 115 (1985) 259.

[15] M. Dupuis, S. Chin and A. Marquez, in: Relativistic and Electron Correlation Effects in Molecules and Clusters, G.L. Malli, ed. (NATO ASI Series, Plenum Press, New York, 1992).

[16] H. Nakano, J. Chem. Phys. 99 (1993) 7983; H. Nakano, MR2D Ver. 2, University of Tokyo, 1995.

[17] T.B. Jones and J.P. Maier, Int. J. Mass Spectrom. Ion Phys. 31 (1979) 287.