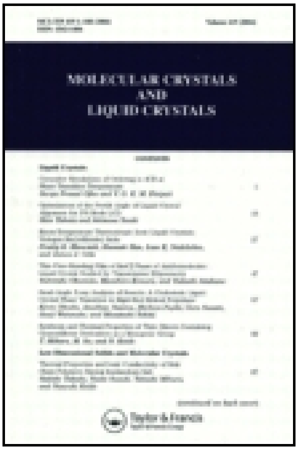

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ELECTRONIC STRUCTURE OF POLYACETYLENE*
— FINITE MODELS OF CIS-FORM —

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Electronic and vibrational structures of finite cis-polyenes are investigated in order to elucidate the origin and mechanism of enhanced IR active vibrational intensities. The remarkable charge polarization generated by one- or two-electron transfer from the polyene segment to the electron accepting dopant is confirmed as the origin, which is common to trans and cis-form of (CH)x.

INTRODUCTION

High electric conductivity of polyacetylene, (CH)x, especially upon the doping by electron donating or electron accepting species, has proved an inherent availability of (CH)x as an excellent organic conductive material [1-3]. Since optical properties of the doped-(CH)x serve for the understanding of this fascinating material through their profound physico-chemical informations, the extensive studies based on spectroscopic approaches have been carried out up-to-date [3-6]. Among the observed phenomena, the occurrence of three intense infrared (IR) absorption bands of the doped-(CH)x has been the focus of current attention ; The observation of these characteristic bands are irrespective of not only the dopant species of electron donor and acceptor but also the geometrical conformation of trans- and cis-forms [7-9]. On the other hand, the evidence of similar behavior

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**Institute of Materials Science, University of Tsukuba of the doped β-carotene as the doped-(CH)x has shed light on the reliability to use finite polyenes in grasping the essential nature of (CH)x, that being an infinite polyene [9-12].

In the preceding paper [13], we have discussed the electronic and vibrational structures of neat and doped trans-(CH)x by means of several kinds of finite polyenes of trans-form, and stressed the importance of charge polarization in accounting for the enhanced IR active vibrational intensities of trans-polyenes.

In order to reinforce the above argument, the present study is devoted to the case of cis-(CH)x. For this aim, molecular orbital (MO) calculations within MINDO/3 approximation and vibrational analyses have been executed on the basis of finite polyenes.

MODEL SYSTEM AND METHOD OF CALCULATION

The finite polyenes with C2h symmetry, C12H14, C12H14(+·), and C12H14(2+), are used for models, where the cation radical and di-cation are regarded to be generated by one- and two-electron transfer from polyene segments to the electron accepting dopant, respectively. Since among two structural isomers of cis-(CH)x, the cis-transoid form is known to be more stable than the trans-cisoid form [14,15], finite polyenes of cis-transoid form are adopted as initial geometries in calculation of geometry optimization which will be discussed later.

MO calculations of closed-shell and open-shell systems are performed using RHF and UHF MINDO/3 methods, respectively. The geometry optimization and calculation of normal vibartion of finite polyenes are carried out by means of the energy-gradient method. That is, the equilibrium geometry is obtained with the metric optimization procedure [16] for which the gradient of potential energy is calculated by MINDO/3 version of its SCF formalism [17]. The normal coordinates corresponding to normal vibrations are given as the eigenvectors of the seqular equation [18,19],

$$\det\left(\partial^2 W/\partial X_i \partial X_j \quad - \quad K\cdot\delta_{ij}\right) = 0$$

$$i,\ j = 1,2,\cdots,\ 3N\ ;\ K = \text{const.}$$

Where W is the potential energy and X_i is the mass-weighted Cartesian coordinate. The masses (in atomic unit) used for atoms are 1.0078 for H and 12.00 for C. The second derivatives of the potential energy are obtained by the numerical differentiation of potential gradients.

The IR intensity, A_i, is calculated with the numerical differentiation of the dipole moment, μ, in the electronic ground state along each normal coordinate, Q_i, by the following formula,

$$A_i = N\pi/3c^2 \cdot (\partial\mu/\partial Q_i)^2$$

Throughout the present calculation, the origin of Cartesian coordinate system is chosen at the center of the gravity of finite polyene.

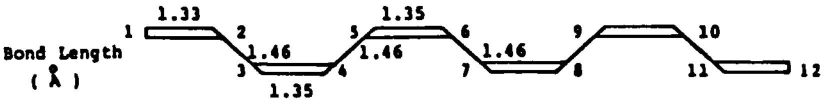
RESULTS AND DISCUSSION

Figure 1 shows the optimized geometries of neutral, cation-radical, and di-cation forms of cis-polyenes, together with the values of net charge and π-bond order. It is seen that the cationic polyene chains tend to be shortened, which may be due to the contraction of electron clouds associated with the loss of one or two electrons. Simultaneously, these cationic polyenes exhibit more polarized charge distribution where the positive and negative charges alternatively spread over the polyene chain, in comparison with the case of neutral polyene. This charge polarization is found to be more remarkable in the di-cation form than the cation-radical form.

It is worthy to note that the loss of one or two electrons causes not only the weakening of bond alternation but also the recombination of π-electron pairing which partly gives rise to the trans-cisoid form in the cis (cis-transoid) polyene, as shown in Figure 1. This result supports our previous prediction [20] that the isomerization from cis- to trans-(CH)x upon the doping should proceed through the continuous internal rotation of trans-cisoid polyene segment which is constructed from the cis-transoid polyene segment located between two doping sites by virtue of the recombination of π-electron pairing.

Now let us consider the normal vibration of cis-polyene. Figure 2 describes the calculated vibrational frequencies and relative intensities, $(\partial\mu/\partial Q_i)^2$, of neutral polyene, $C_{12}H_{14}$, together with the experimental IR spectrum of cis-(CH)x which has been synthesized in our laboratory according to the established procedure [21]. In this figure, the calculated intensities mainly due to the central and terminal vibrational modes of this polyene are distinguished with the

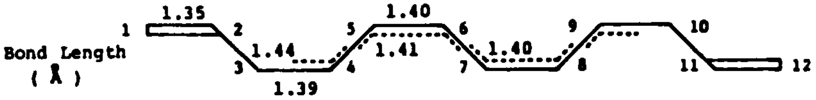
NEUTRAL



Net Charge	C_1	C_2	C_3	C_4	C_5	C_6
	-0.03	+0.04	+0.02	+0.02	+0.02	+0.02

π-Bond Order	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_7
	0.96	0.28	0.92	0.30	0.91	0.30

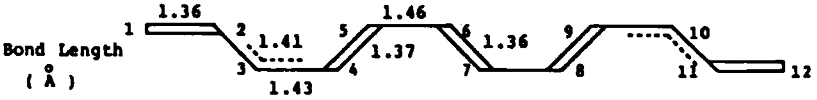
CATION-RADICAL



Net Charge	C_1	C_2	C_3	C_4	C_5	C_6
	+0.07	-0.01	+0.14	+0.00	+0.12	+0.07

π-Bond Order	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_7
	0.85	0.42	0.69	0.56	0.62	0.62

DI-CATION



Net Charge	C_1	C_2	C_3	C_4	C_5	C_6
	+0.29	-0.13	+0.38	-0.11	+0.24	+0.04

π-Bond Order	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_7
	0.80	0.56	0.51	0.80	0.34	0.88

FIGURE 1 Eletcronic and geometrical structures of C12H14, C12H14(+•), and C12H14(2+)

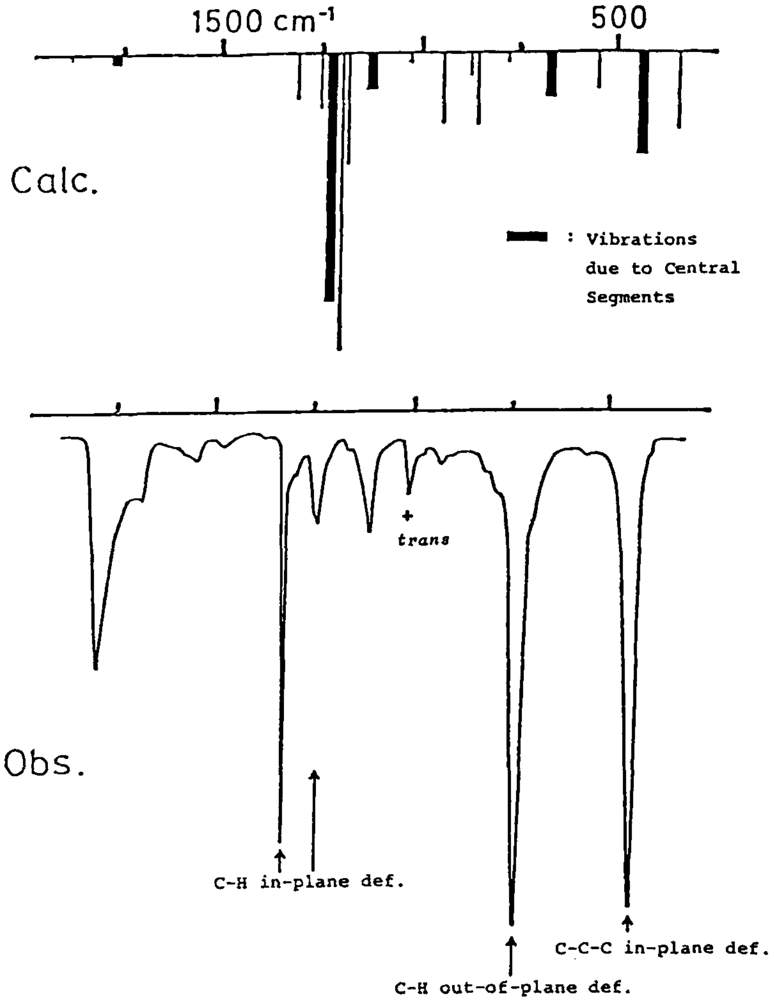


FIGURE 2 Calculated and observed IR spectra (upper : cis-$C_{12}H_{14}$; lower : cis-$(CH)_x$)

thick and thin straight lines, respectively. This figure indicates that the central vibrational frequencies and intensities obtained here well reproduce the global feature of the observed spectrum, and that the assignments of vibrational peaks agree with those of other works [22,23]. These results promotes us to proceed to the vibrational analyses of cationic polyenes.

Table 1 IR Active Vibrational Frequencies (cm^{-1}) and Intensities of C12H14, C12H14(+·), and C12H14(2+)

Band Group	First	Second	Third
	$[\nu_{C=C}]^a$	$[\nu_{C-C} + \delta_{C-H}]^a$	$[\delta_{C-H}]^a$
C12H14	1879 (0.005)	1380 (0.001)	1309 (0.048)
	1835 (0.000)		1243 (0.062)
	1770 (0.007)		1236 (0.284)
			1197 (0.332)
			1189 (0.124)
			1137 (0.040)
C12H14(+·)	1676 (0.277)	1388 (0.566)	1308 (0.073)
	1604 (0.784)		1264 (0.018)
	——		1244 (5.218)
			1217 (0.012)
			1200 (0.059)
			1165 (0.360)
C12H14(2+)	1740 (0.588)	1339 (0.380)	1285 (0.019)
	1596 (73.34)		1254 (0.419)
	1531 (68.93)[b]		1213 (3.286)
			1200 (1.946)
			1182 (0.078)
			1140 (0.254)

[a] main assignment [b] see the body of the manuscript

Since the three IR bands observed for the doped-(CH)x are located at 1397, 1288, and 888 cm^{-1} and these bands are irrespective of trans- and cis-forms [9], the corresponding normal vibrations of cationic polyenes can be selected taking in mind that the present calculation tends to overestimate the vibrational frequencies in this region by ca. 100 to 200 cm^{-1} [13]. The IR active normal vibrations in this region are found to belong to b_u mode for cationic polyenes with C2h symmetry. Table 1 summarizes the vibrational frequencies and relative intensities of b_u-normal vibrations which are classified into three groups abbreviated as first, second, and third groups. It may be straightforward to make main assignment for these vibrational groups. That is, the first group is almost attributed to the C=C stretching vibration ($\nu_{C=C}$), the second the mixed vibration

$(\nu_{C-C} + \delta_{C-H})$ including the C-C stretching and in-plane C-H bending vibrational modes, and the third the δ_{C-H}. These assignments are also rationalized by Figure 3, which shows typical three kinds of vibrations of C12H14(2+) polyene as well as those of C12H14 polyene. Note that although the vibration of di-cation form at 1531 cm^{-1} cited in Table 1 has nature of both $\nu_{C=C}$ and ν_{C-C} modes, in which the contribution of the latter is considerably larger than the former, this vibration is taken into the category of the first group on the basis of its vibrational frequency.

It is seen from Table 1 that the loss of one or two electrons leads to the lower-frequency shift of the $\nu_{C=C}$ vibrations, while the $(\nu_{C-C} + \delta_{C-H})$ and δ_{C-H} vibrations are not so changed. It is also clear that the vibrational intensities in cationic polyenes are largely enhanced, and that the degree of the enhancement is larger in the di-cation form than the cation-radical form, especially for the $\nu_{C=C}$ vibrations. The enhancement of IR active vibrations thus obtained, which is common to the case of trans-polyene [13], is reasonably explained with the aforementioned remarkable charge polarization, since it gives rise to the increase of

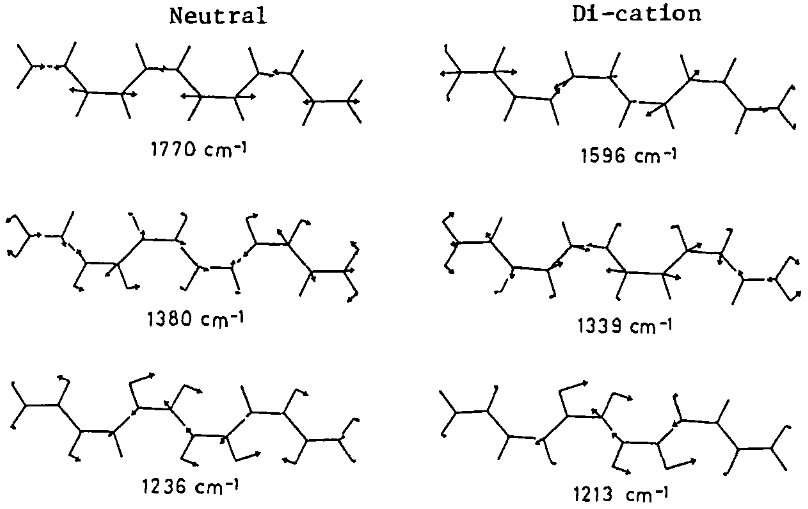


FIGURE 3 Relative magnitude and direction of displacement vectors in IR active normal vibrations of C12H14 and C12H14(2+)

the differentiation rate of the dipole moment in terms of the molecular displacement along the asymmetric normal vibration.

In addition, the vibrational structures of cationic polyenes presented in Table 1 provides a spectral feature with respect to the relative intensity and band width, i.e., the first band group (very strong ; broad), the second (weak ; sharp), and the third (strong ; very broad). This is evidently compatible with the observed pattern of IR spectrum for the doped-(CH)x [8,9], which concomitantly suggests that the broadness of the observed vibrational bands should be attributed to not only the unresolvable component-vibrations of various cationic polyene segments but also those of each band group of one cationic polyene segment concerned here.

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