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Electroabsorption spectroscopy of β-carotene homologs: Anomalous enhancement of $\Delta\boldsymbol{\mu}$

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Electroabsorption spectroscopy was used to determine the change in polarizability ($\Delta\boldsymbol{\alpha}$) and the change in dipole moment ($\Delta\boldsymbol{\mu}$) upon photoexcitation of β-carotene homologs with an increasing number (n) of conjugated C═C double bonds. The $\Delta\boldsymbol{\alpha}$ values increased systematically with increasing n. Although the magnitude of the intrinsic $\Delta\boldsymbol{\mu}$ values of the homologs was negligible because of their centrosymmetric structures, an anomalous increase in the value of $\Delta\boldsymbol{\mu}$ was observed at $n=9$. The stark-broadening mechanism originally proposed by Kulakov and Parschuk [Chem. Phys. Lett. **325**, 517 (2000)] is a possible origin that can generate this anomaly. It is proposed that either the $3\,^1A_g^-$ or another intermediate state whose group symmetry is A_g should be located close in energy to the $1\,^1B_u^+$ state at $n=9$. This increase in the value of $\Delta\boldsymbol{\mu}$ leads to an enhancement of the third-order nonlinear polarizability. We suggest that the energy gap between the *gerade*- and *ungerade*-type excited states is an important factor controlling the magnitude of the optical nonlinearity of carotenoids.

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I. INTRODUCTION

In order to produce the next generation of technologies, such as all-optical switching devices, data processing by using an optical-neural network, etc., and the technology of photonics that utilizes photons instead of electrons to acquire, store, transmit, and process information,[1] it is important to develop materials having the following three key features:[1,2] a large third-order optical nonlinearity, an ultrafast optical response, and a sufficiently high transparency in the required optical-frequency region. π-Conjugated polyene molecules have the potential to fulfill all these requirements, as they can readily satisfy the first and second ones.[3–7] In these molecules, the following two strategies have been suggested as ways of enhancing their optical nonlinearity: elongation of the conjugated polyene chain[3] and introduction of the electron donor and/or acceptor groups.[8] For example, a drastic increase of the third-order optical nonlinearity was reported following the introduction of an electron-withdrawing group into one end of the polyene chain.[8] However, there is a trade-off when n is increased, since this inevitably causes a redshift of the optical-transition frequency, which compromises the third requirement highlighted above. Therefore, it is important to explore strategies that will allow the development of materials that can fulfill all of the above three requirements.

Recently, a gigantic optical nonlinearity was reported in one-dimensional Mott-Hubbard insulators.[9] The origin of this nonlinearity is the large transition dipole moment between optically allowed and forbidden excited states. It is noteworthy, in this case, that the optically forbidden state is located in the immediate vicinity of the optically allowed state. Generally, as the energy gap between optically allowed and forbidden states narrows, the transition dipole moment between them is expected to increase.[10] This interaction between these two excited states plays a key role in the extent of the optical nonlinearity. Therefore, we set out to test if the optimization of these excited-state energies could open the door to a strategy for controlling the performance of nonlinear optical materials.

The PPP-MRD-CI (Pariser-Parr-Pople model Hamiltonian and multireference double excitation configuration interaction) method calculations of the state energies of short polyenes have predicted the presence of several low-lying, allowed, and forbidden excited singlet states: $1\,^1B_u^+$, $1\,^1B_u^-$, $2\,^1A_g^-$, and $3\,^1A_g^-$ states.[11–15] Here the "+" and "−" signs indicate Pariser's notation for the alternating symmetry of polyene excited states (pseudoparity). Optical transitions are allowed between a pair of electronic states having different Pariser's signs. Since the ground state of polyenes that have C_{2h} symmetry has A_g^- symmetry, the optical transition from the ground to B_u^+ state is allowed. However, the one photon transition to B_u^- or the higher A_g^- states ($2\,^1A_g^-$ and $3\,^1A_g^-$) is forbidden. The theoretical calculation and its simple extrapolation, predicted a remarkable trend for the − and + state energies as n increases. For example, the energy of the $3\,^1A_g^-$ state is located above that of the $1\,^1B_u^+$ state for $n\leqslant 8$, while it lies at nearly the same energy as the $1\,^1B_u^+$ state when $n=9$, 10, or 11, and it lies below the energy of the $1\,^1B_u^+$ state when $n\geqslant 12$.[14,16] This remarkable trend is due to the different shapes of the wave functions of the − and + states: The − state has a covalent character, while the + state has an ionic one.[14]

Carotenoids are very important natural pigments in plants and animals, and they have been used extensively as model systems for the study of π-conjugated polyene molecules.[17] The characteristics of the $1\,^1B_u^+$ and $2\,^1A_g^-$ states have been well reported.[18] Recently the $1\,^1B_u^-$- and $3\,^1A_g^-$-state energies were determined by measuring the resonance-Raman excitation profiles of solid carotenoids.[16,19,20] The experimental results showed that the energy gap between the optically forbidden and allowed states varied systematically as a function of n, just as predicted theoretically. In this study, therefore, we set out to investigate the influence of n on the energy gap between the one-photon allowed and the one-photon forbidden excited states of carotenoids and their optical nonlinearity.

The nonlinear optical properties of materials can be determined by electroabsorption (EA) spectroscopy.[21,22] Analysis of the EA spectrum can usually provide information on the change of polarizablity upon photoexcitation ($\boldsymbol{\Delta\alpha}$) and the change of static dipole moment upon photoexcitation ($\boldsymbol{\Delta\mu}$).[21,22] The theoretical background of this analysis has been well established by Liptay,[21] and a large number of studies have confirmed the validity of this method.[22–26] Interested readers should consult the excellent reviews by Boxer and co-worker in Refs. 27 and 28. The two strategies outlined above to increase optical nonlinearity, enhance, respectively, the $\boldsymbol{\Delta\alpha}$ and $\boldsymbol{\Delta\mu}$ values of the materials, i.e., elongation of the conjugated polyene chain enhances $\boldsymbol{\Delta\alpha}$, while introduction of electron donor and/or acceptor groups enhances $\boldsymbol{\Delta\mu}$.

In the present paper a series of β-carotene homologs with a range of n values were synthesized. These homologs have the following characteristics: they have large third-order optical nonlinearity due to one-dimensional electronic delocalization,[5,6] they show an ultrafast optical response, since their excited states relax to the ground state within a few picoseconds,[4,30] and they have centrosymmetric structures. The first and second of these characteristics provide the homologs with potential in applications as optical switching devices.[1] The centrosymmetric structure of the homologs means that they are not expected to have large intrinsic $\boldsymbol{\Delta\mu}$ values.

In π-conjugated polyene molecules, it is generally accepted that an optically forbidden state ($m\ {}^1A_g^-$) lying above the first optically allowed, excited state ($1\ {}^1B_u^+$), plays an essential role in the third-order, nonlinear, optical process.[31–35] Therefore, $m\ {}^1A_g^-$ is usually called an essential state. Previous studies using EA spectroscopy on β-carotene revealed that the transition energy between the ground and the $m\ {}^1A_g$ states is about $3 \sim 4$ eV.[36,37] However, the role of other optically forbidden states located in the vicinity of the $1B_u^+$ state, in regard to optical nonlinearity, has always been ignored. In Mott-Hubbard insulators, the optically allowed and forbidden-state energies locate close to each other, and such a configuration of the excited-state energies enhances their third-order, optical nonlinearity.[9] We expected that the increase of optical nonlinearity would be observed also in β-carotene homologs when the optically allowed and forbidden-state energies are close to each other. By using EA spectroscopy, we systematically determined the optical nonlinear properties of the β-carotene homologs with a series of n number. Based on the predicted dependence of the excited-state energies on n,[11–15] the relationship between the optical nonlinear parameters and the configuration of the excited-state energies was investigated.

II. EXPERIMENTAL SECTION

A. Sample preparation

The chemical structures of β-carotene homologs are shown in Fig. 1. The homologs are named after the number of their carbon atoms as C30-, C36-, C40- (β-carotene), C44-, C46-, and C50-carotene. β-carotene was purchased from Wako Pure Chemical Industries, Ltd. C30-, C36-, C44-, C46-, and C50-carotene were synthesized, respectively, by a reductive dimerization (McMurry reaction) of C15-aldehyde, C18-ketone, C22-aldehyde, C23-ketone, and C25-aldehyde catalyzed by a low-valence titanium compound that was derived from $TiCl_4$.[19] C15-aldehyde was synthesized from C13-ketone (β-ionone) by the use of the Horner-Emmons reaction, followed by a diisobutylaluminum (DIBAL) reduction. In the same way, C22-aldehyde and C25-aldehyde were synthesized from C20-aldehyde (retinal). β-ionone was kindly donated from Kuraray Chemical Co., Ltd., and was used after purification by vacuum distillation. Retinal was synthesized by the hydrolysis of retinyl acetate, followed by MnO_2 oxidation. Retinyl acetate was purchased from the BASF company (Switzerland) and was used after purification with silica-gel column chromatography (diethylether: n-hexane$=$20: 80). C18-ketone and C23-ketone were synthesized, respectively, from C15-aldehyde and C20-aldehyde (retinal) by means of Aldol condensation with acetone. All of the homologs were recrystallized from a hexane or benzene solution, and their ^{1}H-NMR spectra were recorded using a JEOL JNM-LA 400 FT-NMR spectrometer. The assignment of the ^{1}H-NMR signals showed that all the homologs have an all-*trans* configuration.

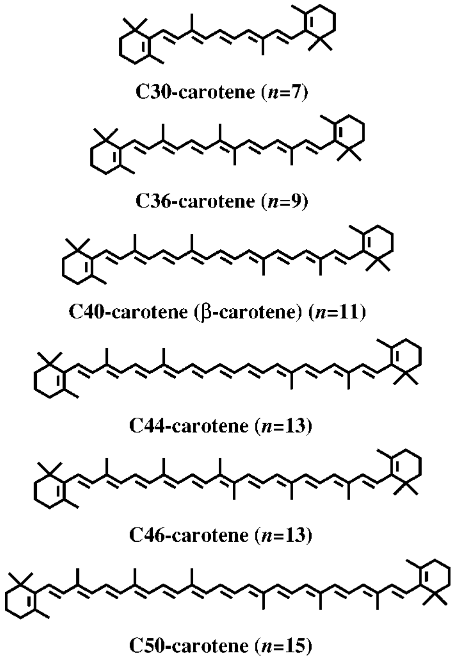

FIG. 1. Chemical structures of β-carotene homologs used in this study. The homologs are named after the number of their carbon atoms. n indicates the number of conjugated C$=$C bonds.

B. Spectroscopic characterization

EA spectra were recorded for methyl methacrylate polymer films (PMMA polymer, Wako Pure Chemical Industries, Ltd.) in which the β-carotene homologs were dispersed isotropically. The films were prepared according to the following procedure. Both the homologs ($\sim$50 mg) and the PMMA polymer (300 mg) were dissolved in benzene (6 ml). A small aliquot of this solution was then dropped onto the surface of a glass substrate on which gold electrodes (gap distance of 50–100 μm) had been installed. The gap distance between the electrodes was determined by optical microscopy to an accuracy of 2 μm. The residual solvent was then removed under reduced pressure. The thickness of the films was determined to be $\sim$3 μm. EA spectra were recorded in the setup described below.[38,39] Light from a 150-W Xe short-arc lamp (Hamamatsu, C7535) was dispersed by a monochromator (Acton Research, SpectraPro 150) and used to irradiate a sample cell. The incident radiation was linearly polarized using a Gran-Thompson prism and guided to the gap between the electrodes on the sample cell. The angle between the electric vector of the incident light and the electric field applied to the sample was set at 54.7° (magic angle). A sinusoidal ac voltage with a frequency $f=500$ Hz generated by a function generator (NF, E-1201A) was amplified to a high voltage (40 kV/cm) through a high-voltage, bipolar amplifier (NF, 4305). The light intensity transmitted by the sample was detected using a silicon photodiode (Hamamatsu, S1336-8BQ). The dc component of the signal was recorded on a digital multimeter (Fluke, 45), while the ac component was amplified by using a dual-phase lock-in amplifier (NF, 5610B). Only the changes (ΔI) of the transmitted light intensity (I) induced by the applied electric field with a frequency of $2f$ were selectively amplified by the lock-in amplifier. Absorption changes (ΔA) induced by the applied electric field were calculated by using the equation $\Delta A=-\ln[(I+\Delta I)/I]/2.303$. The optical-absorption spectra of the β-carotene homologs dispersed in the polymer films were recorded for use in the analysis of their EA spectra. The optical absorption spectra were recorded using a JASCO V-530 UV/VIS spectrophotometer. All of the measurements were performed at room temperature in the dark.

C. Analysis method of electroabsorption (EA) spectra

The absorption change $\Delta A(\nu)$ of β-carotene homologs upon exposure to an externally applied electric field can be written as a linear combination of the first- and second-order derivatives of the absorption spectrum $A(\nu)$. [We have neglected the zero-order derivative contribution to the EA spectra, since it is negligibly small in the present set of homologs.].[21,22,24]

$$\Delta A(\nu) = \frac{1}{30}\left[F\frac{dA(\nu)/\nu}{hd\nu} + H\frac{d^2A(\nu)/\nu}{h^2d\nu^2}\right]|\boldsymbol{E}_{\text{int}}|^2, \tag{1}$$

$$F = 5\,\text{Tr}(\boldsymbol{\Delta\alpha}) + [-\,\text{Tr}(\boldsymbol{\Delta\alpha}) + 3(\boldsymbol{m}\cdot\boldsymbol{\Delta\alpha}\cdot\boldsymbol{m})]\cdot(3\cos^2\chi - 1), \tag{2}$$

$$H = |\boldsymbol{\Delta\mu}|^2[5 + (3\cos^2\chi - 1)(3\cos^2\zeta - 1)]. \tag{3}$$

Here, $\boldsymbol{m}$ is a unit vector of the transition dipole moment. χ is an angle between the applied electric field and the polarization of the incident light. ζ is an angle between $\boldsymbol{\Delta\mu}$ and $\boldsymbol{m}$. $\boldsymbol{E}_{\text{int}}$ is the internal electric field that relates to the external electric field $\boldsymbol{E}_{\text{ext}}$ through a local-field correlation factor f_{L}, $\boldsymbol{E}_{\text{int}}=f_{\text{L}}\boldsymbol{E}_{\text{ext}}$. We estimated this factor under an ellipsoidal cavity approximation[23] and used a value of 1.1 of f_{L} for the β-carotene homologs in the PMMA films. In order to perform similar analyses to those used in the excellent study of the excited-state polarizabilities and dipole moments of diphenylpolyenes by Ponder and Mathies,[23] the external electric field was set so that it related to the applied ac voltage as $|\boldsymbol{E}_{\text{ext}}|^2=1/2|\boldsymbol{E}_{\text{ac}}|^2$.

Equation (1) is a general expression that describes the physical origin of the EA spectra. In the analyses of the EA spectra of the β-carotene homologs the following point was taken into consideration. Equation (1) implicitly assumes a uniform nonlinearity over the entire absorption band. However, this is not always the case for molecules with polyene structure, since the nonlinearity of these molecules is affected by inhomogeneous band broadening.[29,39,40]

When absorption spectra are inhomogeneously broadened, it is necessary to take into account the effect of the nonuniformity of the nonlinearities in order to correctly understand the physical implications of the EA spectra. Therefore, $\boldsymbol{\Delta\alpha}$ is described as a function of Σ that shows the shift of the center frequency of the different subsets within the inhomogeneous band. If the dependence of $\boldsymbol{\Delta\alpha}$ upon Σ is not large, $\boldsymbol{\Delta\alpha}$ can be simply approximated as

$$\boldsymbol{\Delta\alpha} \approx \boldsymbol{\Delta\alpha_0}(1 + \kappa\Sigma).$$

Here, κ is a constant, and $\boldsymbol{\Delta\alpha_0}$ is an intrinsic $\boldsymbol{\Delta\alpha}$ value of the molecule. It has been reported that $\boldsymbol{\Delta\alpha_0}$, as well as $\boldsymbol{\Delta\mu}$, contributes to the coefficient of the second-order derivative term, H, in Eq. (1) (see Ref. 40 for a detailed discussion).

According to these considerations, the EA spectra of the β-carotene homologs can be finally written as

$$\Delta A(\nu) = \frac{1}{6}\left(F_c\frac{dA(\nu)/\nu}{hd\nu} + H_c\frac{d^2A(\nu)/\nu}{h^2d\nu^2}\right)|\boldsymbol{E}_{\text{int}}|^2, \tag{4}$$

$$F_c = \text{Tr}(\boldsymbol{\Delta\alpha_0}), \tag{5}$$

$$H_c = |\boldsymbol{\Delta\mu}|^2 + C\,\text{Tr}(\boldsymbol{\Delta\alpha_0}), \tag{6}$$

$$C = \frac{-\kappa\Sigma^2}{2}. \tag{7}$$

Here the experimental condition ($\chi=54.7°$) was taken into account. According to Eq. (4), the values of F_c and H_c of each β-carotene homolog can be determined by fitting the EA spectrum with a linear combination of first- and second-order derivatives of its absorption spectrum. The $\boldsymbol{\Delta\alpha_0}$ and $|\boldsymbol{\Delta\mu}|$ values of each homolog can then be determined from the F_c and H_c values.

III. RESULTS AND DISCUSSION

Figure 2 shows the optical-absorption spectra of β-carotene homologs in cyclohexane. The concentrations of the molecules were adjusted to an optical density of $\sim$1 (cm^{-1}). The dominant absorption bands can be attributed

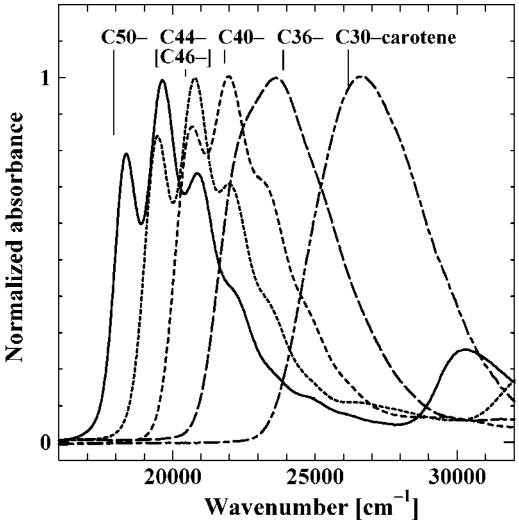

FIG. 2. Absorption spectra of C50- (solid line), C44- (dotted line), C40- (short dashed line), C36- (dashed line), and C30-carotenes (dotted dashed line) in cyclohexane solution. The absorption spectrum of C46-carotene is not shown here, since it shows good overlap with that of C44-carotene. (They have the same *n* number.) The absorbance of the homologs is normalized at their absorption maxima.

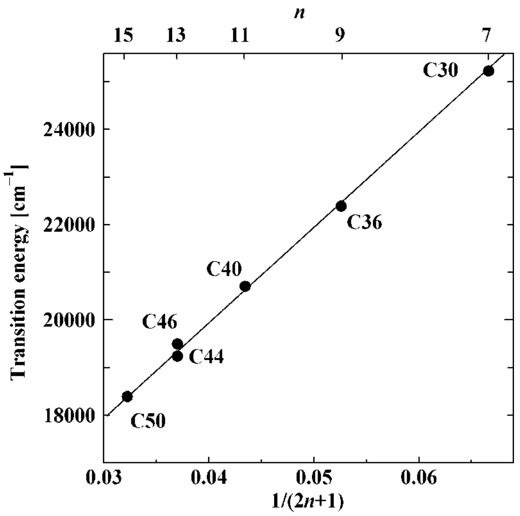

FIG. 3. Relationship between the number of conjugated C=C bonds (n) and the transition energies of $1\,{}^1A_g^- \rightarrow 1\,{}^1B_u^+$ ($0\rightarrow 0$ transition) of β-carotene homologs. The solid line shows the result of the least-square fit of the $1/(2n+1)$ dependence of the transition energies, as predicted by the theoretical calculations by Tavan and Schulten (Ref. 41).

to the optical transition from the $1\,{}^1A_g^-$ state (ground state) to the $1\,{}^1B_u^+$ state (excited state). A *cis*-peak (a characteristic absorption band of *cis* isomers assigned to the $1\,{}^1A_g^- \rightarrow 1\,{}^1A_g^+$ transition) was not found in any of the absorption spectra, since all of the homologs were in the all-*trans* configuration (confirmed by ^{1}H-NMR spectroscopy). An additional absorption band at 30 000 cm^{-1} observed in C50-carotene was attributed to the optical transition from the $1\,{}^1A_g^-$ state to the $2\,{}^1B_u^+$ state, based on its energy. As n increases, there is a systematic decrease in the transition energy between the $1\,{}^1A_g^-$ and $1\,{}^1B_u^+$ states. This is illustrated in Fig. 3. Since the C30- and C36-carotenes gave rise to structureless absorption bands, their absorption spectra were deconvoluted into several Gaussian subbands in order to identify their $0\rightarrow 0$ transition energies. Figure 3 shows that $1\,{}^1B_u^+$ state energies, $\mathrm{E}(1\,{}^1B_u^+)$, scale well as a linear function of $1/(2n+1)$. The relationship between $\mathrm{E}(1\,{}^1B_u^+)$ and n can be described in units of cm^{-1}, as in Eq. (8),

$$E(1\,{}^1B_u^+) = 12038 + \frac{1.9764 \times 10^5}{2n+1}. \qquad (8)$$

This relationship is well accounted for by theoretical calculations using the PPP-MRD-CI method.[13,14]

Figure 4 shows the EA spectra of the β-carotene homologs together with the results of their wave-form analysis. According to the theoretical formula described in Eq. (4), the EA spectra were fitted by a combination of the first- and the second-order derivative wave forms of the corresponding absorption spectra, using a multiregression method. The simulated wave forms are in good agreement with the observed EA spectra and, therefore, the F_c and H_c values could be determined, respectively, as the coefficients of the first- and second-order derivative wave forms. Figure 5 shows the extent that each derivative component contributes to the overall EA spectrum. It is noteworthy here that both the first- and second-order derivative components are required to reproduce the observed EA spectra. Furthermore, the coefficient of the first-order derivative component (F_c) is always positive. As shown in Eq. (5), F_c has a direct relationship to

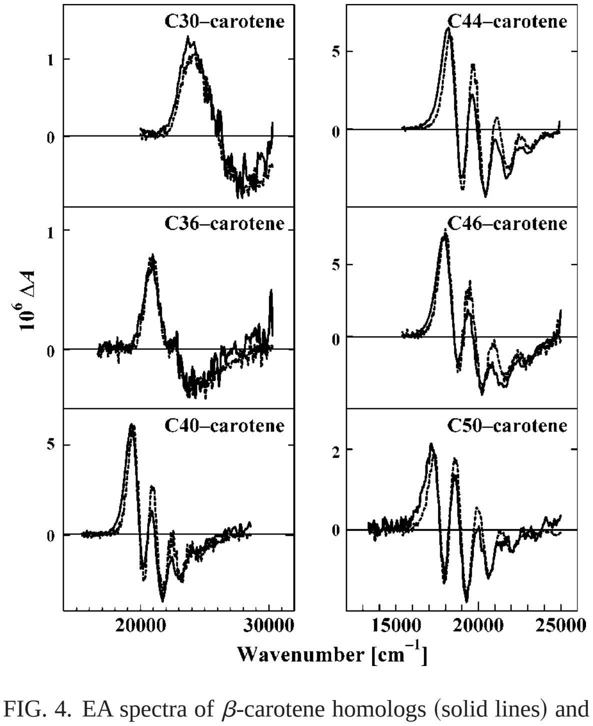

FIG. 4. EA spectra of β-carotene homologs (solid lines) and the wave forms derived from the spectral analysis (dotted lines). The wave forms were derived from a linear combination of the first- and second-order derivatives of the absorption spectra. They reproduce well the experimentally observed EA spectra.

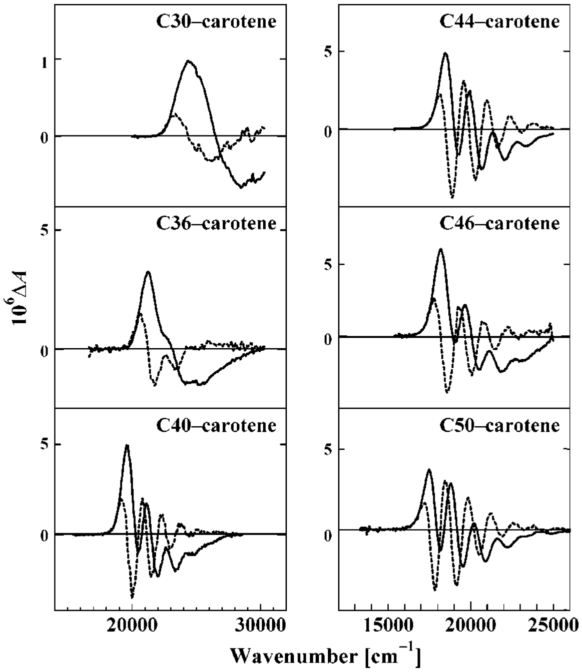

FIG. 5. The solid and dotted lines indicate the calculated first- and second-order derivative components in the EA spectra of β-carotene homologs. They were determined from the wave form analysis of the EA spectra. The dotted lines in Fig. 4 are produced by the simple addition of these two components.

$\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$. Therefore, this finding is an indication that $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ is also always positive with the present set of β-carotene homologs.

A. Dependence of nonlinear optical properties upon *n*

The $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ values of the β-carotene homologs were derived from the experimentally determined F_c values [see Eq. (5)]. The $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ value of β-carotene was estimated to be 818 [Å],[3] a value consistent with previous reports of 890–1030 [Å].[3,37,40,42] Figure 6(a) shows that the value of the $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ increases systematically with *n*. This dependence is well accounted for, since the spatial extent of the exciton state increases according to the elongation of the polyene chain length.[43,44] Ponder and Mathies reported the results of EA measurements on a series of diphenylpolyenes with $n=2–5$.[23] Combining their experimental results with those from the present study, the dependence of $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ on *n* is shown in Fig. 7.

Figure 6(b) shows the dependence of H_c on *n* (closed squares connected by a solid line). This figure reveals two remarkable features. Firstly, the magnitude of H_c becomes larger as *n* increases. Secondly, there is an anomalous enhancement in the value of H_c at $n=9$. According to Eq. (6), H_c can be written as a linear combination of $|\boldsymbol{\Delta\mu}|^2$ and $C\,\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$. The C term can be assumed to be constant for all of the homologs, based on an idea that is supported by our previous observations on hydrazones derived from a series of biological polyenes.[39] Since β-carotene homologs have a centrosymmetric structure, $\boldsymbol{\Delta\mu}$ is naturally expected to be

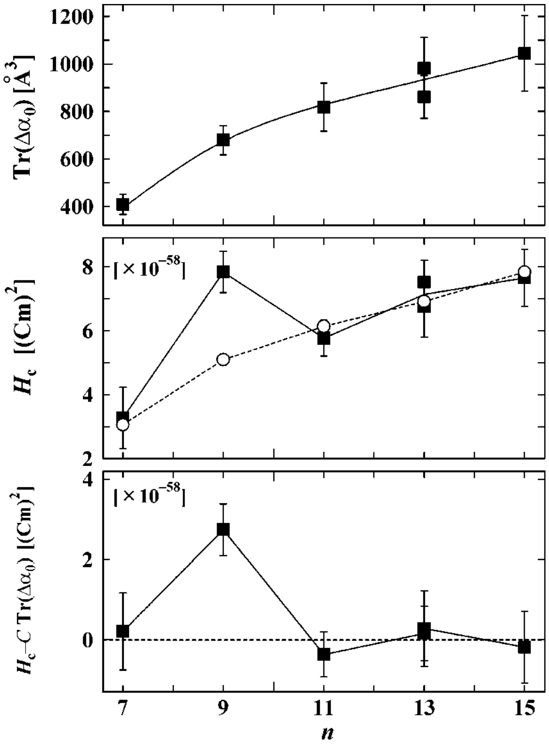

FIG. 6. (a) Dependence of the $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ upon the number *n* of conjugated C═C bonds of β-carotene homologs. The $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ values were directly determined from the F_c values. (b) The dependence of the H_c values (filled rectangles) upon *n*. The open circles connected by a dotted line are the result of fitting, taking the dependence of $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ on *n* into consideration. (c) The dependence of the $H_c - C\,\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ values upon *n*.

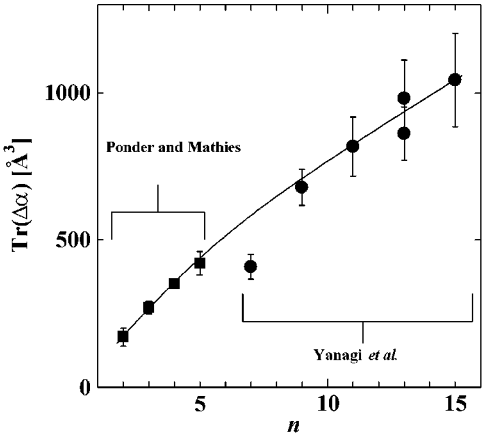

FIG. 7. Dependence of $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ values on the number *n* of C═C conjugated double bonds. The filled circles are the results of the β-carotene homologs, and the filled squares are the results of diphenylpolyenes by Ponder and Mathies. (Ref. 23) Without taking an idea of effective conjugation length into consideration, which is necessary to make a fair comparison of the results between two series of molecules, a systematic increase of the $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ values can be readily realized as the elongation of the conjugated C═C double bonds.

TABLE I. Oscillator strength f and molar extinction coefficient ϵ ($M^{-1}\,cm^{-1}$) of the fundamental absorption band of β-carotene homologs in tetrahydrofuran solution.

	C30	C36	C40	C44	C46	C50
f	1.6 ± 0.1	1.9 ± 0.1	2.2 ± 0.2	2.7 ± 0.1	2.7 ± 0.1	2.9 ± 0.1
ϵ	$(7.3\pm0.2)\times10^4$ at 378 nm	$(9.3\pm0.4)\times10^4$ at 427 nm	$(1.1\pm0.1)\times10^5$ at 458 nm	$(1.4\pm0.1)\times10^5$ at 485 nm	$(1.2\pm0.1)\times10^5$ at 489 nm	$(1.6\pm0.1)\times10^5$ at 512 nm

nearly zero. Thus the systematic increase of H_c can be explained by the dependence of $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ on n. We were able to reproduce the systematic increase of H_c by using the experimentally determined dependence of $\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ on n, and we estimated the contribution of $C\,\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$. The result of this analysis is shown as open circles connected by a dotted line in Fig. 6(b), and the $H_c-C\,\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ values are plotted in Fig. 6(c). The $H_c-C\,\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ values are zero in most of the homologs, when experimental error is taken into consideration. The validity of the assumption that $\boldsymbol{\Delta\mu}$ is zero in the most of the homologs is therefore confirmed by this result. At $n=9$, $H_c-C\,\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ shows a substantial value. According to Eq. (6), this anomaly is due to the presence of a nonzero value of $\boldsymbol{\Delta\mu}$ at $n=9$. Since the structural symmetry leads to $\boldsymbol{\Delta\mu}$ being zero, the striking anomaly at $n=9$ must be explained on the basis of the unique characteristics of the excited electronic states of the π-conjugated system.

Weiser and co-workers suggested that the oscillator strength (transition dipole moment) of a fundamental absorption band is one of the important physical parameters that can generate the second-derivative shape in EA spectra.[45,46] Therefore, we determined the oscillator strength as well as the molar-extinction coefficient of each β-carotene homolog in a solution of tetrahydrofuran, and the results are listed in Table. I. Figure 8 shows the dependence of the oscillator strength on n. Since the simple linear dependence on n of the oscillator strength is well known, we can exclude the possibility that the anomaly of $H_c-C\,\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ at $n=9$ is caused by an anomalous trend of the oscillator strength.

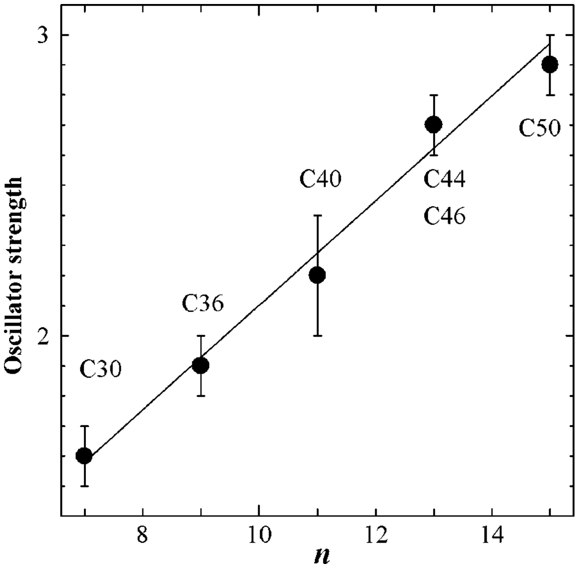

FIG. 8. Relationship between the oscillator strength of β-carotene homologs and the number n of C=C conjugated double bonds. The result clearly indicates the linear dependence of the oscillator strength on n.

Kulakov and Paraschuk have described the following relationship between excited state energies and the line shapes of EA spectra:[47] When the *ungerade*- and *gerade*-type excited states are nearly degenerate (the energy gap between the two states must be less than the width of homogeneous band broadening), a second-order, derivative line shape will appear in the EA spectrum (Stark broadening). On the other hand, when these two excited states are well separated, a first-order, derivative line shape will appear (Stark shift). We have concluded in this work that the second derivative component observed in the EA spectra of the β-carotene homologs is mainly due to an effect of inhomogeneous band broadening. This effect also causes the second derivative component through $\boldsymbol{\Delta\alpha_0}$. However, the anomalous enhancement of $H_c-C\,\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$ at $n=9$ indicates the presence of another mechanism that can generate the second-order derivative component. According to the theory of Kulakov and Paraschuk, if the *ungerade*-type excited state (B_u) and the *gerade*-type excited state (A_g) were nearly degenerate at $n=9$, Stark broadening could account for the anomalous enhancement of $H_c-C\,\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})$.

The second-order derivative component is usually caused by the presence of a static dipole moment. However, the presence of such a static dipole moment is forbidden in one-dimensional, π-conjugated molecules by reason of symmetry. The EA spectra of conjugated polymers showed that the second-order, derivative contribution does not exist in good single crystals,[48] but is apparent in films of the same polymer.[49] It is likely that disorder enables the presence of a static dipole moment. If we take this effect into consideration, another explanation for the anomaly of $\boldsymbol{\Delta\mu}$ can be proposed, i.e., state mixing between the *ungerade*- and *gerade*-type excited states will cause $\boldsymbol{\Delta\mu}$. In order to facilitate this state mixing, the presence of some type of perturbation is required. ($\boldsymbol{\Delta\mu}$ must be generated through an inherent coupling of the $1\,^1B_u^+$ state with an A_g-type excited state.) Theoretical calculation of the molecular structures of various carotenoids has suggested the presence of metastable conformers that have different torsion angles around the C6-C7 bonds at room temperature.[50] Distortion of the molecular structure could be a perturbation that causes the inherent coupling between *gerade* and *ungerade* states. However, the coupling from the torsion of the C6-C7 bond is thought to be weak and ad hoc, as there is no clear evidence for the presence of the perturbation that can cause the inherent coupling. Therefore, we regard the state-mixing mechanism as a less possible origin of the anomalous enhancement of $\boldsymbol{\Delta\mu}$ at $n=9$ than the Stark broadening.

B. Identification of an optically forbidden state that can generate $\Delta\mu$ at $n=9$

If the anomaly of $\boldsymbol{\Delta\mu}$ $[=H_c - C\,\mathrm{Tr}(\boldsymbol{\Delta\alpha_0})]$ at $n=9$ is caused by the Stark-broadening mechanism, as proposed by Kulakov and Paraschuk,[47] then the energy gap between *ungerade*- and *gerade*-type excited states must be less than the width of the homogeneous band broadening of the relevant electronic states. In order to fulfill this requirement the optically forbidden A_g^- state must be located close enough to the allowed $1\,^1B_u^+$ state at $n=9$.

By extrapolation of the PPP-MRD-CI calculations,[14] the $1\,^1B_u^+$, $1\,^1B_u^-$, $2\,^1A_g^-$, and $3\,^1A_g^-$ state energies (in cm^{-1}) are predicted to have the following relationships with n,

$$1\,^1B_u^+ : E = 2.286 \times 10^4 + \frac{1.235 \times 10^5}{2n+1}, \qquad (9)$$

$$1\,^1B_u^- : E = 1.508 \times 10^4 + \frac{2.083 \times 10^5}{2n+1}, \qquad (10)$$

$$2\,^1A_g^- : E = 1.518 \times 10^4 + \frac{1.352 \times 10^5}{2n+1}, \qquad (11)$$

$$3\,^1A_g^- : E = 1.645 \times 10^4 + \frac{2.567 \times 10^5}{2n+1}. \qquad (12)$$

Using these equations, we estimated the following values of the energy gap Δ between the relevant excited states at $n=9$: $\Delta(1\,^1B_u^+ \leftrightarrow 1\,^1B_u^-) = 3317$ cm^{-1}, $\Delta(1\,^1B_u^+ \leftrightarrow 2\,^1A_g^-) = 7064$ cm^{-1}, and $\Delta(1\,^1B_u^+ \leftrightarrow 3\,^1A_g^-) = 604$ cm^{-1}. This result indicates that the energy of the $3\,^1A_g^-$ state is expected to be the closest to that of the $1\,^1B_u^+$ state at $n=9$.

The Resonance-Raman excitation profiles of microcrystals of β-carotene homologs were used to determine the following relationships between the state energies of these excited states as a function of n,[19]

$$1\,^1B_u^+ : E = 1.0834 \times 10^4 + \frac{1.91257 \times 10^5}{2n+1}, \qquad (13)$$

$$1\,^1B_u^- : E = 0.1581 \times 10^4 + \frac{3.44262 \times 10^5}{2n+1}, \qquad (14)$$

$$2\,^1A_g^- : E = 0.9538 \times 10^4 + \frac{1.18033 \times 10^5}{2n+1}. \qquad (15)$$

The Δ values at $n=9$ can be estimated from these resonance-Raman results as follows: $\Delta(1\,^1B_u^+ \leftrightarrow 1\,^1B_u^-) = 1200$ cm^{-1} and $\Delta(1\,^1B_u^+ \leftrightarrow 2\,^1A_g^-) = 5150$ cm^{-1}. Unfortunately, the relationship for the $3\,^1A_g^-$ state was not determined in that study.

According to the above theoretical and experimental results, there are two possible candidates for the excited state that can generate $\boldsymbol{\Delta\mu}$ through Stark broadening. One is the $2\,^1A_g^-$ state, and the other is the $3\,^1A_g^-$ state. The $2\,^1A_g^-$-state energy is predicted to lie well away from that of the $1\,^1B_u^+$ state (more than 5000 cm^{-1} below it). Although the exact energy position of the $3\,^1A_g^-$ state has not been identified, the $3\,^1A_g^-$ state is expected to lie very near in energy to the $1\,^1B_u^+$ state. In 1,3,5-cycloheptatriene, which is a molecule with a polyene structure, an excited-state, homogeneous bandwidth was reported to be ~ 100 cm^{-1} (its excited-state dephasing time is estimated to be ~ 50 fs).[51] The population decay time of the $1\,^1B_u^+$ state in Neurosporene $(n=9)$ was reported to be ~ 20 fs.[52] Thus it is plausible that the homogeneous bandwidth of the homolog at $n=9$ is larger than 100 cm^{-1}. Therefore, it is quite difficult to believe that the $2\,^1A_g^-$ state could generate a remarkable $\boldsymbol{\Delta\mu}$ at $n=9$. In contrast, however, the energy gap between the $3\,^1A_g^-$ and $1\,^1B_u^+$ states could be expected to be small enough to produce the observed $\boldsymbol{\Delta\mu}$. Therefore, we propose that the $3\,^1A_g^-$ and $1\,^1B_u^+$ states should be nearly degenerate at $n=9$.

Recent studies of the ultrafast relaxation kinetics of excited carotenoids have identified the presence of other intermediates [designated as S_x, S^* (S^*_sol), S^*_T, $S^\ddagger$, S_CT] between the $1\,^1B_u^+$ and $2\,^1A_g^-$ states for carotenoid with $n=9$–11.[30,53–77] (A detailed discussion of this issue is presented in recent reviews by Polívka and Sundström[78] and by Hashimoto *et al.*[79]) However, the exact nature of these intermediate states is still not clear, since neither the location of their energies nor their dependence on the polarizability of solvent have been clarified. If one of these intermediate states has A_g-type group symmetry and is close in energy to the $1\,^1B_u^+$ state at $n=9$, $\boldsymbol{\Delta\mu}$ could be generated through the Stark-broadening mechanism. Further experimentation is needed to explore this possibility.

IV. CONCLUSION

In β-carotene homologs, $\boldsymbol{\Delta\alpha}$ values increase systematically with the increase of the polyene chain length. This dependence can be accounted for by the increase in the extent of an exciton state as n becomes larger. The magnitude of the intrinsic $\boldsymbol{\Delta\mu}$ values were determined to be negligible. This is expected, since all of the homologs used in the present study have centrosymmetric structures. However, an anomalous increase of $\boldsymbol{\Delta\mu}$ was observed at $n=9$. The physical background of this anomaly can be explained, based on the Stark-broadening mechanism. We propose that either the $3\,^1A_g^-$ or another intermediate state whose group symmetry is A_g should be located close in energy to $1\,^1B_u^+$ state at $n=9$.

However, further study must be performed in order to completely understand the physical origin of this anomaly. According to the model discussed above, $\Delta\boldsymbol{\mu}$ can only be generated when the energies of the *gerade* and *ungerade* excited states lie close to each other. Since the increase of $\Delta\boldsymbol{\mu}$ leads to the enhancement of the third-order, nonlinear polarizability, the energy gap between those two states is an important factor with which to enhance optical nonlinearity.

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