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model, does suggest that more than one electronic surface might have to be taken into account. Simulation of the spectra with explicit inclusion of more than one potential surface will require more sophisticated computational methods that are presently being developed and applied by several groups.³³⁻³⁹

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Triplet-Sensitized and Thermal Isomerization of All-Trans, 7-Cis, 9-Cis, 13-Cis, and 15-Cis Isomers of β -Carotene: Configurational Dependence of the Quantum Yield of **Isomerization via the T₁ State**

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The products of triplet-sensitized photoisomerization (excitation at 337 nm of the sensitizer, anthracene) and thermal isomerization of β -carotene in *n*-hexane, starting from the all-trans, 7-cis, 9-cis, 13-cis, and 15-cis isomers, were analyzed by HPLC. Direct photoisomerization (excitation at 488 and 337 nm) was also examined for comparison. Three different isomerization patterns were found in both triplet-sensitized and thermal isomerization: pattern A, cis to trans isomerization around each cis bond; pattern B, trans to cis isomerization in the central part of the conjugated chain; and pattern C, cis to another cis isomerization. In the T₁ state, the pattern A isomerization was predominant even for the peripheral-cis (7-cis and 9-cis) isomers and its efficiency was extremely high for the central-cis (13-cis and 15-cis) isomers. In the S_0 state, the pattern B isomerization, instead, was predominant for the peripheral-cis isomers, and the pattern A isomerization was predominant only for the central-cis isomers. The quantum yields of triplet-sensitized isomerization (decrease of the starting isomer per triplet species generated) were determined to be as follows: all-trans, 0.04; 7-cis, 0.12; 9-cis, 0.15; 13-cis, 0.87; and 15-cis, 0.98. In direct photoisomerization, the quantum yield of isomerization at 488-nm (337 nm) excitation was 4 (3) orders of magnitude lower than the above values, the relative values among the isomers being similar to the above. Further, the overall isomerization patterns of direct photoexcitation were similar to those of triplet-sensitized isomerization, supporting the idea that isomerization takes place via the T_1 state even in the case of direct photoexcitation. Carbon-carbon π bond orders of model polyenes in the T_1 and S_0 states were calculated by using the Pariser-Parr-Pople CI theory; bond lengths were optimized by using a bond order-bond length relationship. Isomerization characteristics in the T_1 and S_0 states observed were discussed based on the results of the calculations.

Introduction

Carotenoids (Car) in photosynthetic systems have dual functions of photoprotection and light-harvesting,¹⁻³ and natural selection of carotenoid configurations, in relation to these functions, has been found in the pigment-protein complexes of purple photo-synthetic bacteria.⁴⁻¹¹ In the reaction center (RC), where the photoprotective function involving both triplet energy transfer from bacteriochlorophyll (BChl) and dissipation of the transferred energy by the carotenoid is most important, the 15-cis configuration is selected. In the light-harvesting complex, where the light-harvesting function involving singlet energy transfer from carotenoids in BChl is most important, the all-trans configuration is selected (see a review by Koyama¹²).

It is an intriguing question as to why the 15-cis configuration has been selected by the RC. The configuration must be advantageous over all the possible cis-trans configurations in order to carry out the photoprotective function, and the selection should be ascribed to its T_1 -state property. The T_1 -state properties have been compared among cis-trans configurations by use of a set of isomers of β -carotene: Transient Raman spectroscopy showed that the all-trans, 7-cis, 9-cis, and 13-cis isomers generate their

own T₁ species (we call them the "all-trans", "7-cis", "9-cis", and "13-cis" T_1), but that the 15-cis isomer generates the "all-trans" T_1 .¹³ Transient absorption spectroscopy supported the observation;

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T₁ species generated from all the isomers, except for 15-cis, showed their own $T_n \leftarrow T_1$ absorptions and T_1 lifetimes, but the T₁ species generated from 15-cis showed exactly the same absorption and lifetime as that generated from all-trans.¹⁴ Since the 15-cis isomer isomerizes very efficiently into all-trans via the T_1 state (vide infra), it was concluded that the "15-cis" T_1 isomerizes very rapidly into the "all-trans" T_1 , and that the former is too short-lived to be detected by the above transient Raman and transient absorption spectroscopies.

Based on the above efficient isomerization of the 15-cis carotenoid free in solution, as well as an indication of isomerization in the RC-bound carotenoid,¹⁵ a mechanism of energy dissipation was proposed in which the T₁-state isomerization (or twisting) of the 15-cis carotenoid toward all-trans is involved.^{10,11} In order to substantiate the mechanism, (a) the T_1 -state isomerization from 15-cis to all-trans with a very high quantum yield and (b) the S_0 -state isomerization from all-trans to 15-cis need to be shown as intrinsic properties of carotenoids (free in solution), although the quantum yield or efficiency may be modified by interaction with the apoprotein consisting of pigments and peptides.^{16,17}

A spectroscopic study of triplet-sensitized isomerization using singlet oxygen and methylene blue showed one-way isomerization of β -carotene from 15-cis to all-trans.¹⁸ HPLC analysis (using an aluminum column) of chlorophyll a sensitized isomerization showed that both isomers generated the same steady-state mixture, and that the rate of isomerization from 15-cis to all-trans was 1 order of magnitude higher than that from all-trans to 15-cis.¹⁹ HPLC analysis (using a calcium hydroxide column) of anthracene-sensitized isomerization of isomeric β -carotene showed the relative quantum yield of isomerization in the following order: 15-cis > 13-cis > 9-cis > 7-cis > all-trans.¹³

In the present investigation, we attempted more detailed HPLC analysis of the T_1 - and S_0 -state isomerization, addressing the following three questions: (1) How do the pathways and the quantum yields of the T₁-state isomerization depend on the starting configuration? (2) How do the pathways and the efficiencies of the S₀-state isomerization depend on the starting configuration? (3) If the pathways and the quantum yields (efficiencies) are greatly dependent on the starting configuration, what is the reason for that? We determined isomerization pathways for tripletsensitized and direct photoisomerization, as well as for thermal isomerization, and determined the quantum yields for the photo isomerizations. We also calculated π bond orders for model polyenes by using the Pariser-Parr-Pople (PPP) method including single- and double-excitation configuration interaction (SD-CI). We found that the observed configurational dependence in the T_1 -state (S₀-state) isomerization can be explained in terms of "the triplet-excited region" (the conjugation effect) in the central part of the conjugated chain.

Experimental Section

Preparation, Identification, and Quantification of Isomeric β -Carotene. (a) Preparation of the Starting Isomers. alltrans- β -Carotene was purchased from Wako Pure Chemical Industries and recrystallized from benzene. The 15-cis isomer was a gift from F. Hoffman-La Roche Co. Ltd. The 7-cis isomer was isolated from a mixture of isomers obtained by thermal isomerization (at 200 °C) of the all-trans isomer, while the 9-cis and 13-cis isomers were isolated from an isomeric mixture obtained by I_2 -sensitized photoisomerization of the all-trans isomer. An HPLC technique using calcium hydroxide as adsorbate and 0.5-1.0% acetone in *n*-hexane as the eluent^{20,21} was used in the isolation. The purity of each starting isomer was as follows: all-trans, 98.5%; 7-cis, 97.7%; 9-cis, 97.1%; 13-cis, 96.2%; 15-cis, 97.5%.

(b) Identification of the Product Isomers. The product di-cis isomers, i.e., 7,13'-di-cis, 9,13-di-cis, 9,13'-di-cis, and 9,15-di-cis, were identified by cochromatography with a mixture of thermal isomerization; the assignment of each peak in the chromatogram of the mixture had been established by previous investigations.^{20,21} The product 7,13-di-cis and 7,15-di-cis isomers were newly identified by ¹H NMR spectroscopy in the present investigation; those isomers were obtained by thermal isomerization of the 7-cis isomer and by subsequent purification using HPLC, and their ¹H NMR spectra were recorded in benzene at 7 °C. Details of the NMR measurements were described elsewhere.²²

(c) Quantification of the Starting and the Product Isomers. The composition of isomers for each isomerization measurement was determined by using the area under each peak in the chromatogram and the correction factors at the detection wavelength, 450 nm.²⁰ The correction factors for the newly identified 7,13-di-cis and 7,15-di-cis were assumed to be the same as those for 9,13-di-cis and 9,15-di-cis, respectively. The specific HPLC conditions for the analyses were as follows: column, 4 mm i.d. × 300 mm packed with calcium hydroxide (Nacalai tesque, lot M6E7143, mesh 200-300); eluent, 0.5% acetone in *n*-hexane; and flow rate, 0.5 mL/min.

Triplet-Sensitized Photoisomerization. A mixture of each starting isomer $(5 \times 10^{-5} \text{ M})$ and anthracene $(5 \times 10^{-5} \text{ M})$ in n-hexane was irradiated with the 337-nm pulses from a nitrogen laser (NDC JL-1000L) after *n*-hexane-saturated N_2 gas (> 99.999%) was bubbled through the solution for 30 min. The number of photons absorbed by anthracene was determined by using the ϵ value of anthracene at 337 nm and the number of photons supplied. Triplet anthracene generated was estimated by using the quantum yield of intersystem crossing, 0.75.²³ The efficiency of triplet energy transfer from anthracene to β -carotene was calculated to be 0.95 by using the values of $k_{\rm ET} = 1.1 \times 10^{10}$ mol⁻¹·s^{-1 24} and $k_D = 2.7 \times 10^4$ s⁻¹ (Hashimoto, H., personal communication).

Direct Photoisomerization. (a) 488-nm Excitation. Each isomer $(6 \times 10^{-5} \text{ M})$ in *n*-hexane solution was irradiated with the 488-nm beam (200 mW) of an Ar⁺ laser (NEC GLG-3200) after bubbling with N_2 gas for 30 min. The values of OD_{488} for each isomer were as follows: all-trans, 6.0; 7-cis, 3.6; 9-cis, 3.4; 13-cis, 2.2; and 15-cis, 3.2. [Since isomerization takes place via the T_1 state (vide infra), we attempted to keep the efficiency of energy transfer and annihilation of the long-lived T_1 species the same among the isomers. Thus, the concentration of each isomer was adjusted to be the same, under the conditions where practically all the photons were absorbed.]

(b) 337-nm Excitation. Each isomer $(OD_{337} = 2.5)$ in *n*-hexane solution was irradiated with the 337-nm pulses of the nitrogen laser after bubbling with N_2 gas for 30 min. The concentration of each isomer was as follows: all-trans, 2.5×10^{-4} M; 7-cis, 2.1 $\times 10^{-4}$ M; 9-cis, 1.7 $\times 10^{-4}$ M; 13-cis, 5.1 $\times 10^{-5}$ M; and 15-cis, 3.8×10^{-5} M. [The experiments were originally planned as control experiments for triplet-sensitized isomerization. However, in order to present a set of quantum yields, we assumed, it is preferable to keep the condition of absorbing photons (the OD₃₃₇ value) the same rather than to keep the concentration the same for the above reason, since a large number of photons $(10^{-10} \text{ einstein})$ were applied within a short period of time (10^{-9} s) in the pulsed 337-nm irradiation, in which the number of photons per unit time (10^{-1})

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TABLE I: Chemical Shifts (Isomerization Shifts)^a for Isomeric β-Carotene (ppm)

| | 7,13-cis | 7,15-cis | 7-cis | 13-cis | 15-cis | all-trans |
|--------------|--------------|--------------|--------------|--------------|--------------|-----------|
| 7H | 5.97 (-0.37) | 5.97 (-0.37) | 5.96 (-0.38) | 6.37 (+0.03) | 6.33 | 6.34 |
| 7'H | 6.34 | 6.34 | 6.34 | 6.33 | | |
| 8H | 6.30 (-0.12) | 6.30 (-0.12) | 6.28 (-0.14) | 6.45 (+0.03) | 6.40 (-0.02) | 6.42 |
| 8'H | 6.42 | 6.42 | 6.42 | 6.42 | | |
| 10H | 6.46 (+0.09) | 6.45 (+0.08) | 6.46 (+0.09) | 6.35 (-0.02) | 6.37 | 6.37 |
| 10'H | 6.37 | 6.36 | 6.37 | 6.38 | | |
| 11H | 6.80 | 6.79 (-0.02) | 6.80 | 6.80 | 6.82 | 6.81 |
| 11′ H | 6.80 | 6.81 | 6.81 | | | |
| 12H | 7.07 (+0.57) | 6.51 | 6.51 | 7.06 (+0.56) | 6.51 | 6.50 |
| 12'H | 6.50 | 6.50 | 6.50 | 6.50 | | |
| 14H | 6.14 (-0.20) | 6.90 (+0.56) | 6.34 | 6.14 (-0.20) | 6.88 (+0.54) | 6.34 |
| 14'H | 6.36 (+0.02) | , , | | 6.35 | | |
| 15H | 6.94 (+0.24) | 6.45 (-0.25) | 6.68 (-0.02) | 6.94 (+0.24) | 6.47 (-0.23) | 6.70 |
| 15'H | 6.62 (-0.08) | ,, | , <i>,</i> | 6.63 (-0.07) | . , | |

^a Isomerization shifts with absolute values greater than or equal to 0.02 are shown.

einstein-s⁻¹) is much larger than that in the case of the above 488-nm CW irradiation $(10^{-7} \text{ einstein-s}^{-1})$.]

Thermal Isomerization. Each starting isomer in *n*-hexane solution $(5 \times 10^{-5} \text{ M})$ was sealed in a glass tube and heated at 80 °C in the dark. Thermal isomerization at room temperature was negligible (<1.3% for 1 h).

Actinometry. Actinometry was conducted by using potassium ferrioxalate.^{25,26}

Results

Identification of the 7,13-Di-Cis and 7,15-Di-Cis Isomers by ¹H NMR Spectroscopy. Table I lists the values of chemical shifts for the olefinic protons of the 7,13-di-cis and 7,15-di-cis isomers, the configurations of which have been determined in the present investigation. Chemical shifts for the 7-cis, 13-cis, 15-cis, and all-trans isomers are also shown for comparison. Shown in parentheses are "the isomerization shifts", defined as changes in the values of chemical shifts in reference to those of the all-trans isomer; they are unique to each cis configuration.^{22,27}

The first isomer in the table shows isomerization shifts characteristic of a 7-cis configuration, i.e., the high-field shift (hfs) of the 7H and 8H signals and the low-field shift (lfs) of the 10H signal. It shows also isomerization shifts characteristic of a 13-cis configuration, i.e., the lfs of the 12H and 15H signals and the hfs of the 14H and 15'H signals. Further, it shows the same chemical shifts as those of the all-trans isomer for the 7'-, 8'-, 10'-, 11'-, and 12'H signals, indicating that this part of the isomer is in the all-trans configuration. Thus, the isomer is assigned to the 7,13-di-cis isomer.

The second isomer also shows isomerization shifts characteristic of a 7-cis configuration, i.e., the hfs of the 7H and 8H signals and the lfs of the 10H signal. In addition, it shows isomerization shifts characteristic of a 15-cis configuration, i.e., the lfs of the 14H (14'H) signal and the hfs of the 15H (15'H) signal. Thus, the isomer is assigned to the 7,15-di-cis isomer.

Isomerization Pathways Starting from the All-Trans and Mono-Cis Isomers. Figure 1 shows the configurations of the isomers used in the present isomerization experiments. They are as follows: (a) all-trans, (b) 7-cis, (c) 9-cis, (d) 13-cis, and (e) 15-cis isomers. The cis isomers are classified into (1) peripheral-cis (7-cis and 9-cis) and central-cis (13-cis and 15-cis) isomers, and also into (2) unmethylated-cis (7-cis and 15-cis) and methylated-cis (9-cis and 13-cis) isomers. Isomerization pathways can be characterized by using the above classification of the cis-trans isomers.

(a) Triplet-Sensitized Photoisomerization. Figure 2 shows the results of triplet-sensitized isomerization starting from the (a) all-trans, (b) 7-cis, (c) 9-cis, (d) 13-cis, and (e) 15-cis isomers; anthracene ($E_T = 176 \text{ kJ/mol})^{28}$ was used as the sensitizer.





Figure 1. Configurations of cis-trans isomers of β -carotene used as starting isomers: (a) all-trans, (b) 7-cis, (c) 9-cis, (d) 13-cis, (e) 15-cis.

Product isomers whose amount of generation is larger than 5% of the reduction of the starting isomer are shown in the figure. A primary stage of isomerization, in which the reduction of the starting isomer is less than 12%, showed linear changes in the amounts of the starting and the product isomers as seen in the figure. The following pathways of isomerization are found (starting for each isomer): (a) All-trans isomerizes into 13-cis > 9-cis > 15-cis. (b) 7-Cis isomerizes into all-trans > 9-cis > 7,15-di-cis \approx 7,13'-di-cis. (c) 9-Cis isomerizes into all-trans \gg 9,15-di-cis > 9,13'-di-cis > 9,13-di-cis > 13-cis. (d) 13-Cis isomerizes into all-trans \gg 9-cis. (e) 15-Cis isomerizes only into all-trans.

The above isomerization pathways can be classified into three different patterns: Pattern A, which is defined as cis to trans isomerization of each cis bond, includes the isomerization pathways

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Figure 2. Triplet-sensitized photoisomerization starting from the (a) all-trans, (b) 7-cis, (c) 9-cis, (d) 13-cis, and (e) 15-cis isomers. Product isomers whose amount of generation is larger than 5% of the reduction of the starting isomer are shown.

of (1) 7-cis \rightarrow all-trans, (2) 9-cis \rightarrow all-trans, (3) 13-cis \rightarrow alltrans, and (4) 15-cis \rightarrow all-trans. Pattern B, which is defined as trans to cis isomerization in the central part (the 13=14, 15=15', and 13'=14' bonds) of the conjugated chain, includes the isomerization pathways of (1) all-trans \rightarrow 13-cis > 15-cis, (2) 7-cis \rightarrow 7,15-di-cis > 7,13'-di-cis, and (3) 9-cis \rightarrow 9,15-di-cis > 9,13'-di-cis > 9,13-di-cis. Pattern C, which is defined as cis to another cis isomerization, includes the isomerization pathways of (1) 7-cis \rightarrow 9-cis, (2) 9-cis \rightarrow 13-cis, and (3) 13-cis \rightarrow 9-cis.

Triplet-sensitized isomerization is summarized by using the above isomerization patterns as follows: (1) The pattern A (cis to trans) isomerization is predominant for all the cis isomers, and its quantum yields for the central-cis isomers are much higher than that for the peripheral-cis isomers (15-cis > 13-cis > 9-cis > 7-cis). (2) The pattern B (trans to cis) isomerization takes place only in the all-trans and the peripheral-cis isomers. (3) The pattern C (cis to cis) isomerization causes the generation of the methylated-cis (9-cis and 13-cis) isomers.

(b) Direct Photoisomerization. Figure 3 shows isomerization induced by direct photoexcitation at 488 nm. Here also, product isomers whose amount of generation is larger than 5% of the reduction of the starting isomer are shown in the figure. The

reduction of each starting isomer was limited to within 15% in order to obtain linear relations in the primary photoisomerization. Comparison with Figure 2 shows that the isomerization patterns are extremely similar to the case of triplet-sensitized isomerization, although the quantum yields of isomerization are 4 orders of magnitude lower. Generation of 9-cis from 13-cis was just below the above limit (5%), and it is not shown in Figure 3.

Figure 4 shows isomerization induced by direct photoexcitation at 337 nm. The abscissa and the ordinate scales are different from one panel to another, but both are adjusted so that the quantum yields of isomerization can be compared among the panels as slopes. The following conditions required the selections of the data points and, as a result, of the above different abscissa and ordinate scales: (1) The presence of the cis peak (the ${}^{1}A_{g}^{+} \leftarrow$ ${}^{1}A_{g}^{-}$ transition), whose intensity depends on the configuration,⁷ caused different concentrations among the isomers, when the optical density was adjusted to be the same (see Experimental Section). (2) The same isomerization conditions as above were applied both for the reduction of the starting isomer (<15%) and for the generation of the product isomers shown (their generation was larger than 5% of the reduction of the starting isomer). Comparison with Figure 2 shows that the isomerization pattern



Figure 3. Direct photoisomerization (excitation at 488 nm) starting from the (a) all-trans, (b) 7-cis, (c) 9-cis, (d) 13-cis, and (e) 15-cis isomers. Product isomers whose amount of generation is larger than 5% of the reduction of the starting isomer are shown.

is very similar to the case of triplet-sensitized isomerization, although the quantum yield of isomerization is approximately 3 orders of magnitude lower.

It is to be noted that the overall isomerization pattern (the isomerization pathways and the relative amounts of isomers generated) for direct photoexcitation (at both 488 and 337 nm) is essentially the same as that for triplet-sensitized isomerization. (See below for the differences between the 488- and 337-nm excitation.)

(c) Thermal Isomerization. Figure 5 shows the results of thermal isomerization at 80 °C, starting from the (a) all-trans, (b) 7-cis, (c) 9-cis, (d) 13-cis, and (e) 15-cis isomers. The composition after 1 h of heating is also shown on the right-hand side of each panel. Product isomers whose amount of generation is larger than or equal to 6% of the amount of reduction of the starting isomer are shown in the figure. The following pathways of isomerization are seen (starting from each isomer): (a) All-trans isomerizes into 13-cis > 15-cis \approx 9-cis. (b) 7-Cis isomerizes into 7,13'-di-cis > 7,15-di-cis > 7,13-di-cis. (c) 9-Cis isomerizes into 9,13'-di-cis > 9,15-di-cis > 15-cis. (e) 15-Cis isomerizes into all-trans > 13-cis.

Major differences in the isomerization patterns found for thermal isomerization, when compared to the cases of tripletsensitized and direct photoisomerization, are characterized as follows: (1) The isomerization efficiencies of the central-cis isomers are not so drastically greater than those of the peripheral-cis and the all-trans isomers, the isomerization efficiencies of the starting isomers being in the order all-trans < 7-cis < 9-cis < 13-cis < 15-cis, as in the case of photoisomerization. (2) The pattern A (cis to trans) isomerization is predominant only for the central-cis isomers, and the pattern B (trans to cis) isomerization, instead, is predominant for the peripheral-cis isomers. (3) The pattern C (cis to cis) isomerization generates the central-cis (13-cis and 15-cis) isomers rather than the methylated-cis (9-cis and 13-cis) isomers.

More detailed differences are as follows: (a) Starting from 7-cis, only the pattern B isomerization (\rightarrow 7,13'-di-cis, 7,15-di-cis, and 7,13-di-cis) takes place, and the pattern A and pattern C isomerizations do not occur. (b) Starting from 9-cis, the pattern A isomerization does take place, but its efficiency is as low as the pattern B isomerization. (c) Starting from 13-cis and 15-cis, mutual isomerization between the central-cis isomers (the pattern C isomerization) takes place. As a result, one-way isomerization



Figure 4. Direct photoisomerization (excitation at 337 nm) starting from the (a) all-trans, (b) 7-cis, (c) 9-cis, (d) 13-cis, and (e) 15-cis isomers. Product isomers whose amount of generation is larger than 5% of the reduction of the starting isomer are shown. (The abscissa and the ordinate scales are adjusted so that relative quantum yields can be compared as slopes.)

starting from 15-cis does not take place.

Quantum Yield of Isomerization for Triplet-Sensitized and Direct Photoexcitation. The above characteristics of triplet-sensitized and direct photoisomerization can be described more quantitatively in terms of quantum yields: Table II lists the quantum yield of isomerization ($\Phi_{iso})$ of each starting isomer for triplet-sensitized and direct photoisomerization. For triplet-sensitized photoisomerization, a Φ_{iso} value is defined as the decrease in starting isomer per triplet species generated. For direct photoisomerization, it is defined as the decrease in starting isomer per photon supplied. Hereafter, we denote the former Φ_{iso}^{T} and the latter Φ_{iso}^{D} . The Φ_{ino}^{T} value is as low as 0.04 for the all-trans isomer, and it is almost unity (0.98) for the 15-cis isomer. The value is much higher in the central-cis isomers when compared to the peripheral-cis isomers, and it increases in the order all-trans < 7-cis < 9-cis $\ll 13$ -cis < 15-cis.

The Φ_{iso}^{D} values for excitation at 488 (337) nm are 4 (3) orders of magnitude lower than the Φ_{iso}^{T} values. The relative values of Φ_{iso}^{D} among the isomers for the 488-nm excitation parallel those of Φ_{iso}^{T} . However, the relative values of Φ_{iso}^{D} for the 337-nm excitation do not parallel those of Φ_{iso}^{T} . When the Φ_{iso}^{D} value of

TABLE II: Quantum Yield of Isomerization (Φ_{leo}) of Each Starting Isomer for Triplet-Sensitized and Direct Photoexcitation

| | triplet-sensitized | direct photoexcitation ^b | | | | |
|-----------|--------------------|-------------------------------------|----------------------------|--|--|--|
| isomer | photoexcitation | 488 nm (×10 ⁴) | 337 nm (×10 ³) | | | |
| all-trans | 0.044 0.003 | 0.040 ± 0.001 | 0.10 ± 0.01 | | | |
| 7-cis | 0.119 ± 0.003 | 0.148 ± 0.003 | 0.89 ± 0.03 | | | |
| 9-cis | 0.145 ± 0.005 | 0.185 ± 0.010 | 1.06 ± 0.08 | | | |
| 13-cis | 0.865 ± 0.037 | 0.853 ± 0.021 | 2.18 ± 0.16 | | | |
| 15-cis | 0.976 ± 0.062 | 0.987 单 0.055 | 2.81 ± 0.21 | | | |

^a Defined as decrease in the starting isomer per triplet species produced. ^b Defined as decrease in the starting isomer per photon supplied.

the 15-cis isomer at 337 nm is normalized to unity, the relative values for the rest of isomers are as follows: all-trans, 0.04; 7-cis, 0.32; 9-cis, 0.38; and 13-cis, 0.78. Thus, the relative values of 7-cis and 9-cis are larger and that of 13-cis is smaller, when compared to the relative values of Φ_{iso}^{T} or of Φ_{iso}^{D} at 488 nm. Table III lists the quantum yield of isomerization of each

isomerization pathway, which is defined by using the increase in



Figure 5. Thermal isomerization (at 80 °C), starting from the (a) all-trans, (b) 7-cis, (c) 9-cis, (d) 13-cis, and (e) 15-cis isomers. Product isomers whose amount of generation is larger than or equal to 6% of the reduction of the starting isomer are shown. Shown on the right-hand side of each panel is the composition after 1 h.

the amount of each product isomer (instead of the decrease in the amount of the starting isomer), other definitions for sensitized and direct photoisomerization being the same as the above. We denote, for example, ϕ^{T} (isomer A \rightarrow isomer B) by removing the subscript "iso" and by specifying the isomerization pathway. When the ϕ values are used, the isomerization patterns described above are shown more quantitatively. The values show, for example, for both triplet-sensitized and direct photoexcitation, that the pattern A (cis to trans) isomerization becomes by far more efficient than the pattern B (trans to cis) or the pattern C (cis to cis) isomerization in the order 9-cis \ll 13-cis < 15-cis.

PPP-SD-CI Calculations of π **Bond Orders of Linear Polyenes.** In order to interpret, on a theoretical basis, the set of data obtained for triplet-sensitized and thermal isomerization, it is ideal that the T₁ and S₀ potential surfaces and the effects of geometrical relaxation on the isomerization process are calculated. In fact, this type of calculation has been done for lower polyenes such as butadiene, pentadiene, and hexatriene.^{29,30} However, for a polyene Therefore, we extended the PPP-SD-CI calculation of the π bond orders up to *all-trans*-docosaundecaene as an attempt to interpret theoretically the configurational dependence of the triplet-sensitized (T_i state) and thermal (S_0 state) isomerization. We used a selected set of SD-CI and optimized the bond lengths self-consistently using a bond order-bond length relationship: Briefly, the π bond orders of a state ψ were calculated as

$$n = (M^{1} \Delta \Sigma (c^{+} c^{-} + c^{+} c^{-})) W$$

$$p_{rs} = \langle \psi | / 2 \angle \langle c_{ro} c_{s\sigma} + c_{s\sigma} c_{r\sigma} \rangle \langle \psi \rangle$$

where $c_{r\sigma}^{*}$ and $c_{r\sigma}$ are the fermion creation and annihilation operators, respectively; they create or annihilate an electron with

as high as docosaundecaene (a model for β -carotene) only a neglect of nonbonded differential overlap (NNDO) calculation (without CI) of the bond orders³¹ has been available. The highest polyene for which π bond orders have been calculated by the PPP-SD-CI method (without optimization of the bond lengths) has been dodecahexaene.³²

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TABLE III: Quantum Yield of Isomerization (ϕ) of Each Isomerization Pathway^a for Triplet-Sensitized and Direct Photoexcitation

| starting isomers | isomers produced | | | | | | | | |
|---|---------------------------------------|-------------------------|--------------|-------------------------|-------------------------|--|--|----------|-----------|
| | all-trans | 9-cis | 13-cis | 15-cis | 7,15-cis | 7,13'-cis | 9,13-cis | 9,15-cis | 9,13'-cis |
| | | · · · _ · | Ti | inlet-Sensitiz | ed Excitation (| ×1) ^{b,c} | ······································ | | |
| all-trans | | 0.017 | 0.023 | 0.004 | | -, | | | |
| 7-cis | 0.050 | 0.042 | | | 0.014 | 0.013 | | | |
| 9-cis | 0.094 | •••• | 0.009 | | 0.01 | | 0.009 | 0.018 | 0.015 |
| 13-cis | 0.814 | 0.051 | 0.007 | | | | 01005 | 0.010 | 0.010 |
| 15-cis | 0.976 | 0.001 | | | | | | | |
| | | | Di | ect Excitation | n at 488 nm (X | (10 ⁴) ^{c,d} | | | |
| all-trans | | 0.011 | 0.023 | 0.006 | | , | | | |
| 7-cis | 0.062 | 0.042 | | | 0.023 | 0.021 | | | |
| 9-cis | 0 102 | 0.0.12 | | | 0.020 | 01021 | 0.018 | 0.034 | 0.031 |
| 13-cis | 0.853 | | | | | | 0.010 | 0.054 | 0.051 |
| 15-cis | 0.987 | | | | | | | | |
| | | | Di | ect Excitation | n at 337 nm (X | (10 ³) ^{c,d} | | | |
| all-trans | | 0.029 | 0.061 | 0.013 | n ut 557 min (* | , | | | |
| 7-cis | 0.41 | 0.296 | 0.001 | 0.015 | 890.0 | 0.090 | | | |
| Q cis | 0.76 | 0.270 | | | 0.070 | 0.070 | 0.057 | 0 1 3 3 | 0 1 1 0 |
| 12 010 | 2.06 | 0 1 20 | | | | | 0.057 | 0.155 | 0.110 |
| 15-018 | 2.00 | 0.120 | | | | | | | |
| 15-cis all-trans 7-cis 9-cis 13-cis 15-cis | 0.987 0.41 0.76 2.06 2.81 | 0.029 0.296 0.120 | Din 0.061 | ect Excitation 0.013 | n at 337 nm (× 0.098 | (10 ³) ^{c,d} 0.090 | 0.057 | 0.133 | |

^a Product isomers whose amount of generation is smaller than or equal to 5% of the reduction of the starting isomer are neglected. ^bDefined as increase in the product isomer per triplet species produced. 'Method of excitation (multiplication factor). "Defined as increase in the product isomer per photon supplied.

spin σ on an atomic π orbital χ_r . The expression for the resonance integral was taken from Schulten et al.³² as

$$\beta_{rs} = -2.60 + 3.21(r_{rs} - 1.397)$$

where r_{rs} is the length of the bond (r, s). The Ohno formula³³ was used for the two-center integrals. The CI expansion for the kth state

$$\psi_k = \sum C_{kl} \phi_l$$

consisted of major contributing configurations $\{\phi_i^{(0)}\}$, which were defined by a more restricted CI calculation, plus those of the generated set $\{\phi_m^{(1)}\}\$ having sufficiently large interaction with one or more members of $\{\phi_i^{(0)}\}$.^{34,35} The set $\{\phi_m^{(1)}\}$ was selected according to the relation

$$\left|\frac{\langle \phi_i^{(0)}|H|\phi_m^{(1)}\rangle^2}{\langle \phi_m^{(1)}|H|\phi_m^{(1)}\rangle - \langle \phi_i^{(0)}|H|\phi_i^{(0)}\rangle}\right| > \delta$$

where H is the Hamiltonian operator for the system and δ is a small threshold. The threshold value δ was taken as 3×10^{-3} eV. (We determined with decapentaene that this threshold could duplicate virtually the same bond orders as those calculated by use of the complete set of SD-CI.)

As for the geometry of polyenes, a planar, all-trans configuration was assumed, and all the bond angles were fixed to 120°. (See Discussion for the reason for choosing the planar, all-trans configuration instead of the perpendicularly twisted conformation around the central double bond.) The carbon-carbon bond lengths were optimized self-consistently so that the bond order-bond length relationship³⁶ of

$$r_{rs} = 1.517 = 0.18 p_{rs}$$

was fulfilled. (See Discussion for the necessity of the optimization.)

Figure 6 shows the results of the PPP-SD-CI calculations of the π bond orders for the following linear polyenes: (a) docosaundecaene (a simplified model of β -carotene), (b) octadecanonaene, (c) tetradecaheptaene, and (d) decapentaene. The ordinate scale of each panel shows the π bond order. The abscissa scale shows carbon-carbon double (longer markers) and single



Figure 6. Calculated bond orders for (a) docosaundecaene (a model for β -carotene), (b) octadecanonaene, (c) tetradecaheptaene, and (d) decapentaene. Bond orders were optimized self-consistently by using a bond order-bond length relationship. Bond orders for (e) decapentaene calculated without the above optimization are shown for comparison.

(shorter markers) bonds. (The notation of double and single bonds refers to the S₀ state.) Numbering of the double bonds for β carotene is shown at the top.

In the T₁ state (shown in closed circles and solid lines), the π bond order at each carbon-carbon bond depends strongly on the chain length. In (d) decapentaene (the shortest polyene calcu-

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lated), an inversion of the bond order takes place in the central part upon triplet excitation; e.g., the central C=C (C-C) bond becomes like a "C-C" ("C=C") bond. (We use quotation marks to denote a bond in the T_1 state.) In (a) docosaundecaene (the longest polyene), the trend is greatly diminished; upon triplet excitation, all the C=C and C-C bonds in the central part become carbon-carbon bonds with almost a "one and a half" bond nature (the π bond order, ~0.6). Further, the bond alternation in the S_0 state is retained at both ends. When the chain length increases in the order decapentaene < tetradecaheptaene < octadecanonaene < docosaundecaene, the effect of the bond order inversion decreases, but a similar pattern of spatial distribution of the π bond orders appear, for all the polyenes, in the central moiety of the chain. We call this pattern, which spans approximately five double-bond and four single-bond lengths (in the S₀-state notation), "the triplet-excited region" in the sense that drastic changes in the bond orders take place upon triplet excitation in this particular region, and that the bond alternation in the S_0 state is retained outside of it.

In the S_0 state (shown in open circles and broken lines), the spatial distribution of bond orders is more or less similar irrespective of the length of the polyene chain. There is a clear bond alternation starting from one end to the other. In addition, there is a decrease (increase) in the bond order of the carbon-carbon double (single) bond toward the center of the polyene chain. We call this "the conjugation effect".

Discussion

Isomerization upon Direct Photoexcitation. Except for the factor of 10⁻⁴, an extremely similar set of relative values of quantum yields (Table II) as well as isomerization pathways (Figures 2 and 3 and Table III) were found between the direct excitation at 488 nm and triplet-sensitized excitation. The results strongly suggest that isomerization takes place via the T_1 state even in the case of direct photoexcitation. When the β -carotene molecules are excited up to the optically allowed ${}^{1}B_{u}^{+}$ (S₂) state upon absorption of the 488-nm photons, they are supposed to relax very rapidly down to the optically forbidden $2^{1}A_{g}^{-}$ state, which is actually the S₁ state;^{37,38} subsequently, intersystem crossing to the T_1 (³B_u⁺) state is expected to occur. The quantum yield of intersystem crossing has been believed to be too low to be detected,³⁹ but the T_1 state could be detected by transient Raman spectroscopy using pump-and-probe pulses at 532 nm.⁴⁰

Excitation at 337 nm caused another set of quantum yields of isomerization; the absolute values being 1 order of magnitude higher ($\sim 10^{-3}$) and the relative values among the isomers being slightly different. The results may indicate that another route of intersystem crossing is present, when the molecules are excited up to the much higher ${}^{1}A_{g}^{+}$ state (the cis peak). Actually, both the S_1 and the T_1 states were detected by Raman spectroscopy, and the relative population of the T_1 state was higher when the 355-nm pulses were used for pumping instead of the 532-nm pulses.⁴⁰ Further, in lycopene, a different fluorescence pattern was obtained by excitation at 364 nm to the ${}^{1}A_{g}^{+}$ state (cis peak), instead of excitation at 470 nm to the ${}^{1}B_{u}^{+}$ state,⁴¹ suggesting different pathways of relaxation depending on the excitation wavelength.

Very recently, we examined, by using picosecond transient Raman and transient absorption spectroscopies, the S_1 and T_1 species generated from a set of isomers of β -carotene by direct photoexcitation at 355 nm.⁴² We found the following: (1) No isomerization takes place in the S_1 state, and (2) intersystem

crossing does take place with a quantum yield in the order of 10^{-3} . The results support the idea that isomerization takes place only via the T₁ state, and also the above observation that the quantum vields of isomerization for the 337-nm direct excitation are approximately 3 orders of magnitude lower than those of tripletsensitized isomerization.

Implications of the Natural Selection of Carotenoid Configurations by the Bacterial Reaction Center. The present investigation determined the T₁- and S₀-state isomerization as intrinsic properties of a carotenoid free in n-hexane solution and substantiated the following isomerization properties: (1) The 15-cis isomer, which is commonly found in the RC, showed a quantum yield of isomerization via the T_1 state (Φ_{iso}^T) almost equal to unity and a perfect one-way isomerization specifically into all-trans. Both properties are expected to trigger very efficient and uniform isomerization of the carotenoids toward all-trans in the RC. Intermolecular interaction with the apopeptide, and possibly with the "accessory" BChl, may modify the value of quantum yield. However, since the configurational change must be triggered by triplet excitation of the bound carotenoid, the intrinsic isomerization property of the carotenoid is considered to be most important to cause its configurational change in the RC. (2) The all-trans isomer showed a route of thermal isomerization into 15-cis. This isomerization was found to be not very efficient for the carotenoid free in solution. However, it may be enhanced when assisted by intermolecular interaction with the apoprotein. This isomerization property facilitates the reverse isomerization of the bound carotenoid in the dark.^{10,11}

PPP-SD-CI Calculations of the π **Bond Orders.** In the calculations of the π bond orders for polyenes in the T₁ state, we assumed not a perpendicularly twisted structure around the central carbon-carbon bond but a planar, all-trans structure. The assumption is rationalized on the basis of the following results: (1) Theoretical calculations predict that the planar structure is as stable as, or more stable than, the conformation perpendicularly twisted around the innermost double bond, and that the relative stability depends on the length of the polyene chain. An extended-Hückel calculation⁴³ predicted that the planar structure is more stable in the case of polyenes higher than octatetraene, while an NNDO calculation³¹ predicted that the planar structure becomes more stable for docosaundecaene. Further, even in butadiene, an ab initio MCSCF calculation⁴⁴ predicted that the planar structure is almost as stable as the one-twisted conformation. (2) Resonance Raman spectroscopy and QCFF/PI and CNDO/S calculations of 1,3,5-hexatriene showed the presence of the cis and all-trans T_1 species.⁴⁵ (3) A 2-fold potential curve with a shallow minimum at the cis position and a deep minimum at the trans position has been proposed for some derivatives of stilbene with a large aromatic group on one side.⁴⁶ The conclusion was based on determination of the quantum yield of triplet-sensitized isomerization as well as on transient absorption and transient Raman spectroscopies. (4) Resonance Raman spectroscopy and analysis of triplet-sensitized isomerization of C15-C22 aldehydes (having four to seven double bonds) indicated T_1 potential surfaces with minima at each cis and at the all-trans position.⁴⁷ The conclusion concerning these lower polyenes was based on their T₁ Raman spectra and the quantum yield of triplet-sensitized cis to trans isomerization exceeding 1.0 at higher concentrations, which indicates a complete one-way isomerization from a "cis" T_1 to the "all-trans" T_1 (see refs 46 and 47 for the details). (5) The Raman spectra of T_1 species generated from isomeric β -carotene could be interpreted in terms of a planar cis or trans configuration.¹³ Extremely efficient isomerization in the

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 T_1 state^{13,14} and the quantum yield of triplet-sensitized isomerization as high as 0.98 for the 15-cis isomer (the present result) support a T_1 potential curve with a very shallow minimum at the 15-cis position and a deep minimum at the all-trans position.⁴² All the above results support the presence of the planar, all-trans T_1 species. The present PPP-SD-CI calculations for cis configurations gave essentially the same π bond orders as those for the all-trans configurations (results not shown).

In the present calculation of the π bond orders, we optimized the bond lengths self-consistently using a bond order-bond length relationship given by Coulson and Golebiewski.³⁶ Figure 6e shows the π bond orders calculated for decapentaene without the above optimization; the values of bond orders shown are in complete agreement with those reported by Schulten et al.³² Comparison of panels d and e of Figure 6 clearly shows that this type of optimization is crucial in the calculations of the π bond orders. The values shown in Figure 6a-d were converged after four to seven cycles of self-consistent optimization.

Configurational Dependence of the So- and T1-State Isomerization: An Explanation Using the Calculated π Bond Orders. (a) T_1 -State Isomerization. Calculated π bond orders for docosaundecaene in the T_1 state (Figure 6a) show that the bond orders of the 15=15' and 13=14 bonds in the S_0 state decrease greatly upon triplet excitation (changes in the π bond orders: 0.833 \rightarrow 0.532 and $0.834 \rightarrow 0.585$, respectively), but that the bond orders of the 9=10 and 7=8 bonds do not change appreciably (changes in the bond orders: $0.840 \rightarrow 0.802$, $0.855 \rightarrow 0.865$, respectively). The above values of the T_1 bond orders do explain the order of the quantum yields of isomerization among the cis isomers, i.e., 7-cis (0.865) < 9-cis (0.802) \ll 13-cis (0.585) < 15-cis (0.532). The large difference in the quantum yields of isomerization between the central-cis and peripheral-cis isomers can be explained in terms of the effect of what we call "the triplet-excited region", which is shown to be located in the central part of the polyene chain. The pattern B (trans to cis) and pattern C (cis to cis) isomerizations can also be explained by decreased π bond orders in the central part. However, the preferred generation of the methylated-cis isomers, rather than the unmethylated-cis isomers, cannot be explained by using the present simplified model calculations.

(b) S₀-State Isomerization. Calculated π bond orders for docosaundecaene (a model for β -carotene) in the S₀ state (Figure 6a) show that the C=C bond order decreases from both ends (0.922) toward the center (0.833). The results indicate that isomerization can take place more easily in the central part. First, it explains the pattern A (cis to trans) isomerization around the 15=15', 13=14, and 9=10 bonds of the 15-cis, 13-cis, and 9-cis isomers in this order of efficiencies. Second, it explains the pattern B (trans to cis) isomerization around the 15-15', 13-14, and 13'=14' trans bonds of the all-trans and the peripheral-cis isomers. Finally, it explains the pattern C (cis to another cis) isomerization, which takes place only between the central-cis isomers. Isomerization patterns and efficiencies, which are not so drastically different between the central-cis and peripheral-cis isomers, can be explained in terms of slight differences in the π bond orders among the carbon-carbon double bonds ("the conjugation effect").

Conclusion

Strong dependence of the quantum yield (efficiency) of T_1 -state (S₀-state) isomerization on the starting cis-trans configuration has been found by isomerization experiments, and the result is explained in terms of "the triplet-excited region" ("the conjugation effect") in the central part of the polyene chain predicted by PPP-SD-CI calculations.

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Registry No. all-trans- β -Carotene, 7235-40-7; 7-cis- β -carotene, 83601-92-7; 9-cis- β -carotene, 13312-52-2; 13-cis- β -carotene, 6811-73-0; 15-cis- β -carotene, 19361-58-1; docosaundecaene, 3332-42-1; octadecanonaene, 3227-86-9; tetradecaheptaene, 2423-93-0; decapentaene, 2423-91-8.

Antisymmetric Nonresonant Vibrational Raman Scattering

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Antisymmetric nonresonant vibrational Raman scattering is studied by using group theory, especially a time-reversal symmetry. The results show that under the Born–Oppenheimer (BO) approximation, the antisymmetric transition polarizabilities of even-electron systems are approximately 10^{-4} times as large as symmetric ones, but beyond the Born–Oppenheimer approximation they are 10^{-2} times as large as symmetric transition polarizabilities. For odd-electron systems under the BO approximation, the antisymmetric transition polarizabilities can be nonzero due to time-reversal symmetry. The results verify Buckingham's conjecture of nonzero antisymmetric transition polarizabilities beyond the BO approximation.

1. Introduction

Antisymmetric matter tensors have been important for many years in connection with a resonance Raman scattering,² but antisymmetric nonresonant Raman scattering remains something of a curiosity. It was pointed out recently¹ that infrared and Raman intensities are usually described in terms of the dipole moment and polarizability surfaces. In the Born–Oppenheimer approximation, dipole moment and polarizability of a molecule may be described as functions of nuclear position. However, such a static description does not permit a current density in a diamagnetic molecule. Thus there has been difficulty in incorporating the electronic contribution into the magnetic dipole transition moment in the computation of vibrational circular dichroism.³ Beyond the Born–Oppenheimer approximation or by generalizing

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