TABLE	II: H	Rate	Parame	ters fo	or the	Reaction	and	Deactivation	of
Excited	Singl	et 9-	PA and	Acrid	ine				

	9-PA in methanol	acridine in ethanol ^a
k _F	$5.8 \times 10^7 \mathrm{s}^{-1}$	$4.2 \times 10^7 \mathrm{s}^{-1}$
$k_2 + k_d$	$2.7 \times 10^7 \mathrm{s}^{-1}$	$5.8 \times 10^7 \mathrm{s}^{-1}$
k_3	<10 ⁸ s ⁻¹	$<3 \times 10^{8} \text{ s}^{-1}$
k_4	$6.5 \times 10^{11} \text{ s}^{-1}$	$(5.7-6.3) \times 10^{11} \text{ s}^{-1}$
k _R	$9.3 \times 10^{10} \text{ s}^{-1}$	$3.3 \times 10^{11} \text{ s}^{-1}$
k _M	$1.1 \times 10^{10} \text{ s}^{-1}$	$8.2 \times 10^{10} \text{ s}^{-1}$
k n	$1.85 \times 10^{12} \text{ s}^{-1}$	$(8.6-9.2) \times 10^{11} \text{ s}^{-1}$
Ab	$3.2 \times 10^{10} \text{ s}^{-1}$	
ΔE_3	500 cm ⁻¹	450 cm ⁻¹
ΔE_{4}	1850 cm ⁻¹	1500 cm ⁻¹
ΔE_{b}	860 cm ⁻¹	

^aReference 7.

group of 9-phenylanthracene is different between S_0 and S_1 .¹⁶ On the other hand, Darmanyan¹⁷ studied the temperature dependence of $\Phi_{\rm F}$ and $\Phi_{\rm ST}$ of 9,10-diphenylanthracene in toluene and found that the yield of internal conversion increases with increasing temperature. The preexponential factor and the activation energy

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of the temperature-dependent internal conversion were 1.1×10^{10} s⁻¹ and 1390 cm⁻¹, respectively. This internal conversion was attributed to the sterically hindered rotation of the phenyl group. As the preexponential factor is close to the value for $A_{\rm b}$, the temperature-dependent internal conversion of 9-PA may also be attributed to the sterically hindered rotation of the phenyl group. The adequate deactivation mechanism is obtained by taking account of this internal conversion, which is indicated by a broken line in Figure 2. Then, the temperature dependence of $\tau_{\rm F}$ is satisfactorily described by eq 5.

$$1/\tau_{\rm F} = 1/\tau_{\rm F}^{0} + (k_4 + k_{\rm R} + k_{\rm M} + k_{\rm h}) \exp(-\Delta E_4/kT) + A_{\rm h} \exp(-\Delta E_{\rm h}/kT)$$
(5)

Figure 4a reveals that above 310 K the transition through S_2 is the dominant deactivation process and below 310 K the temperature-dependent internal conversion.

The rate parameters for the deactivation of 9-PA in methanol together with acridine in ethanol are summarized in Table II. In this table, we find that there is no large difference in the corresponding rate parameters between 9-PA and acridine.

Therefore, it is expected that acridine is also an efficient sensitizer for photopolymerization of acrylate monomer.

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Dependence of the Triplet Potential of Retinal Homologues on the Chain Length: **Resonance Raman Spectroscopy and Analysis of Triplet-Sensitized Isomerization**

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The Raman spectra of triplet species produced from the all-trans, 7-cis, and 9-cis isomers of β -ionylideneacetaldehyde (C15 aldehyde) and of β -ionylidenecrotonaldehyde (C17 aldehyde) were recorded. Each isomer of C15 aldehyde showed its own triplet Raman spectrum, while all the isomers of C17 aldehyde showed an identical triplet spectrum. The results were compared with those of isomeric retinal (C20 aldehyde) and retinylideneacetaldehyde (C22 aldehyde) obtained previously. Triplet-sensitized isomerization as well as direct photoisomerization of the all-trans isomer and the complete set of mono-cis isomers of C15, C17, C20, and C22 aldehydes were analyzed by HPLC. Mutual isomerization among the all-trans and mono-cis isomers was seen for C15 aldehyde, while one-way isomerization from each cis to all-trans was seen for C17, C20, and C22 aldehydes. The quantum yield of triplet-sensitized isomerization for each isomer of the above aldehydes was determined. All the results are discussed in terms of triplet potentials with minima at cis and trans positions, the relative stability being dependent on the length of the polyene chain; the cis minima are as stable as the trans minimum for C15 aldehyde, while the cis minima are far less stable than the trans minimum for C17, C20, and C22 aldehydes.

Introduction

Photoisomerization of retinal in rhodopsin (11-cis to all-trans) and in bacteriorhodopsin (all-trans to 13-cis and then back to all-trans) has been selected by nature to trigger a series of configurational changes of the apoprotein, which cause subsequent physiological processes.^{1,2} The reason for the selection should be ascribed to the intrinsic photoisomerization properties of the chromophore having the particular configurations and the particular length of the polyene chain. From this viewpoint, we have been examining the excited-state properties of the isomers of (1)retinal (C20 aldehyde), (2) retinylideneacetaldehyde (C22 aldehyde) having a longer chain than retinal, and (3) β -ionylideneacetaldehyde (C15 aldehyde) and β -ionylidenecrotonaldehyde (C17 aldehyde) having a shorter chain.

Pioneering investigations on the excited states of retinal and the homologues have been done by Das, Becker, and co-workers. Transient absorption spectroscopy of all-trans-C15, -C20, and -C22 aldehydes³ and of all-trans-C17 aldehyde⁴ revealed (1) the triplet decay constants; (2) the λ_{max} and ϵ values of the $T_n \leftarrow T_1$ absorption, the triplet energies estimated from the quenching rate constants for a variety of quenchers, and the dependence of these three parameters on the number of double bonds; (3) the triplet quantum yields, which were discussed in terms of the solventdependent state ordering by using additional data of the $S_n \leftarrow$ S_0 absorption⁵ and of the $S_1 \rightarrow S_0$ emission.⁶

We investigated the excited states, which were produced by flash photolysis from the all-trans, 7-cis, 9-cis, 11-cis, and 13-cis isomers

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Triplet Potential of Retinal Homologues

of C20 and C22 aldehydes by a combination of techniques, i.e. (a) nanosecond transient Raman spectroscopy, (b) analysis by HPLC of photoisomerization, and (c) picosecond time-resolved absorption spectroscopy.

C20 Aldehyde. (1) Raman spectroscopy⁷ detected the most stable 'all-trans' and the second stable '13-cis' triplet species. (We denote the configuration in the excited state with a pair of single quotation marks.) (2) HPLC analysis of direct and triplet-sensitized photoisomerization⁸ showed one-way isomerization of each cis into all-trans. (3) Time-resolved absorption spectroscopy^{8,9} revealed 'cis' to 'trans' isomerization in the T_1 manifold, the rate of which depended on the starting cis configuration.

C22 Aldehyde. (1) Raman spectroscopy¹⁰ detected the 'alltrans' and '9-cis' triplet species. (The presence of the '13-cis' triplet also was suggested.) (2) Time-resolved absorption spectroscopy¹¹ showed "isomeric" singlet-excited species with different spectra and lifetimes, and showed also "isomeric" triplet species produced by subsequent intersystem crossing; cis triplets isomerized into the 'all-trans' triplet as in the case of C20 aldehyde.

In both cases of C20 and C22 aldehydes, photoisomerization was ascribed to a triplet potential surface with shallow minima at cis positions and a deep minimum at the all-trans position. The results motivated a thorough and systematic study including the above aldehydes and other aldehyde with shorter chain lengths. Firstly, we examined the triplet species produced from the all-trans, 7-cis, and 9-cis isomers of both C15 and C17 aldehydes by Raman spectroscopy. Secondly, we examined by HPLC triplet-sensitized photoisomerization (direct photoisomerization was also examined for comparison) starting from the all-trans and all the mono-cis isomers of C15, C17, C20, and C22 aldehydes and determined the quantum yield of isomerization. As a result, we found a discrete change in the type of potential surface between C15 and C17 aldehydes.

Experimental Section

Preparation of Isomeric C15, C17, C20, and C22 Aldehydes. The synthesis of the aldehydes and the isolation of the isomers are described elsewhere.12,13

Transient Raman Measurements. Transient Raman spectra were recorded by a pump-and-probe technique using a jet stream of the sample solution $((1.0-6.0) \times 10^{-3} \text{ M} \text{ isomeric C15 aldehyde})$ or $(2.0-4.0) \times 10^{-3}$ M isomeric C17 aldehyde dissolved in *n*hexane). The details of the experimental setup are described elsewhere.^{10,14} In the present experiments, the 355-nm THG pulses (10 Hz, ~4 mJ/pulse) of a Nd:YAG laser (Quantel YG-480) were used for pumping. For probing, the 385-nm pulses (10 Hz, dye BBQ, 0.5 mJ/pulse) and the 420-nm pulses (10 Hz, dye stilbene 3, 0.7-1.3 mJ/pulse) from a THG-pumped dye laser (Lambda Physic FL-2002) were used for C15 and C17 aldehydes, respectively. Each probe pulse (duration 5 ns) was delayed optically by 5 ns with reference to the pump pulse (duration unstable <20 ns). Spectral data for 5000 (30 000) pulses of exposure were accumulated for C15 (C17) aldehyde, and the spectrum of nhexane was subtracted. The optical slit width was ~ 15 cm⁻¹ and the frequencies were calibrated by using the Raman lines of *n*-hexane, acetone, ethanol, ethyl acetate, and toluene.

Determination of the Composition of the Isomers. Mixtures of the isomers were analyzed by HPLC using a home-packed 4 mm diameter \times 300 mm column of LiChrosorb Si 60 (5 μ m) and

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the eluent, diethyl ether in n-hexane (5% for C15 and C17 aldehydes and 7% for C20 and C22 aldehydes). The detection wavelengths were 300 nm for C15 aldehyde, 350 nm for C17 aldehyde, 360 nm for C20 aldehyde, and 400 nm for C22 aldehyde. Compositions of the isomers were determined by the area under the peak of each isomer, which was corrected with the following $\epsilon_{cis}/\epsilon_{trans}$ factors at the above detection wavelengths: C15 aldehyde, 7-cis 0.545 (the same value assumed for 7,9-di-cis) and 9-cis 0.759; C17 aldehyde, 7-cis 0.626 and 9-cis 0.641; C20 aldehyde, 7-cis 0.989, 9-cis 0.855, 11-cis 0.590, and 13-cis 0.846; and C22 aldehyde, 7-cis 0.989, 9-cis 0.842, 11-cis 0.570, and 13-cis 0.803. (The factors were determined after the determination of the ϵ values at λ_{max} in *n*-hexane.)

Isomerization Experiments. A sensitizer for each aldehyde, i.e., benzil or Zn-TPP ((5,10,15,20-tetraphenyl-21H,23H-porphinato)zinc) was selected in order to satisfy the following conditions. (1) There is a *complete* region of wavelength which is absorbed not by the aldehyde but by the sensitizer. (2) The triplet energy can be transferred from the sensitizer to the aldehyde. Benzil $(E_T = 223.7 \text{ kJ} \cdot \text{mol}^{-1})^{15}$ was used for C15 aldehyde $(E_T = 188 \text{ kJ} \cdot \text{mol}^{-1})^3$ and C17 aldehyde $(E_T = 150-160 \text{ kJ} \cdot \text{mol}^{-1})^{.16}$ Zn-TPP ($E_{\rm T}$ = 153.4 kJ·mol⁻¹)¹⁷ was used for C20 aldehyde ($E_{\rm T}$ = 149,¹⁸ 159,¹⁹ or $\leq 140^{16}$ kJ·mol⁻¹) and C22 aldehyde ($E_T = 121^{20}$ or 1483 kJ-mol⁻¹).

Actually, sensitized isomerization was performed for 1.0×10^{-4} M of each isomeric aldehyde in *n*-hexane solution. The concentrations of the sensitizers were 1.0×10^{-2} M benzil (Wako Pure Chemicals, S.G.) for C15 and C17 aldehydes, and 2.5×10^{-5} M Zn-TPP (Aldrich, synthetic) for C20 and C22 aldehydes. Light from a 250-W halogen lamp, which was passed through both water filter and a Toshiba glass filter (V-Y42 for benzil or V-Y52 for Zn-TPP), was used for irradiation. Before irradiation, nitrogen gas saturated with *n*-hexane was bubbled through the sample solution for 1 h. An aliquot $(30 \ \mu L)$ of sample solution (total 4 mL) kept under nitrogen atmosphere was taken by a syringe through a rubber cap after each span of irradiation, and then it was subjected to HPLC analysis.

Direct photoisomerization was conducted in *n*-hexane solution under nitrogen atmosphere by irradiating the 337-nm light pulses (1 Hz, 5 mJ/pulse) from a N_2 gas laser (NDC JL-1000L); OD at 337 nm was adjusted to be 1.0, 1.0, 2.5, and 1.0 for C15, C17, C20, and C22 aldehydes, respectively.

Determination of Quantum Yield of Sensitized Isomerization. The quantum yield of sensitized isomerization was defined as decrease in the amount of the starting isomer per triplet molecule produced. For C15 and C17 aldehydes, sensitized isomerization was conducted by exciting the sensitizer (benzil) with 430-nm pulses (10 Hz, \sim 1.5 mJ/pulse) from a dye laser (Lambda Physik FL-2002, stilbene 3) which was pumped with the THG pulses of a Nd:YAG laser (Quantel YG-480). n-Hexane solutions containing 1×10^{-4} M isomeric aldehyde and $(1.4-2) \times 10^{-3}$ M benzil (7-9% absorption) were irradiated. Absorbed photons were determined by actinometry using potassium ferrioxalate.^{21,22} To determine the quantum yield of triplet-sensitized isomerization $(\Phi_{\rm iso}^{\rm T})$, the values of $\Phi_{\rm ISC} = 0.92$ for benzil²³ and $\Phi_{\rm ET} = 0.94$ were used; $\Phi_{\rm ET}$ was calculated by using $k_{\rm ET} = 1 \times 10^9 \, {\rm M}^{-1} \, {\rm s}^{-1}$ and $k_{\rm D}^{-1}$ $= 150 \ \mu s.^{24}$

For C20 and C22 aldehydes, sensitized isomerization was conducted by exciting the sensitizer (Zn-TPP) with 532-nm pulses (10 Hz, 1 mJ/pulse) from the Nd:YAG laser (SHG). An n-

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Figure 1. Cis-trans configurations of (a) C15, (b) C17, (c) C20, and (d) C22 aldehydes: (1) all-trans, (2) 7-cis, (3) 9-cis, (4) 11-cis, and (5) 13-cis isomers. Isomers of which triplet species have been detected by nanosecond transient Raman spectroscopy are indicated with an asterisk.

hexane solution containing 1×10^{-4} M isomeric aldehyde and 5 \times 10⁻⁵ M Zn-TPP (10% absorption) was irradiated, and the absorbed photons were determined by actinometry using Reinecke's salt.²⁵ To determine the quantum yield of triplet-sensitized isomerization, the values of $\Phi_{ISC} = 0.88$ for Zn-TPP²⁶ and $\Phi_{ET} = 0.99$ were used; Φ_{ET} was calculated by using $k_{ET} = 1 \times 10^9$ M⁻¹ $s^{-1.27}$ and $k_D^{-1} = 1200 \ \mu s.^{28}$

Results

Triplet Raman Lines and Their Empirical Assignments. Figure 1 shows the configurations of the cis-trans isomers of C15, C17, C20, and C22 aldehydes. Depending on the position of the cis bend in the polyene chain, the cis isomers are classified into terminal-bent and central-bent isomers. Depending on the presence and absence of the methyl group attached to the cis bend, they are also classified into methylated-cis and unmethylated-cis isomers. Presumably, each isomer keeps the original configuration immediately after excitation to the T_1 state.

Empirical assignments of Raman lines in the T_1 state can be done by referring to the assignments of those in the S₀ state, which have been established by calculations of normal vibrations, by comparison of the Raman spectrum of the parent species with those of deuterated species, and by spectral comparison among the isomers. Analyses of the Raman spectra of isomeric retinal, 12,29,30 isomeric retinal homologues, 13 and isomeric β -carotene^{31,32} in the S₀ state have revealed the following characteristics of Raman lines of biological polyenes.

(a) Key Raman Modes. The key Raman modes are as follows: (1) The C=O stretching mode which gives rise to a weak line above 1600 cm⁻¹. (2) The C=C stretching mode giving rise to a very strong line in the 1600-1500-cm⁻¹ region. (3) Asymmetric and symmetric C-H in-plane (ip) deformations of the methyl



Figure 2. T₁ Raman spectra of (a) C15 and (b) C17 aldehydes; the triplet species was produced from the (1) all-trans, (2) 7-cis, and (3) 9-cis isomers. Pumping at 355 nm; probing at 385 nm for C15 aldehyde and at 420 nm for C17 aldehyde.

groups attached to the polyene backbone which appear in the 1450-1350-cm⁻¹ region. (4) A coupled mode associated with the unmethylated-trans group (trans-C-CH=CH-C), i.e., a pair of C-H bendings coupled with the C=C stretching (an Ag type mode of the local symmetry C_{2h}). We call this "UT mode", and it appears in the 1270-1260-cm⁻¹ region. (5) A coupled mode associated with the unmethylated-cis group (cis-C-CH=CH-C), i.e., the C-H ip bendings coupled with the C=C stretching (an A₁ type mode of local symmetry $C_{2\nu}$). This "UC mode" also appears in the 1270-1260-cm⁻¹ region. (6) A coupled mode associated with the methylated-trans group (trans-C-CH= C*Me-C), i.e., the C-H ip bending coupled with both the methyl ip rocking and the C*-C stretching. This "MT mode" appears in the 1230-1220-cm⁻¹ region. (7) The same type of coupled mode associated with the methylated-cis group (cis-C--CH=-C*Me-C). This "MC mode" also appears in the 1230-1220-cm⁻¹ region. (8) The C-C stretching lines which appear in the 1200-1000-cm⁻¹ region.

(b) General Rules in Raman Intensity. (1) Those vibrational modes which take place in the central part of the extended (all-trans) polyene chain tend to give rise to the highest Raman intensity among the same type of vibrational modes. (2) Vibra-

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TABLE I: Empirical Assignments of T₁ Raman Lines (cm⁻¹) of C15 and C17 Aldehydes^a

	C15 aldehyde		C17 aldehyde	C20 aldehyde ^b	C22 aldehyde ^b	
all-trans	7-cis	9-cis	all-trans	all-trans	all-trans	
1614, 'C=O' str	1614, 'C=O' str	1614, 'C=O' str 1576, 'C ₇ =C ₈ ' str	1607, 'C=O' str	1600, 'C=O' str	1648, 'C=O' str	
1556, 'C ₉ = C_{10} ' str	1550, ' $C_9 = C_{10}$ ' str 1442, methyl asym def	1550, 'C ₉ = C_{10} ' str	1552, 'C ₉ = C_{10} ' str 1435, methyl asym def	1553, ' $C_{11} = C_{12}$ ' str	1550, ' $C_{11} = C_{12}$ ' str 1421, methyl asym def	
1398, methyl sym def	1398, methyl sym def	1398, methyl sym def 1291, 'UT' $(C_7 = C_8)$	1379, methyl sym def	1342, methyl sym def 1302, 'UT' ($C_7 = C_8$)		
1262, 'UC' $(C_7 = C_8)$	1264, 'UC' $(C_7 = C_8)$			1260, 'UT' $(C_{11} = C_{12})$	1270, 'UT' (C ₁₁ =C ₁₂)	
1220, M Γ (C ₉ =C ₁₀)	1218, MI ($C_9 = C_{10}$)	1224, 'M1' ($C_9 = C_{10}$)	1225, $MT'(C_9=C_{10})$	1188, 'C ₁₀ -C ₁₁ ' str	1201, ' $C_{10}-C_{11}$ ' str	

^aSee text for description of normal modes. ^bRaman frequencies from ref 10.

tional modes in the vicinity of a cis bend also tend to cause very high Raman intensity.

The above characterization of Raman lines in the S_0 state should be applicable to the Raman lines in the T_1 state, if the molecules keep essentially the planar cis or trans configurations upon triplet excitation, although changes in the bond lengths and in the force constants of the carbon-carbon bonds can cause some shifts of the related modes. Empirical assignments of triplet Raman lines described below will show that the above expectation is the case. (Hereafter, a pair of single quotation marks will be used to denote the vibrational modes in the T_1 state.)

Figure 2a shows the Raman spectra of the triplet species produced from the (1) all-trans, (2) 7-cis, and (3) 9-cis isomers of C15 aldehyde. The Raman spectra are different from one another, indicating that triplet species with different structures are generated. (It is obvious that the triplet species produced from the 9-cis isomer shows a unique spectral pattern; see the Raman lines at 1576 and 1291 cm^{-1} . The triplet species from 7-cis and that from all-trans show similar spectral patterns, because the structures of the polyene side chain are expected to be similar (see Figure 1). However, the former shows, when compared to the latter, a lower 'C==C' stretching Raman line at 1550 cm⁻¹, a unique Raman line at 1442 cm⁻¹, and two Raman lines in the 1300-1200-cm⁻¹ region having different frequencies and intensities.) The Raman lines can be assigned by assuming that the triplet species keep essentially the original configurations shown in Figure 1; the Raman line at 1614 cm⁻¹ which is commonly found in spectra 1-3 is assigned to the 'C=O' stretching. Raman spectrum 1 is characterized by the Raman lines of the $C_9 = C_{10}$ stretching at 1556 cm⁻¹, the methyl symmetric 'C-H' ip deformation at 1398 cm⁻¹, and the 'MT' mode at 1220 cm⁻¹ (associated with the methylated $C_9 = C_{10}$ bond); all of the vibrational modes are expected to take place in the central part of the extended chain of the 'all-trans' triplet. A weak line at 1262 cm⁻¹ is assigned to the 'UT' mode associated with the unmethylated $C_7 = C_8$ double bond. Spectrum 2 is characterized by the Raman lines of the $C_9 = C_{10}$ stretching at 1550 cm⁻¹, the methyl asymmetric (symmetric) 'C-H' ip deformation at 1442 (1398) cm⁻¹, and the 'MT' mode at 1218 cm⁻¹ (associated with $C_9 = C_{10}$), all of which are taking place in the central region of the all-trans part of the '7-cis' triplet. The spectrum is characterized also by the 'UC' mode at 1264 cm⁻¹ localized at the cis bend. Spectrum 3 is characterized by the Raman lines of the 'C₉= C_{10} ' stretching at 1550 cm⁻¹, the methyl symmetric 'C-H' ip deformation at 1398 cm⁻¹, and the 'MC' mode at 1224 cm⁻¹, all of which are taking place at the cis bend of the '9-cis' triplet. The C==O stretching mode taking place adjacent to the cis bend in this isomer shows the highest intensity among the isomers. The spectrum is characterized also by the $C_7 = C_8$ ' stretching at 1576 cm⁻¹ (shoulder) and the 'UT' mode at 1291 cm⁻¹ on the β -ionone side of the cis bend. Except for the 'C=O' stretching (1614 cm⁻¹) and the methyl 'C-H' ip deformation (1398 cm⁻¹), each vibrational mode has its own frequency. The above assignments are listed in Table I.

Comparison of the frequencies of the T_1 Raman lines with those of the S_0 Raman lines¹³ reveals the lengthening of the C=O and C=C bonds upon excitation of the molecule to the T_1 state. The T_1 'C=O' stretching line is shifted to the lower frequency by ~55 cm⁻¹ when compared to the S₀ C=O stretching line. The 'C=C' stretching line is also shifted to the lower frequency by 60 cm⁻¹. However, the C=O and C=C stretching frequencies (1614 and ~1550 cm⁻¹) still reflect the double-bond character. In addition, all the Raman lines could be assigned by assuming the original cis or trans configuration. Therefore, it is concluded that C15 aldehyde takes a planar cis or trans configuration in the T₁ manifold; the possibility of 7- or 9-perpendicular (twisted ~90°) conformation is excluded (at least as major components).

Figure 2b shows the Raman spectra of the triplet species of C17 aldehyde produced from the (1) all-trans, (2) 7-cis, and (3) 9-cis isomers. All the Raman spectra are identical within the limit of experimental errors, indicating that the same triplet species is generated. The Raman lines can be assigned in terms of an all-trans configuration: The weak Raman line at 1607 cm⁻¹ is assigned to the 'C==O' stretching and the strong line at 1552 cm⁻¹ is assigned to the central ' $C_9 = C_{10}$ ' stretching. The very weak lines at 1435 and 1379 cm⁻¹ are assigned to the methyl 'C-H' ip deformations (asymmetric and symmetric). The Raman line at 1225 cm⁻¹ is assigned to the 'MT' mode (associated with $C_9 = C_{10}$). The Raman line at 1151 cm⁻¹ is assigned to the $C_{10}-C_{11}$ stretching. (The corresponding line is not found for C15 and C20 aldehydes but is found for C22 aldehyde. See below.) All the Raman lines except for the 'C=O' stretching at 1607 cm⁻¹ are assigned to the vibrational modes in the central part of the extended 'all-trans' triplet.

Low-frequency shifts of the 'C=O' and 'C=C' stretchings upon triplet excitation by 78 and 43 cm⁻¹, respectively, indicate the lengthening of the double bonds, but they still keep the doublebond character. The 'C-C' stretching frequencies in the T_1 state are similar to those in the S_0 state; no drastic changes in the C-C bond order is expected. All the T_1 Raman lines could be assigned in terms of a single, planar all-trans configuration.

The above assignments have provided a basis for the assignments of the T_1 Raman lines of C20 and C22 aldehydes investigated previously;¹⁰ the results are summarized in Table I. Previous assignments for the 'C=O' and 'C=C' stretchings as well as the 'UT' modes¹⁰ are now confirmed by comparison with C15 and C17 aldehydes. The present data have enabled additional assignments of the 'C-C' stretching Raman lines by assuming the general rule that those modes taking place in the central part of the extended chain give rise to the highest intensities. The Raman line at 1151 (1149) cm⁻¹ of C17 (C22) aldehyde is assigned to the 'C₁₀-C₁₁' ('C₁₄-C₁₅') stretching (the 'C-C' stretching mode of the MeC=CH-CH=CH group on the carbonyl side). The Raman line at 1188 (1201) cm⁻¹ of C20 (C22) aldehyde is assigned to the 'C₁₀-C₁₁' stretching (the 'C-C' stretching mode of the MeC=C-CH=CH group in the central part).

Figure 3 summarizes the Raman lines of 'all-trans' triplet species of all the aldehydes. Thus, all the T_1 Raman lines of the isomeric aldehydes have been assigned consistently in terms of (a) the key Raman modes and (b) the general rules in Raman intensity. Conclusive assignments will be given when a set of Raman data of deuterated species and the results of normal-coordinate calculations become available.

Triplet Structures As Revealed by Raman Spectroscopy. Isomeric triplet species of C15-C22 aldehydes which have been



Figure 3. Comparison of the T_1 and S_0 Raman lines of all-trans (a) C15, (b) C17, (c) C20, and (d) C22 aldehydes. Raman lines are classified into strong, medium, and weak; solid (broken) lines show T_1 (S_0) Raman lines. The 'C=O' (\bullet) and C=O (\bullet) stretchings, the 'C=C' (O) and, C=C (\bullet) stretchings, the 'UT' (∇) and UT (∇) modes, and the 'MT' (∇) and MT (∇) modes are indicated. The 'C-C' stretchings of the MeC= CH-CH=CH groups in the central part (\diamond) and on the carbonyl side (\bullet) are also indicated. The wavy line indicates the triplet-excited region.

detected by nanosecond transient Raman spectroscopy are marked with an asterisk in Figure 1. They are the 'all-trans', '7-cis' and '9-cis' triplets of C15 aldehyde; the 'all-trans' triplet of C17 aldehyde; the 'all-trans' and '13-cis' triplets of C20 aldehyde; and the 'all-trans', '9-cis' and ('13-cis') triplets of C22 aldehyde. The results indicate the following: (1) The 'all-trans' triplet is stable and is detected for all the aldehydes. (2) For C15 aldehyde with the shortest polyene chain, 'cis' triplets have comparative stability with the 'all-trans' triplet. (3) For C17 aldehyde with the second shortest chain, 'cis' triplet species are too unstable to be detected. (4) For C20 and C22 aldehydes with a longer chain, 'methylated-cis' (9-cis or 13-cis) triplet species with an extended all-trans part of more than five double bonds long (including one in the β -ionone ring) are stable enough to be detected. (5) No indication of perpendicular (twisted) triplet species has been obtained for all the aldehydes.

Comparison of the (S_0) C=C stretching frequency with the (T_1) 'C=C' stretching frequency as well as comparison of the C=O stretching frequency with the 'C=O' stretching frequency, for all the all-trans aldehydes, lead us to the idea of "a triplet-excited region" with a similar magnitude and a limited span of structural changes (see the wavy lines in Figure 3):

The C==C stretching frequency in the S_0 state (o) decreases when the length of the polyene chain increases; it is 1607, 1595, 1575, and 1563 cm⁻¹ for C15, C17, C20, and C22 aldehydes, respectively. This is naturally ascribed to an increased conjugation for the longer polyene chains, which is reflected by the frequency of the central C==C stretching. On the other hand, the 'C==C' stretching frequency in the T₁ state (O) is constant and does not depend on the chain length; it is 1556, 1552, 1553, and 1550 cm⁻¹ for C15, C17, C20, and C22 aldehydes, respectively. The results strongly suggest that the effect of triplet excitation is not delocalized but localized in the central part and that the bond order of the central 'C==C' bond is almost the same for all the aldehydes.

The C=O stretching frequency in the S_0 state (•) is almost constant but slightly affected by the chemical structure in the carbonyl end; it is 1668, 1684, 1664, and 1680 cm⁻¹ for C15, C17, C20, and C22 aldehydes, respectively. On the other hand, the 'C=O' stretching frequency in the T₁ state (•) does reflect the chain length, not linearly but discretely. It is 1614, 1607, 1600, and 1648 cm⁻¹ for C15, C17, C20, and C22 aldehydes, respectively, indicating that the frequency shift upon triplet excitation is 54, 77, 64, and 32 cm⁻¹. The effect of triplet excitation for C22 aldehyde is much smaller than that for C15, C17, and C20 aldehydes. The results indicate that the span of "the triplet-excited region" is limited and does not reach the carbonyl end in the case of C22 aldehyde having the longest chain. In the case of β - apo-8'-carotenal (C30 aldehyde), the C=O and 'C=O' stretching frequencies have been determined to be 1682 and 1657 cm⁻¹, respectively.³³ The frequency shift is 25 cm⁻¹, supporting the above interpretation.

The above results suggest that the ordinary span of the triplet-excited region is approximately six double bonds long. This is probably the reason why the 'all-trans' triplet is the most stable for C17, C20, and C22 aldehydes, since the all-trans isomer has the longest extended chain among the isomers. C15 aldehyde, however, has a chain only four double bonds long; the tripletexcited region must be strongly compressed. This must be the reason why the 'all-trans' triplet is as unstable as other 'isomeric' triplet species (see below).

Pathways of Triplet-Sensitized Isomerization. Figure 4a shows the results of triplet-sensitized isomerization of C15 aldehyde starting from the (1) all-trans, (2) 7-cis, and (3) 9-cis isomers. The composition (%) of the isomers at different irradiation is shown together with the composition after a long exposure (photostationary state). Isomerization pathways are summarized as follows: (1) All-trans isomerizes mainly into 7-cis; (2) 7-cis isomerizes mainly into all-trans; and (3) 9-cis isomerizes mainly into 7-cis and all-trans. Generation of 7,9-di-cis is also observed.

Figure 4b shows the triplet-sensitized isomerization of C17 aldehyde starting from the (1) all-trans, (2) 7-cis, and (3) 9-cis isomers. In contrast to the case of C15 aldehyde, an approximate one-way isomerization from cis to trans is seen: (1) All-trans isomerizes only partially into 9-cis and 7-cis; (2) 7-cis and (3) 9-cis isomerize efficiently into all-trans.

Figure 4c shows the triplet-sensitized isomerization of C20 aldehyde starting from the (1) all-trans, (2) 7-cis, (3) 9-cis, (4) 11-cis, and (5) 13-cis isomers. (1) All-trans is very stable and hardly isomerizes; (2) 7-cis, (3) 9-cis, and (4) 11-cis isomerize very efficiently into all-trans; and (5) 13-cis slowly isomerizes into all-trans. 13-Cis is also generated from other cis isomers in small amounts.

Figure 4d shows the triplet-sensitized isomerization of C22 aldehyde starting from the (1) all-trans, (2) 7-cis, (3) 9-cis, (4) 11-cis, and (5) 13-cis isomers. All-trans is stable and reluctant to isomerize; (2) 7-cis, (3) 9-cis, (4) 11-cis, and (5) 13-cis isomerize very efficiently into all-trans.

To summarize the isomerization pathways of all the aldehydes: (a) C15 aldehyde is characterized by mutual isomerization among all-trans, 7-cis, and 9-cis and also by generation of 7,9-di-cis. (b) C17 aldehyde is characterized by one-way isomerization from 7-cis or 9-cis to all-trans. (c) C20 aldehyde is characterized by one-way isomerization from 7-cis, 9-cis, or 11-cis to all-trans and also by the second stable 13-cis. (d) C22 aldehyde is characterized by one-way isomerization from 7-cis, 9-cis, 11-cis, or 13-cis into all-trans.

The composition of the isomers in the photostationary state is in the order: (a) 7-cis > 7,9-di-cis > all-trans > 9-cis for C15 aldehyde; (b) all-trans > 9-cis > 7-cis for C17 aldehyde; (c) all-trans \gg 13-cis > 9-cis for C20 aldehyde; and (d) all-trans \gg 13-cis > 9-cis for C22 aldehyde. The following is to be noted: (1) The all-trans isomer is by far the most stable among the isomers for C17, C20, and C22 aldehydes, but the 7-cis isomer is the most stable for C15 aldehyde. (2) The 7,9-di-cis isomer is produced in a considerable amount for C15 aldehyde. (3) The unmethylated-cis (7-cis) isomer remains in the stationary state for C15 and C17 aldehydes. (4) The unmethylated-cis isomers (7-cis and 11-cis) are missing, and only the methylated-cis isomers for C20 and C22 aldehydes.

Quantum Yield of Triplet-Sensitized Isomerization. Table II lists the values of quantum yield of triplet-sensitized isomerization (Φ_{1so}^{T}) at the concentration of aldehydes 1×10^{-4} M. We found a strong dependence of the Φ_{1so}^{T} values on the concentration (this important observation has not been published as far as the authors know). Therefore, the true quantum yield of isomerization should be obtained when the Φ_{1so}^{T} value is extrapolated to infinite dilution.

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Figure 4. Triplet-sensitized isomerization of (a) C15, (b) C17, (c) C20, and (d) C22 aldehydes, starting from the (1) all-trans (\bullet), (2) 7-cis (O), (3) 9-cis (Δ), (4) 11-cis (\star), and (5) 13-cis (\Box) isomers. The 7,9-di-cis isomer of C15 aldehyde is indicated by \diamond . Changes in the isomeric composition (%) caused by irradiation of the sensitizer are shown together with the compositions after 30 min of exposure (a photostationary state). Amounts less than 1% are not shown.

TABLE II: Quantum Yield^a of Triplet-Sensitized Isomerization^b

	aldehyde				
isomers	C15	C17	C20	C22	
all-trans	0.7	0.1	0.1	0.1	_
7-cis	0.5	0.7	0.8	1.0	
9-cis	0.8	0.8	0.8	0.9	
11-cis			0.9	0.7	
13-cis			0.2	0.5	

^a Defined as decrease in the starting isomer per triplet species produced. ^b Concentration of isomeric aldehyde at 1×10^{-4} M.

Here, we present approximate values at the particular concentration in order to characterize isomerization via the triplet state (only one digit is given from this reason). The values of quantum yield of isomerization are in general agreement with the relative quantum yield discussed above. The Φ_{iso}^T values are characterized as follows: (1) The value for all the isomers of C15 aldehyde, ≥ 0.5 , indicates very efficient mutual isomerization. (2) The values

for the 7-cis and 9-cis isomers of C17 aldehyde (≥ 0.7) are much higher than that for the all-trans isomer (0.1), a fact which indicates efficient cis \rightarrow trans one-way isomerization. (3) The values for the 7-cis, 9-cis, and 11-cis isomers of C20 aldehyde (≥ 0.8) are much higher than the value for the all-trans isomer (0.1), indicating very efficient cis \rightarrow trans one-way isomerization. The value for the 13-cis isomer (0.2) indicates that $cis \rightarrow trans$ isomerization is less efficient. (4) The values for the 7-cis (1.0), 9-cis (0.9), 11-cis (0.7), and 13-cis (0.5) isomers of C22 aldehyde are much higher than the value for the all-trans isomer (0.1), indicating very efficient cis \rightarrow trans one-way isomerization. (5) The least stable isomer is 9-cis for C15 and C17 aldehydes, 11-cis for C20 aldehyde, and 7-cis for C22 aldehyde. The central-bent isomer is the least stable for C15, C17, and C20 aldehydes and an unmethylated-cis isomer is the least stable for C20 and C22 aldehydes.

Preliminary experiments on the concentration dependence of the $\Phi_{\rm iso}^{\rm T}$ value showed that those isomers of C15, C17, C20, and C22 aldehydes showing the $\Phi_{\rm iso}^{\rm T}$ value above 0.7 at the concen-



Figure 5. Dependence of the quantum yield of triplet-sensitized isomerization on concentration for 11-cis-C20 aldehyde.

tration of 1×10^{-4} M give rise to the Φ_{iso}^{T} value exceeding 1.0 when the concentration is increased. Figure 5 shows a typical example, i.e., the case of the 11-cis isomer of C20 aldehyde. When the concentration was increased up to 4.8×10^{-3} M, the value of Φ_{iso}^{T} increased as high as 5.5. The fact indicates that the 'all-trans' triplet species is very stable so that it functions as an additional sensitizer to isomerize the 11-cis isomer. In other words, the following chain reaction is expected to take place

$${}^{3}S^{*} + cis \rightarrow S + {}^{3}cis^{*}$$

 ${}^{3}cis^{*} \rightarrow {}^{3}trans^{*}$
 $trans^{*} + cis \rightarrow trans + {}^{3}cis^{*}$

3

where ³S*, ³cis*, and ³trans* indicate the sensitizer, the 11-cis isomer, and the all-trans isomer all in the T_1 states. (1) Efficient one-way isomerization from cis to trans in the T_1 manifold, (2) a sufficiently long lifetime of the 'all-trans' triplet, and (3) a small difference in the triplet energies between the cis and trans isomers should make the above chain reaction possible.

Isomerization by Direct Photoexcitation. We examined isomerization by direct photoexcitation for the following reasons: (1) Since triplet species probed by transient Raman spectroscopy were produced by direct photoexcitation, it provides a basis for the interpretation of the Raman results. (2) Since isomerization by direct photoexcitation can take place via both the singlet and triplet states, comparison of it with the above triplet-sensitized isomerization may help to characterize isomerization via the triplet state. (3) Since direct photoexcitation and subsequent intersystem crossing can supply a much larger amount of triplet energy than the present sensitizers (the difference in the triplet energies between the sensitizer and each aldehyde was less than 50 kJ·mol⁻¹), the photostationary state compositions and the pathways of direct photoexcitation can be different from those of sensitized isomerization.

Figure 6 compares the photostationary state compositions for the triplet-sensitized isomerization (S) and for the direct photoexcitation (D). (The compositions after long exposure starting from different isomers shown in Figures 4 and 7 were averaged.) In each aldehyde, the stationary-state composition for direct photoexcitation is similar to that for sensitized excitation. Since the stationary-state composition is a reflection of the balance of the quantum yield of isomerization starting from each isomer in the mixture, the result indicates that the relative quantum yields of isomerization are similar in both cases. The above observation suggests (1) that isomerization by direct photoexcitation mainly takes place via the triplet state, and (2) that the triplet isomerization mainly takes place along the relaxed T₁ potential surface and does not depend on the excess triplet energy supplied. One distinct difference between the sensitized and direct photoisomerization is concerned with the relative amount of the all-trans isomers in the photostationary state; the all-trans configuration (cis configurations) tends to be more (less) stabilized in the T_1 state. This result is consistent with the idea of the triplet-excited region described above, because the extended all-trans configuration is advantageous over the cis configurations to accommodate it.

Figure 7 compares an early stage of direct photoisomerization for (a) C15, (b) C17, (c) C20, and (d) C22 aldehydes, starting from the (1) all-trans, (2) 7-cis, (3) 9-cis, (4) 11-cis, and (5) 13-cis



Figure 6. Stationary-state isomeric composition (%) for (a) C15, (b) C17, (c) C20, and (d) C22 aldehydes for triplet-sensitized (S) and direct (D) photoisomerization; all-trans (\bullet), 7-cis (\circ), 9-cis (\triangle), 7,9-di-cis (\diamond), and 13-cis (\Box) isomers. Compositions after long exposure starting from different cis-trans isomers are averaged.

isomers. Comparison of Figures 4 and 7 shows that isomerization pathways for direct excitation are similar to those for sensitized excitation. Distinct differences between the direct and sensitized photoisomerization are as follows.

In the case of direct photoexcitation, the quantum yields of isomerization for isomeric C15 aldehyde are much lower than those for isomeric C17, C20, and C22 aldehydes. The result is consistent with the fact that the triplet species of each starting isomer of C15 aldehyde was detected by transient Raman spectroscopy. Since the quantum yield of intersystem crossing³ as well as the quantum yield of triplet-sensitized isomerization (Table II) of C15 aldehyde are in similar order of magnitudes to those of C17-C22 aldehydes, the above difference may be ascribed to the relation between the S_1 potential surface and the T_1 potential surface (the geometries of the potential minima and the barrier heights), and possibly to the process of intersystem crossing.

The quantum yields of isomerization of the 11-cis isomers of C20 and C22 aldehydes relative to those of other isomers are found to be different between direct and sensitized photoisomerization. As Figure 7 shows, the relative quantum yields for direct excitation are in the order 7-cis > 9-cis > 13-cis \approx 11-cis \gg all-trans for both C20 and C22 aldehydes. On the other hand, those for sensitized excitation were in the order 11-cis > 7-cis \approx 9-cis \gg 13-cis \gg all-trans for C20 aldehyde, and 7-cis > 9-cis > 11-cis > 13-cis \gg all-trans for C22 aldehyde (see Table II). The results suggest that the 11-cis configuration is greatly destabilized in the T_1 state. This observation is also consistent with the idea of the triplet-excited region; the central-bent 11-cis configuration should be the least advantageous in accommodating the triplet-excited region.

Discussion

The T_1 Potentials with Minima at the Cis and Trans Positions; the Relative Energies of the Minima Dependent on the Chain Length. The T_1 potential curves around the C==C bonds (starting from the all-trans configuration) of ethylene, butadiene, hexatriene, octatetraene, and higher polyenes have been calculated by various investigators.³⁴⁻³⁹ The degree of approximation has been different from one calculation to another, and there are some discrepancies among the results. However, the main conclusions are in agreement: (1) In ethylene, perpendicularly (90°) twisted conformation is stable. (2) In butadiene, the conformation of one twisted-one planar is more stable than that of both planar or that of both twisted. (3) In hexatriene, the conformation of one twisted around the central double bond is preferred to that of all planar or to that of one twisted around a terminal double bond. (4) In

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Figure 7. Direct photoisomerization of (a) C15, (b) C17, (c) C20, and (d) C22 aldehydes, starting from the (1) all-trans (\bullet), (2) 7-cis (\circ), (3) 9-cis (Δ), (4) 11-cis (\star), and (5) 13-cis (\Box) isomers. \diamond indicates the 7,9-di-cis isomer. Changes in the isomeric compositions (%) caused by irradiation of the 337-nm pulses are shown together with the compositions after 5000 pulses of exposure (photostationary state). Amounts less than 1% are not shown.

lower polyenes, peripheral double bonds are resistant to twisting. The conformation of one twisted around the innermost double bond is preferred to the all planar one; the energy difference between them decreases when the length of the polyene chain is increased.

The dependence on the chain length of the relative stability between the planar conformation and the central-twisted conformation of higher polyenes has been predicted differently. Hoffmann³⁵ predicted that the planar configuration is more stable in the case of polyenes higher than octatetraene, while Baird and West³⁶ predicted that the planar configuration is more stable for a polyene as high as 11 conjugated double bonds long (a model for β -carotene). Most recently, Aoyagi et al.³⁹ predicted that the planar conformation is almost as stable as the one-twisted conformation even for butadiene. No theoretical calculations concerning the cis configurations are available, and the planar conformation always meant the planar all-trans configuration.

All the present experimental results concerning C15-C22 aldehydes (four to seven conjugated double bonds long) indicated the presence of both cis and trans "planar" configurations. In other words, the results support the idea of a 2-fold T_1 potential around each 'C=C' bond with minima at cis and trans positions: Transient Raman spectroscopy of isomeric C15 aldehyde has provided evidence for the planar cis and trans configurations. Transient Raman spectroscopy of the all-trans isomers of C17, C20, and C22 aldehydes showed that they are in the planar 'all-trans' configuration in the T_1 state. The 'C=C' and 'C-C' stretching frequencies indicated an elongated 'C=C' bond and an ordinary 'C-C' bond in the T_1 state; however, no indication of a perpendicularly twisted carbon-carbon bond having "a single and a half" bond character has been found.

Transient Raman spectroscopy of the cis isomers of C17, C20, and C22 aldehydes has shown very fact cis \rightarrow trans isomerization; the Raman spectra of triplet species generated from the 7-cis and 9-cis isomers of C17 aldehyde, the 7-cis, 9-cis, and 11-cis isomers of C20 aldehyde, or the 7-cis and 11-cis isomers of C22 aldehyde agreed with the Raman spectrum of the triplet species generated from the all-trans isomer (all-trans triplet) of each aldehyde. Those cis triplet species were considered to be too short-lived to be detected by the present nanosecond transient Raman spectroscopy; the '13-cis' triplet of C20 aldehyde,⁷ and the '9-cis' and '13-cis' triplets of C22 aldehyde¹⁰ were long-lived enough to be detected. The above interpretation has been supported by picosecond transient absorption spectroscopy;^{8,9,11} actually, 'cis' to 'trans' isomerization in the T1 manifold has been detected for each 'cis' triplet.

All the above resonance Raman results indicate a T_1 potential surface with minima at various cis positions and with a minimum at the all-trans position, the relative depth of which is dependent of the chain length. The results showed that the cis and trans potential minima are comparable in the case of C15 aldehyde but that the minimum at the all-trans position is by far the deepest in the case of C17, C20, and C22 aldehydes.

Triplet-sensitized isomerization has provided additional evidence for the above view of the T_1 potential surface. The quantum yield of triplet isomerization showed definitely (1) mutual isomerization among the 'cis' and 'trans' configurations for C15 aldehyde, and (2) one way 'cis' \rightarrow 'trans' isomerization for C17, C20, and C22 aldehydes. The mutual isomerization for C15 aldehyde supports the idea of the T_1 potential having cis and trans minima with comparable energies. The one-way isomerization for C17, C20, and C22 aldehydes is a strong support for the 2-fold T_1 potential with shallow minima at 'cis' positions and a deep minimum at the all-trans position.

It is difficult to explain the one-way isomerization in terms of a T₁ potential having an additional minimum at the perpendicular position, which is expected to give rise to a mixture of the cis and trans isomers. In particular, the quantum yield of isomerization exceeding 1 observed for some cis isomers of the C17, C20, and C22 aldehydes at higher concentrations (indicating a chain reaction including energy transfer from the 'all-trans' triplet to a cis isomer) provides conclusive evidence for the above 2-fold potential. Here, it is crucial that only the 'all-trans' triplet is produced from the 'cis' triplet adiabatically and that it is long-lived enough to facilitate efficient energy transfer. (It is to be remembered that the S_0 potential has a maximum at the perpendicular position, which should cause very efficient relaxation from the T_1 state if there were a T_1 potential minimum at this position.)

A unique idea proposed in the present investigation is that of the triplet-excited region detected by transient Raman spectroscopy. It seems to determine the relative energies of the cis and trans potential minima and to function as a driving force of isomerization in the T_1 manifold. It is supposed to have a span of about six conjugated double bonds long. It can be accommodated by the all-trans isomers of C17, C20, and C22 aldehydes; extremely stable 'all-trans' triplets are thus explained. It explains also unstable 'cis' triplets, in particular, the extremely unstable '11-cis' (central-bent) triplets of C20 and C22 aldehydes; the central-bent isomers do not have an extended part long enough to accommodate it. It can be barely accommodated by the '13-cis' triplet of C20 aldehyde and by the '9-cis' and '13-cis' triplets of C22 aldehyde having an extended all-trans part of five conjugated double bonds long; therefore, their triplet species show considerable stability. In the case of C15 aldehyde, it cannot be accommodated by any isomer; all the triplet species including 'all-trans', '7-cis', and '9-cis' are unstable. Thus, all the present observations can be explained nicely in terms of the triplet-excited region.

The present results have shown that the relative energies among the potential minima are dependent on the chain length. It is tempting to relate the present results to the natural selection by rhodopsin and bacteriorhodopsin of the particular configurations and the particular chain length of retinal as the chromophore. It is interesting to note (1) the most efficient one-way isomerization from 11-cis to all-trans of C20 aldehyde has been selected by rhodopsin to trigger a series of reactions and (2) a set of stable configurations, i.e., the all-trans and 13-cis configurations of C20 aldehyde has been selected by bacteriorhodopsin to carry out a cyclic transformation. However, in order to establish the idea, the same line of experiments should be extended to the unprotonated and protonated Schiff bases of isomeric C15-C22 aldehydes. It is also necessary to prove that the photoisomerization

in rhodopsin and bacteriorhodopsin takes place via the T_1 state.

Comparison with the Results of Other Investigations. Finally, we compare the present results of retinal homologues with those of related compounds by other investigators from the viewpoint of the T_1 potential around a C=C bond: Dependence of triplet-sensitized isomerization of retinal homologues on the length of the polyene chain was first studied by Ramamurthy and Liu,⁴⁰ and it was shown that the isomerization properties of dienes and trienes were completely different from those of the higher members of the series. The difference was ascribed to different structures in the T_1 state, i.e., perpendicular ones in dienes and trienes, and planar ones in higher polyenes. Their proposal of a 2-fold T₁ potential with minima at the cis and trans positions for higher polyenes is in good agreement with our present proposal; they classified C15 aldehyde (four conjugated double bonds) into "a higher polyene". Very recently, Liu and co-workers have found independently the concentration effect of photoisomerization of 7-cis-C20 aldehyde (communicated by one of the referees), which is in agreement with the present observation.

The T₁ potential of stilbene with a minimum at the perpendicular position has been established by isomerization experiments using sensitizers with different triplet energies.^{41,42} On the other hand, a 2-fold T_1 potential with a shallow minimum at the cis position and with a deep minimum at the trans position also has been established by Tokumaru, Arai, and co-workers⁴³ for some stilbene derivatives with a large aromatic group on one side, e.g., 1-anthryl-3,3-dimethyl-1-butene, based on evidence including the analysis of triplet-sensitized isomerization with sensitizers having different triplet energies, the determination of quantum yields at various concentrations, and transient absorption and transient Raman spectroscopies. (1) One-way isomerization from cis to trans, (2) the quantum yield of sensitized isomerization exceeding 1 at higher concentrations, and (3) detection of only the 'trans' triplet species by transient Raman spectroscopy reported closely parallel our present observations. Conjugated double bonds in the present aldehydes may have the same function as the aromatic group in the above stilbene derivatives in lowering the energy of the 'trans' triplet.43

The T_1 potential of 1,3,5-hexatriene has been studied by Wilbrandt and co-workers44 based on transient Raman data and their theoretical interpretation. They explained the Raman data in terms of 'trans' and 'cis' triplets, although they were careful enough not to exclude the possibility of the presence of the 'perpendicular' triplet. Their work clearly shows a strategy to be used in the interpretation of the transient Raman data.

The T_1 potential of C20 aldehyde also has been studied by Wilbrandt and co-workers by means of a combination of triplet-sensitized isomerization27,45 and transient Raman spectroscopy.⁴⁶ Their values of quantum yields of isomerization at 2×10^{-4} M^{45} i.e., 1.0 ± 0.2 for 11-cis and 0.15 ± 0.05 for all-trans, are in rough agreement with our values at 1×10^{-4} M, i.e., 0.9 for 11-cis and 0.1 for all-trans. They also showed that the composition of the photostationary state mixture does (does not) depend on the triplet energy of the sensitizer when it is below (above) the triplet energy of 'all-trans'. They interpreted the triplet Raman spectra as a mixture of triplet species, which is contradictory to our interpretation. We feel that our picosecond transient ab-

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sorption studies^{8,9,11} have provided conclusive evidence for our interpretation. We believe picosecond transient Raman spectroscopy and femtosecond transient absorption spectroscopy of isomeric C20 aldehyde will resolve the contradiction in the near future.

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Absolute Raman Cross Sections for Cyclohexane, Acetonitrile, and Water in the **Far-Ultraviolet Region**

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Absolute Raman cross sections with excitation at wavelengths between 266 and 200 nm have been determined for the CH and CN stretching modes of acetonitrile, the symmetric OH stretch of water, and the CH stretches of cyclohexane. The measurements have been performed both directly, using an integrating cavity method, and indirectly, by reference to methane gas as an external standard. The two methods agree to within 35% or better in all cases. The cross sections are fit to Albrecht A-term frequency dependences to permit interpolation and modest extrapolation from the measured points. These solvent Raman bands can now be employed as internal standards for the determination of absolute resonance Raman cross sections of solutes in the far-UV spectral region.

Introduction

It has long been known that resonance Raman intensities contain information about the structure and dynamics of the resonant molecular excited state. Early resonance Raman intensity studies focused on either Raman spectra (the relative intensities of different vibrations at a given excitation frequency) or excitation profiles (the dependence of the Raman intensity on excitation frequency).¹ Excitation profiles were usually measured relative to a solvent Raman band or an added nonresonant species such as sulfate or cacodylate as an internal standard. The frequency dependence of the internal standard Raman cross section was often assumed to follow either a pure ν^4 dependence (totally nonresonant scattering) or a single-state Albrecht A-term preresonance with the lowest allowed electronic state. While these were questionable assumptions, they often did not lead to serious uncertainties in the excitation profile band shapes, particularly when the profiles covered a rather narrow range of frequencies in the visible region of the spectrum. More recently, however, there has been increasing interest in the measurement of excitation profiles in the far-UV region,²⁻⁶ where the internal standard cross sections are expected to be more strongly frequency dependent, as well as in the use of absolute UV resonance Raman cross sections to probe solvation dynamics.⁷ For these purposes it is essential to have direct measurements of the internal standard absolute cross section as a function of excitation frequency in the far-ultraviolet region.

Recently several groups have addressed this need through different experimental methods. Dudik et al.8 developed a method based on ratioing the Raman intensity to the laser scattering from a suspension of BaSO₄ powder which enabled them to measure the frequency dependence of the differential Raman cross section for several substances in aqueous solution well into the UV region. Their absolute cross sections were scaled to a single primary measurement on benzene in the visible.⁹ Bischel and Black¹⁰ employed a very direct method, based essentially on measuring the solid angle of collection and the efficiency of their collection optics, to measure absolute differential cross sections for several gases down to 193 nm. The excellent agreement of their results with high-quality calculations on H₂ provided confidence in the accuracy of their measurements. Trulson and Mathies11 developed

an integrating cavity technique that allowed them to measure directly the total Raman cross sections for cyclohexane, benzene, and aqueous cacodylate from 647 to 240 nm. Schomacker et al.¹² also employed a direct method, based on first measuring the total Rayleigh plus Raman cross section and then ratioing the Raman to the Rayleigh, to determine absolute cross sections for benzene in the visible to near-UV region. Finally, very recently Fodor et al.⁶ applied the relative method of ref 8 to obtain cross sections for aqueous sulfate and for water down to 193 nm.

At the time we began this work, no direct measurements on liquids had been reported at wavelengths below 240 nm, and the relative measurements of Dudik et al. extended only to 220 nm. We set out to provide ourselves and other workers with reliable solution-phase standards down to 200 nm by applying the integrating cavity method of Trulson and Mathies¹¹ to cyclohexane, acetonitrile, and water, with comparison to methane gas as an external standard¹⁰ used to verify our results. The data are fit to a single-state A-term frequency dependence, providing a convenient fitting function with which to interpolate and, if necessary, slightly extrapolate to wavelengths other than those used in this study. It is now comparatively straightforward to employ these

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