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Sensitized Photoisomerization of *all-trans-* and 11-*cis*-Retinal

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Abstract: The photoisomerization of *all-trans*-retinal (all-trans) and 11-*cis*-retinal (11-cis) sensitized by a range of sensitizers (porphyrins, Zn-porphyrins, naphthacene and a Zn-phthalocyanine) with varying triplet energies above and below the vertical triplet energy of *all-trans*-retinal (E_T = 149 kJ/mol) has been investigated by continuous illumination and HPLC analysis of the products. The composition of the photostationary states, the relative isomerization quantum yields of all-trans and 11-cis, and the primary product ratios are reported. One photon-one bond isomerizations are dominant. With Zn-TPP as sensitizer it is shown that 11-cis and possibly all-trans undergoes one photon-two bond isomerizations as well. The quantum yields of photoisomerization of 11-cis sensitized by biphenyl (E_T = 275 kJ/mol) and anthracene (E_T = 178 kJ/mol) were found to be identical. Absolute measurements allowed evaluation of the overall triplet isomerization quantum yield of 11-cis, $\Phi^T_{iso}(11\text{-cis}\rightarrow) = 1.0 \pm 0.2$, from which the corresponding quantity for all-trans, $\Phi^T_{iso}(\text{trans}\rightarrow) = 0.15 \pm 0.05$, was obtained. The overall photoisomerization quantum yield of 11-cis with direct excitation at 254 nm was determined as $\Phi^d_{iso}(11\text{-cis}\rightarrow) = 0.42 \pm 0.05$ assuming all-trans and 13-cis to be the primary products. Quenching rate constants of several of the sensitizer triplet states by retinal were measured by laser flash photolysis. Possible mechanisms that could account for the experimental results are discussed, and it is concluded that the photoisomerizations most likely involve the retinal triplet states as intermediates. Within this model the observed sensitizer triplet energy dependence of the primary product ratios suggests that the triplet states of the different retinal isomers are different mixtures of triplet excited species, and that the composition of these mixtures depends on the starting isomer as well as on the sensitizer triplet energy for energies below the vertical triplet energy of *all-trans*-retinal. In the light of a review of the existing literature on the direct and the sensitized photoisomerization of retinals these conclusions suggest substantial corrections to the accepted picture of retinal photochemistry.

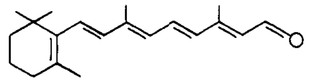
Retinals have important biological functions as chromophores in rhodopsin and bacteriorhodopsin. Since the early recognition that geometric isomerization of the retinal moiety occurs upon light absorption by rhodopsin,[1] the photochemistry and photophysics of retinals have received much attention and several reviews have appeared.[2-5] In spite of these efforts several points, particularly in relation to photoisomerization, remain controversial.

Intersystem crossing quantum yields of *all-trans*-retinal (all-trans) and selected cis isomers in polar[6-8] and nonpolar solvents[6,7,9-15] have been reported. For all isomers the values are considerably lower in polar (0.1-0.2) than in nonpolar solvents (0.4-0.7) with excitation around 350 nm. This effect has been discussed in terms of a solvent-dependent shifting of the $n\pi^*$- and $\pi\pi^*$-type singlet excited states, but with the lowest triplet state being of $\pi\pi^*$-type in all solvents.[4b,8,15] On the other hand, these current state diagrams of the retinal excited states[4b] predict the intrinsic photochemical properties of the retinal triplet states to be largely independent of solvent. Finally, the intersystem crossing yields are dependent on the excitation wavelength.[8,12,13]

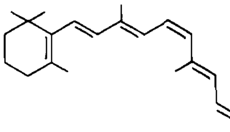
The triplet states formed from the various isomers all have similar decay rate constants[8,11] and they are easily detected through their strong absorptions around 460 nm. The possibility that the triplet states from different geometric isomers may be identical as judged from the respective triplet-triplet absorption spectra has been a matter of controversy.[8,10,11,14,16-18a,b] Recently, resonance Raman spectroscopy also has been applied to studies of the triplet states of retinal isomers.[17,19,20] The triplet energy of all-trans has been estimated to be 159[21] and <140 kJ/mol[22] by energy-transfer experiments while S_0-T_1 absorption measurements give a vertical triplet energy of 149 kJ/mol.[23]

The isomerization of retinals can be induced thermally or photochemically. Iodine-catalyzed thermal isomerization yields a mixture containing ca. 60% all-trans.[24-26] Analysis by HPLC has allowed accurate determination of the free energy differences between the various isomers.[25,26] Since the first quantitative study of retinal photoisomerization by direct excitation[27] several investigations of direct and triplet-sensitized photoisomerization have appeared. Raubach and Guzzo[28] reported the first study of the triplet-sensitized isomerization of all-trans, 13-cis, and 11-cis

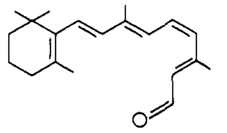
Chart I



All-trans-retinal



12-S-trans, 11-cis-retinal



12-S-cis, 11-cis-retinal

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isomers. Using biacetyl as sensitizer they obtained $\Phi^{T}_{\mathrm{iso}}(\mathrm{trans}\rightarrow) = 0.17$ and $\Phi^{T}_{\mathrm{iso}}(11\text{-cis}\rightarrow) = 0.75$. $\Phi^{T}_{\mathrm{iso}}(\mathrm{trans}\rightarrow)$ and $\Phi^{T}_{\mathrm{iso}}(11\text{-cis}\rightarrow)$ are the total quantum yields of isomerization from the triplet states. The values were discussed in terms of eq 1

$$\Phi^{d}_{\mathrm{iso}}(i\rightarrow) = \Phi^{S}_{\mathrm{iso}}(i\rightarrow) + \Phi_{T}(i)\Phi^{T}_{\mathrm{iso}}(i\rightarrow) \qquad (1)$$

where

$$\Phi^{d}_{\mathrm{iso}}(i\rightarrow) = \sum_{j\neq i}\Phi^{d}_{\mathrm{iso}}(i\rightarrow j)$$

and

$$\Phi^{S}_{\mathrm{iso}}(i\rightarrow) = \sum_{j\neq i}(i\rightarrow j)$$

and

$$\Phi^{T}_{\mathrm{iso}}(i\rightarrow) = \sum_{j\neq i}(i\rightarrow j)$$

are the overall quantum yield of isomerization on direct excitation and the total quantum efficiencies of isomerization from the singlet and triplet states, respectively. $\Phi_{T}(i)$ is the intersystem crossing yield of the retinal isomer in question. Equation 1 as such is general at any wavelength, but the use of eq 1 is limited by the fact that the values of $\Phi^{T}_{\mathrm{iso}}(i\rightarrow)$ are only obtainable from a sensitized experiment.

Rosenfeld et al.[10] remeasured Φ_{T}, Φ^{d}_{iso}, and Φ^{T}_{iso} for 11-cis and all-trans. They found the individual values of Φ^{T}_{iso} to be considerably lower than those given by Raubach and Guzzo, and also the ratio $\Phi^{T}_{\mathrm{iso}}(11\text{-cis}\rightarrow)/\Phi^{T}_{\mathrm{iso}}(\mathrm{trans}\rightarrow)$ was changed significantly from ca. 4.4 to >75. Rosenfeld et al.[10] also reported that the direct and triplet-mediated photoisomerization of 11-cis is insensitive toward the presence of oxygen from which they concluded that a thermalized triplet cannot be involved in the isomerization process. Waddell et al.[29] reinvestigated the photoisomerization of retinals using for the first time HPLC as an analytical tool. Concerning all-trans and 11-cis this work essentially confirmed the results obtained by Rosenfeld et al.[10] Furthermore, Waddell et al.[29] reported $\Phi^{T}_{\mathrm{iso}}(13\text{-cis}\rightarrow) = 0.15$ and $\Phi^{T}_{\mathrm{iso}}(9\text{-cis}\rightarrow) = 0.20$, i.e. the triplet states of the mono-cis isomers had similar isomerization efficiencies. Sensitized photoisomerization of retinal and lower homologues has also been reported by Ramamurthy and Liu.[30a] Unfortunately, the NMR analysis used in this work only allowed distinction between 7-*cis*- and 7-*trans*-retinals. The content of 7-cis was found to be negligible.

The direct photoisomerization of all-trans has been reinvestigated several times emphasizing aspects such as wavelength and solvent dependence,[31-34] effect of deuterium substitution,[35] and temperature dependence.[36] The regioselectivity observed in the photoisomerization of retinal and retinal analogues has recently been discussed in terms of medium-induced barriers of rotation.[37] Apart from giving useful information on the mechanistic details of the photoisomerization process these studies have, however, also contributed further to the confusion that exists about many quantitative aspects of retinal photochemistry. Pertinent examples are the various values for Φ^{d}_{iso} and the ratios of primary products 13-cis/9-cis in the photolysis of all-trans. Since the first report of $\Phi^{d}_{\mathrm{iso}} = 0.06 - 0.2$ for all-trans,[27] values of 0.04,[29] 0.08,[31] and 0.12[36] have been reported for the same reaction under similar conditions. The ratio, $\Phi^{d}_{\mathrm{iso}}(\mathrm{trans}\rightarrow 13\text{-cis})/\Phi^{d}_{\mathrm{iso}}(\mathrm{trans}\rightarrow 9\text{-cis})$ of the primary products formed from all-trans has been given as 4.0,[31] 3.6,[32] 7,[35] and 6.7[36] for photolysis at 350 nm in hexane or 3-methylpentane.

Also the photoisomerization of 11-cis has been reinvestigated by continuous as well as pulsed excitation methods. Menger and Kliger[38] studied the photoisomerization of 11-cis in methylcyclohexane and methanol by laser flash photolysis at 337 nm (N_2-laser). From the shape of the kinetic traces they concluded that a slow isomerization from the triplet dominates in methylcyclohexane, whereas a fast isomerization from the singlet state occurs in methanol. Moreover, they pointed out that the lack of oxygen effect cannot be used as argument for excluding the possible involvement of a thermalized triplet state. The latter argument has its origins in the extensive work on stilbene photoisomerization[39] and it has later been substantiated by experiment.[40] With respect to the singlet and triplet contributions in the direct photoisomerization of 11-cis it has been argued that the slow grow-in of absorbance noticed by Menger and Kliger[38] can equally well be interpreted as ground-state recovery and that singlet contributions cannot be excluded on this basis alone.[8,14] Rosenfeld et al.[41] studied the sensitized photoisomerization of 11-cis using various sensitizers with triplet energies ranging from 289 to 176 kJ/mol. Surprisingly, they found that Φ^{T}_{iso} for 11-cis had a strong dependence on the sensitizer triplet energy. The values of Φ^{T}_{iso} varied from ca. 0.15 to 1.0 on going from the high to the low energy sensitizers. The photoisomerization of 11-cis in hexane induced by pulsed laser excitation at 347 nm was studied thoroughly by Veyret et al.[14] Apart from the contributions mentioned above, this work confirmed that 11-cis and all-trans have different triplet–triplet absorption spectra. From an analysis of the difference absorbances observed at various wavelengths immediately after the pump pulse the authors concluded that isomerization of 11-cis takes place from an internally excited first triplet state. This conclusion, which is in agreement with Rosenfeld et al.,[10] is doubtful as the underlying data analysis contains a serious, but hitherto unnoticed, error. From their apparent triplet–triplet difference absorption spectra of 11-cis and all-trans

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Veyret et al.[14] constructed the absolute triplet–triplet absorption spectra making two important assumptions: (i) isomerization does not occur from a relaxed triplet state as indicated by the lack of oxygen effect, and (ii) the amount of all-trans produced after decay of all excited states is equal to the amount of triplet all-trans present at the end of the pulse. Arguments against the first assumption have been mentioned above. The second assumption was explicitly used to neglect the presence of ground-state all-trans immediately after the pulse. The extinction coefficients obtained from this treatment of the experimental data were then used to analyze the absorbance versus pulse energy data mentioned above and, not surprisingly, this analysis showed that no ground-state all-trans was produced during the pump pulse. Hence, Veyret et al.[14] reached a conclusion which in fact was inherent in their analysis of the experimental data. Finally, in this overview of retinal photochemistry it also should be mentioned that the photochemistry of retinal analogues with other patterns of methyl substitution,[42-46] of lower and higher homologues, and of retinal complexes[50,51] has been reported.

Lately, we have been interested in the triplet-state photochemistry of biological polyenes and simpler model compounds. We have shown that *all-trans-β*-carotene undergoes trans–cis isomerization when sensitized by chlorophyll *a* or naphthalene.[57a] Torsional distortion was also discussed on the basis of time-resolved resonance Raman spectroscopy for carotenoids,[52-54] retinals,[17,14] and certain methyl-substituted hexatrienes.[55,56]

In the present paper[57b] we report on similar experiments with *all-trans-* and 11-*cis*-retinal though with other sensitizers. We have attempted to resolve the apparent state of confusion which exists with regard to the photochemistry of retinals by addressing the following questions: (i) Can all-trans isomerize from the triplet state? (ii) What are the quantum yields and product distributions of the triplet isomerizations? (iii) Do the retinals undergo one photon–two bond isomerizations from the triplet state? (iv) What is the role of the sensitizer triplet energy on Φ^{T}_{iso}(11-cis→)?

In designing an experiment involving sensitized isomerization of retinal it is important to excite the sensitizer selectively. In particular, selective excitation of the sensitizer is important if reliable photostationary states are wanted. This means that the sensitizers should have absorptions in the visible as far away from the absorption of retinal as possible. The sensitizer should also have a high efficiency of triplet formation, and preferably a long triplet lifetime in order to mediate efficient formation of retinal triplet states at relatively low concentrations of retinal. Low concentrations of retinal minimize possible aggregation and interaction with the sensitizer singlet excited state. Finally, the sensitizer should not interfere with the analysis of the photoinduced isomeric mixture. When quantum yields are determined, partial direct excitation of the retinal substrate is less critical as corrections usually are possible in these cases. On the basis of these considerations the triplet states of the retinals were produced by sensitized photolysis by using various hydrocarbons, porphyrins, and phthalocyanins with triplet energies above and below that of retinal as sensitizers. The porphyrins and phtalocyanins are sensitizers that satisfy the mentioned requirements, whereas contributions from direct excitation cannot be avoided with the hydrocarbon sensitizers. Product analysis was performed by normal-phase HPLC.

Experimental Section

Chemicals. *all-trans*-Retinal (99.0–99.3%) was purchased from Sigma and used as received. In some experiments *all-trans*-retinal (>99.6%) from Roche A/S was used. 11-*cis*-Retinal (>99.5%) was kindly supplied by Dr. W. E. Scott, Hoffmann La Roche, NJ, and used as received. Samples of 13-*cis*- (99.7%) and 9-*cis*-retinal (99.7%) were supplied by Roche A/S. Zinc–octaethylporphin (Zn–OEP), octaethylporphin (H_2-OEP), zinc–tetraphenylporphin (Zn–TPP), and tetraphenylporphin (H_2-TPP) were obtained from Porphyrin Products and used as received. The sample of H_2OEP contained ca. 0.3% of the corresponding chlorin as estimated from the absorption spectra. The remaining sensitizers did not contain any detectable (absorption and HPLC) impurities. Zinc–mesoporphyrin IX–dimethyl ester (Zn-MP-DME) was prepared from mesoporphyrin-IX-dimethyl ester (H_2-MP-DME) (gift from Dr. T. With or purchased from Koch-Light) by using published procedures.[58] Zinc-tetra-*tert*-butylphtalocyanine (Zn-Pc-(t-Bu)$_4$) was kindly supplied by Dr. S. Gaspard. Naphthacene (Eastman Kodak) was recrystallized from benzene; anthracene (Merck scintillation) and biphenyl (BDH) were used as received. Benzene (Ferak p.a. or Merck, Uvasol), toluene (Merck, Uvasol), and cyclohexane (Ferak p.a. or Fluka für die Spektroskopie) were used as received. In particular, no precautions were taken to dry these solvents.

Illumination. Illuminations (except at 254 nm) were made with a 250-W projector lamp filtered through 25 mm of H_2O or with a Schott KL 1500 light source equipped with a Schott KG 1 heat filter and fiberoptic output. The light filtered by appropriate 3-mm colored glass edge filters was collimated onto the sample cells. Schott GG 475 (naphthacene), OG 530 (H_2-TPP, Zn-TPP, Zn-MP-DME, H_2-OEP, Zn-OEP), or OG 590 (Zn-Pc-(t-Bu)$_4$) glass filters (3 mm) were used as longwave pass and calibrated Schott NG filters were used as attenuation filters when necessary. In the experiments involving sensitization by Zn-TPP the light intensities with OG 530 filter were approximately 100 mW/cm^2 without neutral density filters in the beam. The diameter of the light beam was ca. 1.5 cm. The sample cells were either cylindrical homemade Pyrex cells with 1.5-cm diameter and 1.8-cm path length or cylindrical suprasil cells (Hellma) with 2.1-cm diameter and 2.0-cm path length. With the Pyrex cells the bulk solutions were deoxygenated by Ar-bubbling and the cells filled with the syringe technique.[59] Thereby one cell was prepared for each illumination dose. With the suprasil cells the samples were deoxygenated by Ar-bubbling directly in the cell and usually each sample was used for three illuminations, taking out 150 μL after each illumination. The latter technique was used for experiments involving naphthacene, Zn-OEP, and H_2-OEP.

For illumination at 254 nm a low-pressure Hg-arc (Pen Ray 11 SC-1) with a G 275 (Ultraviolet Products) filter was used. From the transmission of the filter and spectral distribution of the emitted light we estimate that 88 ± 2% of the output was in the 253.7-nm line. The sample was placed 12.7 cm from the lamp. The light intensity was measured with a Hilger-Schwarz thermopile (FT 16-769) which had a response of 22 mV/mW on the active area 0.9 × 0.05 cm. The sample cell for these experiments was a cylindrical suprasil cell with 1.5-cm diameter and 0.3-cm path length. Samples were deoxygenated by bubbling with Ar and the cell filled by using the syringe technique.[59] Under

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Table I. Absorption Data of Sensitizers[a]

	wavelength, nm [ϵ, 10^4 M^{-1} cm^{-1}]				
Zn-MP-DME (B)	405 [30.4]	534 [1.60]	570 [2.60]		
Zn-OEP (T)		533 [1.65]	570 [3.06]		
H_2-OEP (T)		500 [1.49]	532 [1.13]	570 [0.726]	624 [0.694]
Zn-TPP (B)	423 [53.6]	513 [0.306]	550 [2.28]	589 [0.360]	
Zn-TPP (T)		513 [0.286]	551 [2.21]	589 [0.296]	
H_2-TPP (B)	420 [47.4]	515 [2.02]	549 [0.834]	591 [0.570]	647 [0.390]
H_2-TPP (T)		515 [1.93]	549 [0.793]	592 [0.542]	648 [0.353]
naphthacene (T)	397 [0.229]	420 [0.432]	446 [0.823]	476 [0.915]	
Zn-Pc-(t-Bu)$_4$ (T)	348 [6.02]	612 [3.52]	649 [3.05]	679 [23.3]	

[a] Solvents: B = benzene and T = toluene. The Soret bands were not measured in all cases.

the experimental conditions the incident intensity on the cell was 62.2 μW cm^{-2}. The incident number of photons was calculated for each of the spectral lines between 253.7 and 404.7 nm by using the known relative spectral distribution. In calculating quantum yields four effects were taken into account: (i) direct excitation of 11-cis at 254 nm, (ii) direct excitation of 11-cis at $\lambda > 254$ nm, (iii) excitation of sensitizer (when present) at 254 nm followed by triplet energy transfer to 11-cis, and (iv) excitation of sensitizer (when present) at 254 nm followed by sensitizer fluorescence reabsorbed by 11-cis. In the presence of sensitizers the solutions absorbed 93.7% of the incident radiation at 254 nm over a path length of 3 mm, whereas the solution containing 11-cis only absorbed 43.1% at 254 nm. In the calculations the following data were used: $\Phi_f = 0.1$, $\Phi_T = 0.84$, $k_1 \leq 10^4$ s^{-1}, $k_{ET} = 3 \times 10^9$ M^{-1} s^{-1} for biphenyl and $\Phi_f = 0.27$, $\Phi_T = 0.71$, $k_1 \leq 10^4$ s^{-1}, $k_{ET} = 2.5 \times 10^9$ M^{-1} s^{-1} for anthracene.[41,60–62,87] Φ_f, Φ_T, k_1, and k_{ET} are fluorescence yield, triplet yield, triplet decay rate constant, and triplet energy transfer rate constant from the sensitizer to 11-*cis*-retinal, respectively.

Sample Analysis. Samples were analyzed for isomeric composition by normal-phase HPLC by using a system that consisted of a Waters Model 600 A pump, a Rheodyne 7125 injector, a 25 × 0.46 cm steel column packed with Nucleosil Si 50-5, and a Kontron 720 LC spectrometer equipped with a 8-μL flow cell. Analysis was performed at 360 nm, but representative samples were analyzed at 250 nm as well. The eluent (1 mL/min) was usually n-heptane containing 8–10% diethyl ether, but in some experiments 4% diethyl ether in n-heptane was used. The samples dissolved in benzene or toluene were injected (20 μL) without further sample preparation.

All samples were HPLC analyzed immediately after preparation and illumination. Usually each sample was analyzed at least twice with several hours between each analysis. Occasionally some samples were reanalyzed the next day. All samples illuminated in the presence of sensitizers were stable in the dark. The samples illuminated with unfiltered light (Schott KL 1500, $\lambda > 350$ nm) in the absence of sensitizers showed changes in the isomeric composition that occurred on a time scale of several hours in the dark. These changes will be discussed further in the text. Experiments were performed at ambient temperature (20–22 °C) and all preparations were made in nearly complete darkness.

Isomer compositions were calculated from the peak heights which were corrected for differences in retention time between different isomers and for differences in extinction coefficients at 360 nm. The latter values were determined from the absorption spectra of 9-cis, 11-cis, and 13-cis, measured in this work by stopped-flow HPLC on authentic samples, combined with ϵ_{max} values given by Hubbard and Wald.[63] For 9,13-dicis and 7-cis the relative extinctions at 360 nm were determined from spectra reported in the literature.[64,65] The relative extinction coefficients $\epsilon_{trans}/\epsilon_{cis}$ at 360 nm are the following: 7-cis, 1.014; 9-cis, 1.217; 11-cis, 1.738; 13-cis, 1.198; 9,13-dicis, 1.316. Under the conditions used for HPLC analysis of the retinals we observed that some of the porphyrins eluted as double peaks. This effect is due to splitting caused by the benzene or toluene in the injected volume. The effect of the injected solvent on the peak shape of the retinal peaks was negligible. Retinal isomers were identified from the relative retention times, from their absorption spectra recorded by stopped-flow HPLC of individual peaks, and from their absorbance ratios $\epsilon_{360}/\epsilon_{250}$. Also, the 9-cis, 11-cis, and 13-cis isomers were compared with authentic samples.

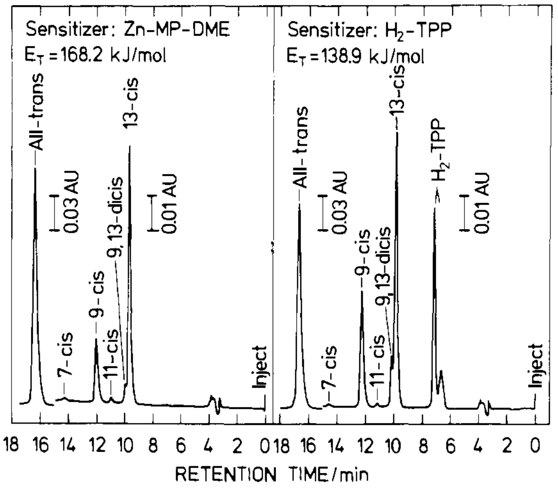

Figure 1. Chromatograms of photostationary states obtained with H_2-TPP and Zn-MP-DME as sensitizers. Concentration of sensitizer: 5×10^{-5} M. Concentration of retinal: 2×10^{-4} M. Solvent: Ar-saturated benzene. Illumination with $\lambda > 530$ nm. Analysis at 360 nm. Eluent: 10% diethyl ether in n-heptane, 1 mL/min.

Absorption spectra of solutions containing the sensitizers and sensitizers in the presence of retinal were recorded by using the Kontron 720 LC as a conventional spectrophotometer.

Laser Flash Photolysis. The excitation was performed with 530-nm-light pulses of 25-ns duration from a frequency -doubled Nd-doped glass laser (VD 230, CILAS, CGE) on an experimental setup described previously.[66,67]

Results

Photostationary States. The sensitizers used in this work all have relatively strong absorptions in the visible. Data concerning the optical absorptions are collected in Table I. Absorption spectra were also recorded in the presence of *all-trans*-retinal. For naphthacene we did not observe any changes in the absorption spectrum other than those ascribable to the weak absorption tail of retinal by addition of 2×10^{-4} M all-trans. For the remaining sensitizers no changes were observed up to 10^{-3} M all-trans.

Illumination of 2.0×10^{-4} M *all-trans*- or 11-*cis*-retinal in Ar-saturated benzene or toluene containing the sensitizer (5.0×10^{-5} M except for Zn-Pc-(t-Bu)$_4$ where the concentration was 4.4×10^{-6} M) with appropriately filtered visible light (see Experimental Section) results in isomerization of the retinal substrate, and after sufficient illumination a photostationary state is produced. The isomeric compositions of the retinal mixtures were analyzed by HPLC as exemplified in Figure 1 and the photostationary states obtained with the various sensitizers are tabulated in Table II along with the triplet energies of the sensitizers. In Figure 2 the variations of the photostationary states as a function of the sensitizer triplet energy are depicted.

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Table II. Composition of Photostationary States (%)[a]

sensitizer[b] E_T kJ/mol	substrate (2×10^{-4} M)	trans	13-cis	11-cis	9-cis	9,13-dicis	7-cis
Zn-MP-DME	all-trans	72.9	18.7	0.6	5.9	1.5	0.3
170.8	11-cis	72.6	18.9	0.8	6.2	1.5	nd
Zn-OEP 169.8	all-trans	72.9	19.3	0.5	5.7	1.5	0.2
H_2OEP[c] 155.8	all-trans	73.0	19.0	0.5	6.0	1.4	0.2
Zn-TPP	all-trans	71.7	19.9	0.5	6.1	1.7	nd
153.4	11-cis	71.2	19.8	0.8	6.1	1.7	0.3
H_2-TPP	all-trans	63.3	20.7	0.4	11.1	4.4	0.2
138.9	11-cis	63.4	20.5	0.9	11.0	4.3	nd
naphthacene[d] 122.5	all-trans	56.6	21.2	0.2	17.1	4.7	0.2
Zn-Pc-(*t*-Bu)$_4$[e] 109.0	all-trans	<58.6	19.3	0.1	17.3	>4.7	~0.2
direct[f]	all-trans (5×10^{-4} M)	27.0	54.5	6.3	6.8	5.2	<0.2
thermal[g]	all-trans (2.4×10^{-4} M)	61.8	23.2	0.1	10.9	4.0	

[a] All samples were Ar-saturated. Solvent: benzene or toluene. Absolute error limits on yields are ±0.2% as estimated from multiple analysis. Sensitizer concentrations and optical filters as given in text. In some cases the 7-cis region of the chromatograms were recorded at sensitivities too low for detecting 7-cis. This is indicated by nd. [b] Sensitizer triplet energies from Darwent et al.[68] [c] Triplet energy from Gouterman and Khalil.[69] [d] Triplet energy from Berlman.[70] [e] Triplet energy assumed equal to unsubstituted Zn-Pc. [f] Obtained with an unfiltered Schott KL 1500 lamp. Analysis after dark storage for 40 h (see text). Solvent: toluene. [g] Iodine catalyzed isomerization in the dark (ref 26). Solvent: *n*-heptane.

Essentially identical photostationary states were obtained with all-trans and 11-cis (Table II) and the total amount of retinal was conserved to within 1–2% during the approach to the photostationary states. No signs of isomers other than those listed in Table II were observed in the sensitized isomerization experiments. In particular, no signs of thermally unstable products were observed from the $\epsilon_{360}/\epsilon_{250}$ ratios or by analyzing the samples after several hours (see Experimental Section). Illumination of all-trans or 11-cis (2×10^{-4} M) in Ar-saturated benzene or toluene with light above 530 nm (OG 530 filter) but without added sensitizer did not induce any isomerization of the retinal within illumination times comparable to those necessary for obtaining photostationary states in the presence of sensitizers. Illumination of all-trans under similar conditions, but with light filtered through the GG 475 filter used with naphthacene induced some isomerization of the substrate. The rate of the direct isomerization without sensitizer under these conditions was approximately 8% of the total isomerization rate in the presence of naphthacene. As the inner filter effect reduces the direct contribution when naphthacene is present, we estimate that direct isomerization contributed less than 5% to the total observed isomerization rate in the naphthacene sensitization experiments.

The photostationary states were dependent upon the energy of the sensitizer below the vertical triplet energy of retinal (1.54 eV, 149 kJ/mol). As shown in Table II and Figure 2 the photostationary concentration of all-trans decreases, whereas the photostationary concentrations of 9-cis and 9,13-dicis increase with decreasing sensitizer triplet energy. The photostationary concentrations of 11-cis and 13-cis are apparently only slightly dependent on the sensitizer triplet energy.

In addition to the sensitized photoisomerization experiments we have also investigated the photostationary states obtained by direct irradiation of all-trans in Ar-saturated toluene with unfiltered light from the tungsten sources. These experiments were complicated by an apparent disappearance of ca. 30% of the total amount of retinal without any signs of unexpected new products except for a small peak appearing before 13-cis in the chromatogram ($k' = 2.05$ compared with $k' = 2.47$ for 13-cis where k' is the chromatographic capacity factor). Similar observations were made with Ar-saturated cyclohexane as solvent. Upon standing at room temperature in the dark, HPLC analysis at 360 nm showed that the peak appearing at the 13-cis retention time (13-cis peak) had increased while the other peaks were essentially unchanged. Hence, the missing material seemed to revert to 13-cis thermally. We studied this phenomenon in more detail by photolyzing 5×10^{-4} M all-trans in Ar-saturated toluene with unfiltered light from the Schott KL 1500 light source for 20 min. HPLC analysis at 360 and 250 nm (9% diethyl ether in *n*-heptane as eluent) immediately after photolysis and after storage in the dark at room temperature for ca. 40 h revealed the following: (i) Peaks corresponding to known retinal isomers accounted for 68.4% of the retinal immediately after photolysis but for 90.5% after 40 h. (ii) All peaks, except 13-cis and 9,13-dicis, had unchanged heights during storage when measured at 360 and 250 nm. (iii) The 13-cis peak increased by a factor 1.70 at 360 nm but was essentially unchanged at 250 nm. (iv) The 9,13-dicis peak in-

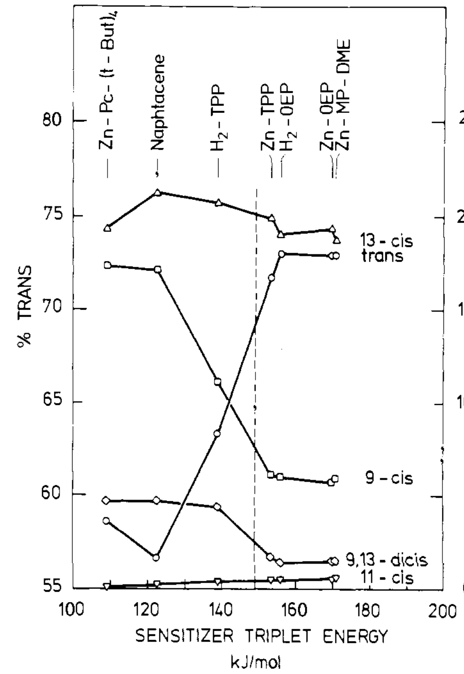

Figure 2. Composition of the photostationary states versus the sensitizer triplet energy. The vertical broken line indicates the vertical triplet energy of *all-trans*-retinal. All-trans: left scale. Cis isomers: right scale.

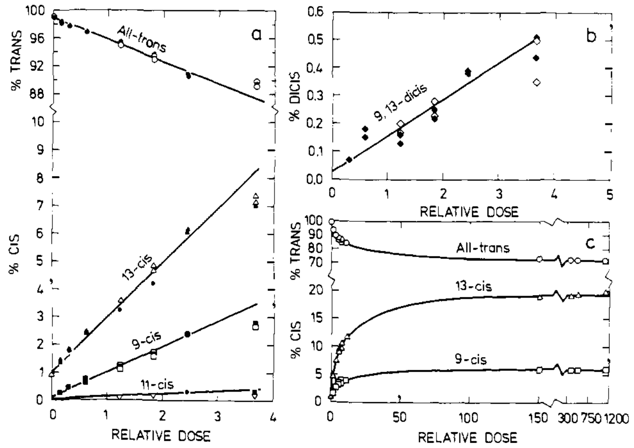

Figure 3. Distribution of retinal isomers versus total incident illumination dose in Zn-TPP-sensitized photoisomerization of all-trans. (a) Disappearance of all-trans and formation of major mono-cis products at the initial stage of photolysis. (b) Initial formation of 9,13-dicis. 9,13-dicis was not detected before illumination. (c) Attainment of a photostationary state upon prolonged illumination. Only all-trans, 13-cis, and 9-cis are shown for clarity. Total retinal: 2×10^{-4} M. Zn-TPP: 5×10^{-5} M. Solvent: Ar-saturated benzene. Illumination with a projector lamp through an OG 530 filter. The dose unit corresponds to 100 s with a neutral density filter of OD = 2. Filled and unfilled points correspond to two independent series of experiments.

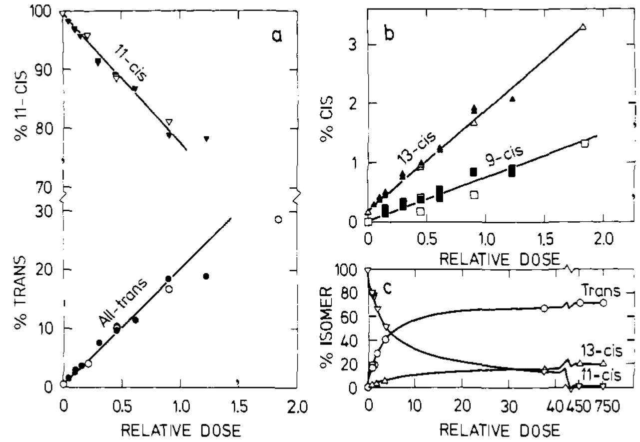

Figure 4. Distribution of retinal isomers versus total incident illumination dose in Zn-TPP-sensitized photoisomerizaiton of 11-cis. (a) Disappearance of 11-cis and formation of all-trans. (b) Initial formation of 9-cis and 13-cis. (c) Attainment of a photostationary state upon prolonged illumination. Only 11-cis, all-trans, and 13-cis are shown for clarity. Other conditions are as for Figure 3.

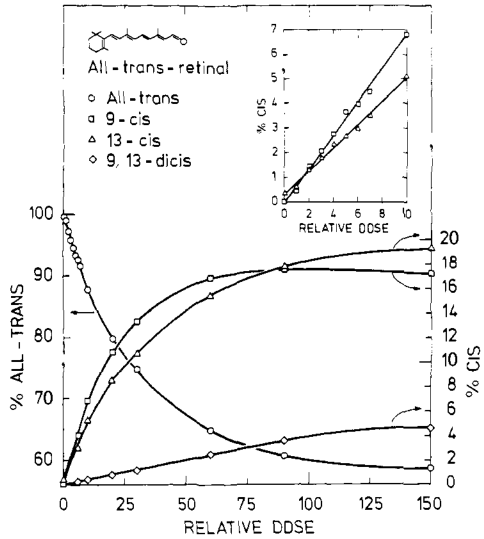

Figure 5. Distribution of retinal isomers versus total incident illumination dose in Zn-Pc-(t-Bu)$_4$-sensitized photoisomerization of all-trans. Only the major products are shown. Insert: Initial formation of 9-cis and 13-cis. Total retinal: 2×10^{-4} M. Zn-Pc-(t-Bu)$_4$: 4.4×10^{-6} M. Solvent: Ar-saturated benzene. Illumination with a Schott KL 150 through an OG 590 filter. The dose unit corresponds to 60 s without the neutral density filter.

creased by a factor 1.4–1.5 at 360 and 250 nm. (v) The unknown component eluting before 13-cis nearly disappeared during the same time. Repeating this experiment but with 4% diethyl ether in n-heptane as eluent revealed a splitting of the 13-cis peak into two components with k'values of 5.61 and 5.89, respectively. The absorption spectra of the two components recorded by stopped-flow HPLC showed that the peak at $k' = 5.89$ had a spectrum identical with 13-cis while the peak at $k' = 5.61$ gave a spectrum with $\lambda_{\rm max} = 302$ nm, $\epsilon_{360}/\epsilon_{250} = 1.07$, and $\epsilon_{\rm max}/\epsilon_{360} = 1.50$. The significance of these observations will be discussed below. Included in Table II is the composition of the photostationary state obtained by direct photolysis in Ar-saturated toluene and subsequent storage in the dark. Also included in Table II are data from the literature[26] on iodine-catalyzed thermal isomerization of retinal.

Quantum Yields and Primary Products. The composition of the photostationary states does not give information about the primary products of the sensitized photoisomerizations or about the relative photoisomerization efficiencies of various isomers. This information is contained in the apparent relative photoisomerization yields that for small conversions in a sensitized photoisomerization experiment can be approximated by

$$\Phi^{\rm app}_{\rm iso}(\rm i \to j) = \Phi^{\rm D}_{\rm T}\Phi^{\rm i}_{\rm ET}\Phi^{\rm T}_{\rm iso}(\rm i \to j) \qquad (2)$$

where

$$\Phi^{\rm i}_{\rm ET} = k^{\rm i}_{\rm ET}[\text{isomer i}]/(k^{\rm D}_{\rm T} + k^{\rm i}_{\rm ET}[\text{isomer i}]) \qquad (3)$$

$\Phi^{\rm D}_{\rm T}$ is the triplet yield of the sensitizer (donor); $\Phi^{\rm i}_{\rm ET}$ is the triplet energy transfer yield from sensitizer to isomer i (at concentration [isomer i]) of substrate; $\Phi^{\rm T}_{\rm iso}(\rm i \to j)$ is the isomerization yield from isomer i to isomer j via the triplet state; $k^{\rm i}_{\rm ET}$ and $k^{\rm D}_{\rm T}$ are the rate constants of energy transfer from sensitizer to isomer i and of sensitizer triplet decay, respectively. For a given set of sensitizer/substrate the relative values of $\Phi^{\rm app}_{\rm iso}(\rm i \to j)$ will give directly the relative values $\Phi^{\rm T}_{\rm iso}(\rm i \to j)$ as $\Phi^{\rm D}_{\rm T}$ and $\Phi^{\rm i}_{\rm ET}$ cancel out. Likewise, relative values of $\Phi^{\rm T}_{\rm iso}(\rm i \to j)$ for two different isomers can be obtained from the apparent yields provided that the experiments are made under conditions where the values of $\Phi^{\rm i}_{\rm ET}$ are close to unity. Hence, in order to obtain relative yields it is necessary to follow the reactions as functions of the total illumination doses. This was done in most detail with the Zn-TPP (5×10^{-5} M) sensitized photoisomerizations of all-trans (2×10^{-4} M) and 11-cis (2×10^{-4} M) and the data are presented in Figures 3 and 4. In these experiments all-trans and 11-cis were illuminated under identical conditions. Figure 3 shows that 13-cis and 9-cis are the major primary products in the sensitized photoisomerization of all-trans. The 9,13-dicis isomer, however, also grows in linearly with the illumination dose. Although the data are scattered this suggests that 9,13-dicis is a primary product from all-trans. Similarly, Figure 4 shows that all-trans is the major primary product from 11-cis and that also 9-cis and 13-cis grow in linearly with illumination dose as if they are primary products, too. Finally, Figures 3 and 4 demonstrate that photostationary states are produced upon prolonged illumination. Similar data were obtained for all-trans and 11-cis with Zn-MP-DME, H_2-TPP, and naphthacene, whereas the sentizations by Zn-Pc-(t-Bu)$_4$, Zn-OEP and H_2-OEP were investigated only with all-trans as substrate. The results obtained with Zn-Pc-(t-Bu)$_4$ and all-trans, illustrated in Figure 5, are noteworthy because the triplet energy of Zn-Pc-(t-Bu)$_4$ is ca. 40 kJ/mol below the vertical triplet energy of retinal. In spite of the considerable endothermicity we estimate that the overall photoisomerization efficiency of all-trans is only 2–3 orders of magnitude lower with Zn-Pc-(t-Bu)$_4$ than with ZnTPP. From the initial slopes values for the relative apparent isomerization yields of all-trans and 11-cis, $\Phi^{\rm app}_{\rm iso}(\text{11-cis}\to)/\Phi^{\rm app}_{\rm iso}(\textit{trans}\to)$, and the relative yields of the major primary products 9-cis and 13-cis,

Table III. Apparent Quantum Yield Ratios and Rate Constants[a]

sensitizer E_T (kJ/mol)	substrate	$\Phi_{iso}^{app}(11\text{-cis}\rightarrow) / \Phi_{iso}^{app}(\text{trans}\rightarrow)$	$\Phi_{iso}^{T}(\rightarrow 13\text{-cis}) / \Phi_{iso}^{T}(\rightarrow 9\text{-cis})$	k_{ET}, 10^9 M^{-1} s^{-1}
Zn-MP-DME 170.8	all-trans	6.1 ± 0.9	2.0 ± 0.2	3.6 ± 0.4
	11-cis		2.6 ± 0.5	
Zn-OEP 169.8	all-trans		1.9 ± 0.2	
H_2OEP 155.8	all-trans		1.9 ± 0.2	
Zn-TPP 153.4	all-trans	6.9 ± 0.6	2.0 ± 0.2	0.96 ± 0.05
	11-cis		2.3 ± 0.1	0.80 ± 0.07
H_2-TPP 138.9	all-trans	6.3 ± 0.7	1.6 ± 0.1	1.2 ± 0.2
	11-cis		1.8 ± 0.4	
naphthacene 122.5	all-trans	19.5 ± 2	1.19 ± 0.05	
	11-cis		0.84 ± 0.10	
Zn-Pc-(*t*-Bu)$_4$ 109.0	all-trans		0.69 ± 0.07	0.00015

[a] Solvents: Ar-saturated benzene or toluene.

Table IV. Relative Apparent Quantum Yields of Triplet Photoisomerization[a,b]

	product					
substrate	total	all-trans	13-cis	11-cis	9-cis	9,13-dicis
11-cis	1.00	0.895	0.082		0.036	
all-trans	0.144		0.090	0.0053	0.042	0.0061

[a] Sensitizer: Zn-TPP. Solvent: Ar-saturated benzene. [b] Obtained from the initial slopes in Figures 3 and 4. Estimated relative error limits are ±10% for the total and for the major one-bond isomerization yields, ±15% for the major two-bond isomerization yields, and up to ±25% for the minor yields.

$\Phi_{iso}^{T}(\rightarrow 13\text{-cis})/\Phi_{iso}^{T}(\rightarrow 9\text{-cis})$, were obtained. These data are collected in Table III. Moreover, the results obtained with Zn-TPP sensitization of all-trans and 11-cis (Figures 3a,b and 4a,b) allowed evaluation of the individual relative isomerization quantum yields. Normalizing the initial rates to the total initial rate of 11-cis isomerization we obtained the values collected in Table IV.

As mentioned above Rosenfeld et al.[41] have reported that $\Phi_{iso}^{T}(11\text{-cis}\rightarrow)$ is dependent on the sensitizer triplet energy for energies above the vertical triplet energy of retinal. As such an energy dependence obviously is of interest in connection with our work, we have attempted to reproduce the experiments with biphenyl and anthracene sensitization. Illumination with a low-pressure Hg arc (main emission at 254 nm) of 5×10^{-5} M 11-cis in Ar-saturated cyclohexane either alone or in the presence of 2×10^{-5} M anthracene or 2×10^{-4} M biphenyl gave the results shown in Figure 6. Besides all-trans, HPLC analysis of the samples without sensitizers revealed a product tentatively assigned as 13-cis.[71a] The solutions containing the sensitizers had equal optical densities (1.20 ± 0.05 over a 3-mm path length) at 254 nm. As the triplet yields of anthracene (0.71) and biphenyl (0.84) are similar the data in Figure 6 suggest the immediate qualitative conclusion that the triplet isomerization yields of 11-cis are similar when sensitized with biphenyl (E_T = 275 kJ/mol) and anthracene (E_T = 178 kJ/mol). Calibration of the light intensity allowed evaluation (Experimental Section) of $\Phi_{iso}^{T}(11\text{-cis}\rightarrow)$ and $\Phi_{iso}^{d}(11\text{-cis}\rightarrow)$ (at 254 nm) as $\Phi_{ET} > 0.9$ (eq 3) for both anthracene and biphenyl. Assuming Φ_{iso}^{d} to be independent of wavelength we obtain $\Phi_{iso}^{d}(11\text{-cis}\rightarrow) = 0.40$ at 254 nm after correction for light absorbed at longer wavelengths. Use of the accepted value $\Phi_{iso}^{d}(11\text{-cis}\rightarrow) = 0.24$ for excitation around 360 nm[29] in the correction for light absorbed above 254 nm gives a slightly higher value $\Phi_{iso}^{d}(11\text{-cis}\rightarrow) = 0.43$ at 254 nm. Hence, we consider 0.42 ± 0.05 to be the best estimate for $\Phi_{iso}^{d}(11\text{-cis}\rightarrow)$ at 254 nm.[71a] Similarly, we obtain $\Phi_{iso}^{T}(11\text{-cis}\rightarrow) \leq 1.1$ in the case of biphenyl sensitization and $\Phi_{iso}^{T}(11\text{-cis}\rightarrow) \leq 1.2$ for anthracene sensitization. Also these values depend slightly on the value of $\Phi_{iso}^{d}(11\text{-cis}\rightarrow)$ used for corrections with respect to excitation above 254 nm. Consequently, we consider $\Phi_{iso}^{T}(11\text{-cis}\rightarrow) = 1.0 \pm 0.2$ as a reliable estimate for the triplet isomerization yield of 11-cis. Assuming the same value of Φ_{iso}^{T} for 11-cis in the case of Zn-TPP sensitization we finally obtain $\Phi_{iso}^{T}(\text{all-trans}\rightarrow) = 0.15 \pm 0.05$ by using an average value of 6.5 ± 0.5 for the relative triplet isomerization yields of 11-cis and all-trans (see Table III).

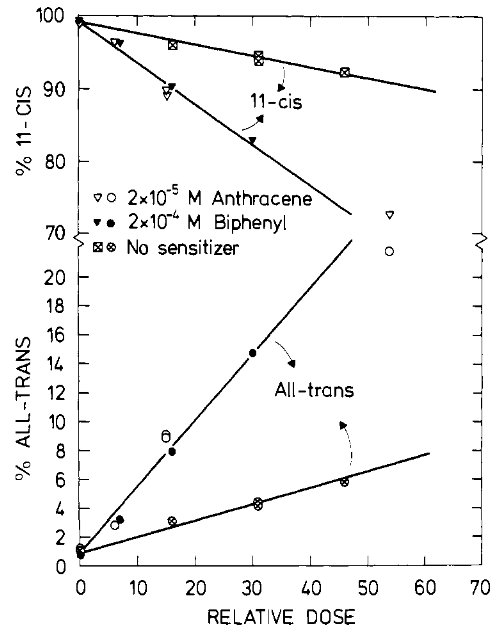

Figure 6. Initial distribution of 11-cis and all-trans[71a] versus total incident illumination dose upon photolysis of 11-cis at 254 nm. The two sets of lines correspond to illumination without sensitizer and with 2×10^{-5} M anthracene or 2×10^{-4} M biphenyl as sensitizer. Total retinal: 5×10^{-5} M. Solvent: Ar-saturated cyclohexane. The dose unit corresponds to 1 s, and the incident light intensity was 62.2 μW cm^{-2}.

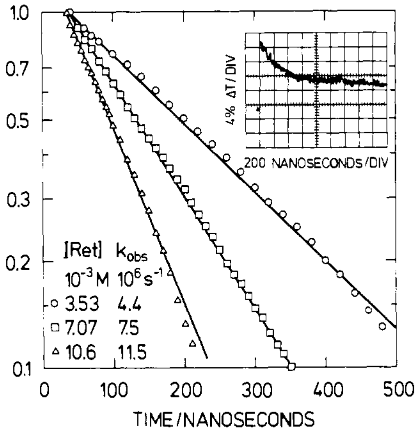

Figure 7. Logarithmic plots of the initial normalized changes observed in laser flash photolysis of Zn-TPP in the presence of all-trans. Zn-TPP: 1.4×10^{-4} M. Solvent: Ar-saturated benzene. Excitation: 530 nm. Monitoring: 500 nm. Path length: 1 cm. Insert: Oscillogram obtained with 3.53×10^{-3} M all-trans showing the initial changes in absorbance.

Energy-Transfer Rate Constants. Triplet energy transfer from Zn-MP-DME, Zn-TPP, H_2-TPP, and Zn-Pc-(*t*-Bu)$_4$ to all-trans was studied by laser flash photolysis of 0.5–1.5 × 10^{-4} M Ar-saturated solutions of the sensitizers containing various concentrations (10^{-3}–10^{-2} M) of all-trans. In the case of Zn-TPP we also studied the energy transfer to 11-cis. The solutions were excited at 530 nm and the subsequent changes in transient ab-

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(71) (a) The isomer compositions of the unsensitized samples and the quantum yield $\Phi_{iso}^{d}(11\text{-cis}\rightarrow)$ were calculated assuming 13-cis to be the other major product as indicated by the HPLC analysis. During the revision of the manuscript Prof. R. S. H. Liu informed us that the direct photoisomerization of 11-cis at 360 nm has been reinvestigated in his laboratory. At this wavelength he finds 11,13-dicis to be formed together with all-trans. It is possible that the product assigned to 13-cis in our 254-nm illumination is in fact 11,13-dicis. If this proves to be the case our results correspond to $\Phi_{iso}^{d}(11\text{-cis}\rightarrow) = 0.64$ instead of 0.42. (b) Pekkarinen, L.; Linschitz, H. *J. Am. Chem. Soc.* **1960**, *82*, 2407–2411.

Table V. Energies Related to Sensitized Photoisomerization (eV)[a]

sensitizer	E_S	E_T	ΔE_S[c]	ΔE_T[c]	τ_S,[d] ns	E_{ox}	E_{red}	E_{CT}[e] (Ret = A)	E_{CT}[f] (Ret = D)
Zn-MP-DME	2.16	1.77	0.70	−0.23	2	0.50		2.23	
Zn-OEP	2.14	1.76	0.72	−0.22	2.2	0.63	−1.61	2.36	>3.16
H_2-OEP	1.99	1.61	0.87	−0.07		0.81	−1.46	2.54	>3.01
Zn-TPP	2.05	1.59	0.81	−0.05	2.7	0.71	−1.35	2.44	>2.90
H_2-TPP	1.86	1.43	1.00	0.11	13.6	0.95	−1.05	2.68	>2.60
naphthacene[b]	2.58	1.27	0.28	0.27	5.2	0.77	−1.55	2.50	>3.10
Zn-Pc(t-Bu)$_4$	1.83	1.13	1.03	0.41	3.8	0.68	−0.89	2.41	>2.44

[a] Excited-state energies and singlet lifetimes of porphyrins (except H_2-OEP) and Zn-Pc-(t-Bu)$_4$ (assumed equal to Zn-Pc) in organic solvents are from Darwent et al.[68] For H_2-OEP the excited singlet energy is obtained from the absorption spectrum (toluene) and the triplet energy (EPA) from Gouterman and Khalil.[69] Redox potentials of porphyrins (versus SCE) from Felton.[82] Redox potentials measured in DMF or DMSO (oxidations) and butyronitrile or CH_2Cl_2 (reductions). Redox potentials for Zn-Pc-(t-Bu)$_4$ are from Darwent et al.[68] [b] Excited-state energies from Berlman[70] and singlet lifetime from Wilkinson.[83] Redox potentials (versus SCE, CH_3CN, and DMF) from Siegerman[84] and Murov.[60] [c] Based on $E_S = 2.86$ eV and $E_T = 1.54$ eV for *all-trans*-retinal. The singlet energy is the mean value of $h\nu_{abs}$(hexane)[63] and $h\nu_{fl}(C_6H_{12})$.[14] The triplet energy (CCl_4) is from Raubach and Guzzo.[23] [d] Lifetimes (ns) of the excited singlet states. [e] Energy of charge-transfer exciplex with retinal as acceptor. Based on the equation $E_{CT} = E_{ox}(D) - E_{red}(A) + 0.35$ V as obtained from Weller.[81] Retinal redox potentials (versus SCE) are as follows: $E_{red} = -1.38$ V (CH_3CN)[85] and $E_{ox} > 1.20$ V (THF).[86] [f] Energy of charge-transfer exciplex with retinal as donor.

sorbance were followed at selected wavelengths in the range 470–520 nm where the triplet states of the porphyrins and the retinals have overlapping absorptions. As expected from the relative values of the triplet extinction coefficients of the sensitizers and retinals,[15,19,71b,72] a decrease of transient absorbance was observed at 500 nm in the case of Zn-TPP whereas an increase occurred at 500–520 and 470–490 nm for Zn-MP-DME and H_2-TPP, respectively. Typical results for Zn-TPP and all-trans are shown in Figure 7. The insert of Figure 7 shows a biphasic decay where both the fast and slow phases follow apparent first-order kinetics. The rate constants for the slow phase were all in the range $1.2\text{–}2 \times 10^5$ s^{-1} and showed no dependence on the retinal concentration. The apparent first-order rate constants for the fast phase were on the other hand dependent on the retinal concentration as exemplified in Figure 7. This behavior is most simply interpreted in terms of simple collisional triplet energy transfer between sensitizer and acceptor followed by decay of the acceptor triplet state. The first-order rate constants for the slow phase decay should then be equal to the decay rate constant (ca. 1.2×10^5 s^{-1}) of the retinal triplet state,[10,11] and the measured values support this assumption reasonably well. The observed first-order rate constants for the fast phase should be given by

$$k_{obs} = k_1^D + k_{ET}[\text{retinal}]$$

where k_1^D is the sensitizer decay constant. Consequently, k_{ET} is obtained as the slopes of the linear plots of k_{obs} versus [retinal]. The values of k_{ET} thus obtained are collected in Table III. The decay of the Zn-Pc-(t-Bu)$_4$ triplet state (monitored at 500 nm) was unaffected by the addition of 10^{-2} M all-trans. Only by increasing the concentration of all-trans to 1.1×10^{-1} M did we observe an increase in the first-order decay constant, k_{obs}, from $(6.4 \pm 0.5) \times 10^3$ to $(2.3 \pm 0.2) \times 10^4$ s^{-1}. This corresponds to a k_{ET} of $(1.5 \pm 0.3) \times 10^5$ M^{-1} s^{-1} which, however, only can be regarded as an estimate of the true rate constant. The sensitizers studied by laser flash photolysis all have triplet energies (Table II) slightly above and below the vertical triplet energy of all-trans. Hence, reversible energy transfer between sensitizer and retinal is highly probable. With large retinal concentrations resulting in triplet equilibration which is much faster than the decay of the donor and acceptor triplet states, the observed rate constants for the fast phase can be approximated by

$$k_{obs} = k_1^D + k_{ET}[\text{retinal}] + k_{-ET}[D]$$

where k_{-ET} is the rate constant for reverse energy transfer from triplet retinal to sensitizer at concentration [D]. In the treatment used here reversible energy transfer would show up as apparent intercepts in the k_{obs} versus [retinal] plots which are larger than expected from the known values of k_1^D. The slopes, however, would still represent k_{ET}. In the experiments with Zn-TPP (1.4×10^{-4} M and $k_1^D = 3.2 \times 10^3$ s^{-1}) we did get intercepts of $1.2 \pm 0.3 \times 10^6$ and $1.7 \pm 0.5 \times 10^6$ s^{-1} for all-trans and 11-cis, respectively, suggesting that reversible energy transfer is occurring.

Discussion

Photostationary States and Primary Products. The currently accepted values of $\Phi_{iso}^T(\text{trans}\rightarrow)$ (<0.002–0.003) and its cis isomers (0.15–0.20) are those obtained by Rosenfeld et al.[10] and Waddell et al.[29] (for recent reviews see ref 4 and 5). These values imply that the triplet-sensitized photostationary states obtained from any of the retinal isomers should contain nearly 100% all-trans if the sensitizer transfers energy to each isomer with similar efficiencies which we have shown to be the case for Zn-TPP sensitization of all-trans and 11-cis (Table III). This prediction is in obvious conflict with our results (Table II) provided that the mechanisms of the sensitized photoisomerizations all involve formation of triplet retinal followed by geometric isomerization of the triplet excited retinals. Besides triplet-mediated isomerization other conceivable mechanisms that could explain the observed isomerizations are as follows: (i) direct excitation of retinal; (ii) excitation of ground-state complexes between the sensitizers and retinal followed by retinal isomerization; (iii) singlet energy transfer from sensitizer to the retinal followed by isomerization of the retinal within the excited-state manifolds; (iv) formation of charge-transfer exciplexes from either singlet-excited or triplet-excited sensitizer followed by retinal isomerization within the exciplex.

The direct excitation of the retinals can safely be excluded on the basis of our experiments involving illumination of retinal with filtered light in the absence of sensitizer which show no direct isomerization except in the case of the filter combination used with naphthacene. Any significant involvement of ground-state complexes between the sensitizers and retinal is unlikely for several reasons. First, no signs of complexation were observed in the absorption spectra of the sensitizers upon addition of 10^{-3} M retinal. More specifically we did not observe any spectral changes characteristic of adding a fifth axial ligand to a Zn-porphyrin.[73-76] Neither did we observe spectral changes that could indicate formation of charge-transfer complexes.[77-79] Second, the photostationary states and the primary product ratios (Tables II and III) obtained with H_2-OEP, Zn-TPP, and H_2-TPP do not indicate that ligation to zinc, unobserved in the absorption spectra, determines the photochemistry. Finally, the results obtained by

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sensitization with naphthacene (this work) and anthracene (using γ-radiolysis; N.-H. Jensen, unpublished) show that the triplet energy rather than chemical structure is the important factor in determining the photochemistry. Hence, we exclude mechanisms involving ligand photoisomerization via intramolecular energy transfer that have been suggested for metalloporphyrin-sensitized photoisomerization of azastilbenes.[80] To estimate the relative importance of the remaining mechanisms more detailed consideration of the energetics is needed. In Table V we have collected the data necessary for comparing the energies of the excited and charge-transfer states that possibly could be involved in the photoisomerization processes. Long-range singlet-energy transfer by a dipole mechanism from the sensitizers to retinal is impossible as there is no overlap between the sensitizer fluorescence and retinal absorption in all the cases. Singlet-energy transfer by a collisional mechanism also seems unlikely on account of the substantial endothermicities combined with the short sensitizer singlet lifetimes that prevail for all the sensitizers.

Turning now to the possibility of forming charge-transfer (CT) exciplexes we have calculated the energies of the exciplexes with retinal acting as acceptor and donor. The energies of the CT states were estimated by using the formula of Weller.[81] From Table V it can be seen that all possible CT states are of substantially higher energy than all of the sensitizer triplet states and most of the sensitizer singlet states. Only Zn-MP-DME, Zn-OEP, and naphthacene have singlet energies comparable to the energies of the CT states. However, a predominant involvement of sensitizer singlet state ($^1D^*$) quenching through formation of a singlet charge-transfer state can be ruled out for two reasons: (1) even for a diffusion-controlled quenching ($^1D^* + \text{Retinal} \rightarrow {}^1CT$) the actual concentration (2×10^{-4} M) of retinal should only result in quenching of less than 1% of the short-lived (ns lifetime) sensitizer singlet state; (2) the similarities of the overall photoisomerization efficiencies (data not shown) and of the photostationary states (Table II) for Zn-OEP, Zn-MP-DME, H_2-OEP, and Zn-TPP sensitization are not correlated with the differences between $E_S - E_{CT}$ of these molecules. A large decrease of overall efficiency for H_2-OEP and Zn-TPP would be expected on account of the 0.4–0.5-eV endothermicities in contrast with the 0.1–0.2-eV endothermicities for the two other porphyrins. Thus, quenching of the sensitizer triplet state by triplet-energy transfer to retinal followed by retinal isomerization from the triplet manifold seems to be the only likely mechanism. Consequently, we are faced with the problem of explaining sensitizer triplet energy dependent changes observed in the photostationary states (Table II and Figure 2), in the relative triplet isomerization efficiencies of all-trans and 11-cis (Table III), and in the primary product ratios $\Phi^T_{iso}(\rightarrow 13\text{-cis})/\Phi^T_{iso}(\rightarrow 9\text{-cis})$ (Table III). Also, the sensitized photoisomerization observed with naphthacene and Zn-Pc-(t-Bu)$_4$, for which triplet-energy transfer to retinal is substantially endothermic, should be considered. Accordingly, we will in the following paragraphs discuss how the sensitizer triplet energy may influence the "nature" and reactivity of the retinal triplet states. Likewise, we will consider the possible role of reversible triplet-energy transfer in the overall isomerization processes.

The energy-dependent changes in the photostationary states seem to be reminiscent of the changes observed for stilbene with triplet sensitizers of different energies.[39] In the case of stilbene the observed photostationary states (PSS) could be accounted for by the general expression

$$\frac{[\text{cis}]_{PSS}}{[\text{trans}]_{PSS}} = \frac{k_{ET}^{trans}\,\Phi^T_{iso}(\text{trans}\rightarrow\text{cis})}{k_{ET}^{cis}\,\Phi^T_{iso}(\text{cis}\rightarrow\text{trans})} \qquad (4)$$

and the measured values of the rate constants for energy transfer to trans and cis, k_{ET}^{trans} and k_{ET}^{cis}. The isomerization quantum yield of the triplet stilbene, $\Phi^T_{iso}(\text{trans}\rightarrow\text{cis}) = 1 - \Phi^T_{iso}(\text{cis}\rightarrow\text{trans})$, was assumed to be independent of the sensitizer triplet energy. Hence, the stilbene photostationary states were explained within a model where (i) trans and cis form one identical triplet state and (ii) the "nature" of the triplet state is independent of the sensitizer triplet energy.[87] The present work on retinal has yielded results that could be taken as support for a common triplet mechanism. The occurrence of one photon–two bond isomerization (e.g. 11-cis → 13-cis) would be an expected feature if the isomers formed one fully equilibrated triplet state. Moreover, the efficiencies of forming 9-cis and 13-cis seem to be identical within the limits of error (Table IV) for all-trans and 11-cis when sensitized by Zn-TPP. Again this result could indicate a common triplet for 11-cis and all-trans. In fact, this kind of argument has recently been used in favor of a common triplet in a conjugated imine.[88] Thus, extension of the stilbene model to a multiisomer system as retinal is tempting, but several experimental observations show that the picture is more complicated for retinal. First, as mentioned in the introduction, there is strong evidence supporting the idea that the different retinal isomers form spectroscopically distinct triplet states.[17] Second, the energy-dependent changes in the primary product ratios $\Phi^T_{iso}(\rightarrow 13\text{-cis})/\Phi^T_{iso}(\rightarrow 9\text{-cis})$ show that the reactivity of the triplet states from all-trans and 11-cis is dependent on the sensitizer triplet energy for energies below the vertical triplet energy of all-trans. These reactivity changes could reflect energy-dependent changes in the "nature" of the triplet states, or they could be the result of reversibility in the energy-transfer process. At energies above the vertical triplet energy neither the present results nor our previous resonance Raman measurements[17] indicate any energy dependence in the "nature" and reactivity of the triplet states from all-trans and 11-cis.

The structural differences between the ground states and the excited triplet states of the retinal isomers are largely unknown. Theoretical calculations on the excited states of various polyene systems[89-93] as well as the apparently general occurrence of triplet-mediated isomerization,[39,57a,94-97] however, suggest that torsional and other relaxations in the excited triplet states are likely. Previously, we have suggested a model for the triplet states derived from β-carotene.[54,57a] In this model it was proposed that *all-trans-β*-carotene forms a mixture of triplet excited species, each being twisted around one particular C=C double bond, whereas each of the cis-isomers was proposed to form only one triplet excited species being twisted around the formal cis double bond. In terms of the triplet potential energy surface this model suggests that excitation of the trans isomer populates several local minima on the potential energy surface while excitation of each of the cis isomers only populates one local minimum. A similar model for the retinal triplet states would give difficulties in explaining the energy-dependent changes of the primary product

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ratios (Table III) observed for 11-cis, whereas the changes observed for all-trans could be explained by an energy dependence of the distribution of the excited retinals in the various potential energy minima, i.e., a mixture of different triplet species. Thus the observed changes in the product ratios for 11-cis suggest that 11-cis as well as all-trans form triplet states which are mixtures of different triplet species, and that the compositions of these mixtures (i.e. the "nature" of the triplet states) are dependent upon the sensitizer triplet energy. Moreover, such an extension of the previous model could easily accommodate the observations of one photon–two bond isomerization in the triplet states of retinal (present work) and β-carotene (Y. Koyama and N.-H. Jensen, unpublished results).

The endothermicities of the triplet energy transfer reactions involving H_2-TPP, naphthacene, and Zn-Pc-(*t*-Bu)$_4$ are substantial. The major effect of an energy-deficient sensitizer on the overall photoisomerization efficiency would be a low efficiency of the energy-transfer process. This efficiency (eq 3) is, however, determined not only by the rate constant of energy transfer but also by the intrinsic lifetime of the sensitizer. The lifetimes of the sensitizers, $1/k_T^D$, for this work are all in the 100-μs range[68,98] and consequently they are very sensitive to quenching by added substrates. The triplet energy transfer rate constants (Table III) for the exothermic sensitizers Zn-MP-DME and Zn-TPP as well as H_2-TPP, for which triplet-energy transfer is endothermic, are all close to or above 10^9 M^{-1} s^{-1}. These values appear normal as compared to the value of 1.2×10^9 M^{-1} s^{-1} reported for the quenching of protoporphyrin IX dimethyl ester by retinal.[99] With respect to the energy-transfer efficiency (eq 3) these values ensure essentially complete quenching of the sensitizer triplet states with a retinal concentration of 2×10^{-4} M. For the strongly endothermic sensitizers, naphthacene and Zn-Pc-(*t*-Bu)$_4$, the energy-transfer rate constants are far less certain. Only an estimate of 1.5×10^5 M^{-1} s^{-1} could be obtained for Zn-Pc-(*t*-Bu)$_4$, and for naphthacene the rate constant is unknown. If the energy-transfer processes to retinal in the endothermic region were strictly vertical the rate constants should follow an Arrhenius-type relation[100]

$$k_{ET} = k_{ET}^{o}(\exp(\Delta E/RT) + 1)^{-1} \qquad (5)$$

where k_{ET}^{o} ideally would be the rate constant for a diffusion-controlled process. In this context, however, it is probably a better choice to use a value for an exothermic process involving reactants with similar structures. With use of $k_{ET}^{o} = 5 \times 10^9$ M^{-1} s^{-1} eq 5 predicts $k_{ET} = 1.2 \times 10^5$ M^{-1} s^{-1} for naphthacene and $k_{ET} = 5 \times 10^2$ M^{-1} s^{-1} for Zn-Pc-(*t*-Bu)$_4$. In the latter case the measured energy-transfer rate constant is 300 times larger than that calculated for a strictly vertical energy-transfer process. However, the measured value predicts $\Phi_{ET} = 4.7 \times 10^{-3}$ in good agreement with the observed efficiency (vide supra). Hence, the measured energy-transfer rate constant and the observed photoisomerization efficiency for Zn-Pc-(*t*-Bu)$_4$/all-trans are consistent with each other but in conflict with the predictions based on a strictly vertical energy-transfer process.

With a structurally flexible acceptor like retinal the concept of "non-vertical" energy transfer (see e.g. ref 101 and 102) might be relevant. Within the so-called hot band model[30a–c,102,103] this would mean that thermally activated structural deformation (e.g. torsional motion) prior to a vertical energy-transfer step would lower the retinal triplet excitation energy by an amount larger than the energy used for the thermal activation. Thereby the rate constants for endothermic energy transfer can be substantially larger than expected for a vertical energy-transfer process without structural deformation. For the well-documented system anthracene/*cis*-stilbene the measured energy-transfer rate constants[87,104] are approximately 5 orders of magnitude larger than predicted from eq 5.

Thus, it appears that a modest degree of "nonvertical" character in the endothermic energy transfer to retinal can accommodate the experimental observations at least in the case of the Zn-Pc-(*t*-Bu)$_4$/all-trans system. Moreover, assuming that the endothermic "nonvertical" energy transfer processes follow mechanisms similar to the hot band model,[30a–c] it appears likely that endothermic energy transfer might induce some regioselectivity as the changes in potential energy surface shapes on going from the ground state to the triplet state probably are different for different coordinates. Hence, the energy-dependent changes in the primary product ratios at low sensitizer triplet energies could possibly be the result of "nonvertical" excitation along some preferred coordinate whereby the composition of the mixture of triplet species is changed. More specifically, the decrease in $\Phi_{iso}^{T}(\rightarrow 13\text{-cis})/\Phi_{iso}^{T}(\rightarrow 9\text{-cis})$ by decreasing sensitizer triplet energy would suggest that the C_9–C_{10} torsional coordinate is preferred relative to the C_{13}–C_{14} torsional coordinate with respect to endothermic "nonvertical" excitation.

The substantial increase found for the apparent isomerization yield ratio $\Phi_{iso}^{app}(11\text{-cis}\rightarrow)/\Phi_{iso}^{app}(\text{trans}\rightarrow)$ on going from H_2-TPP to naphthacene (Table III) can be due to a higher efficiency of highly endothermic energy transfer to 11-cis relative to all-trans resulting in a higher Φ_{ET} for 11-cis than for all-trans. That the observed change in $\Phi_{iso}^{app}(11\text{-cis}\rightarrow)/\Phi_{iso}^{app}(\text{trans}\rightarrow)$ should be due to energy-dependent changes of the $\Phi_{iso}^{T}(11\text{-cis}\rightarrow)/\Phi_{iso}^{T}(\text{trans}\rightarrow)$ ratio seems unlikely as no changes occur on going from Zn-TPP to H_2-TPP. For these sensitizers the Φ_{ET} values are close to unity.

The effect of reversible triplet-energy transfer[97,100] should also be considered in this context. The rate constant for triplet-energy transfer from triplet all-trans to naphthacene is 2.6×10^9 M^{-1} s^{-1}.[22] Together with the concentration of naphthacene used (5×10^{-5} M) and the intrinsic triplet lifetime of all-trans a back-transfer efficiency of ca. 0.5 is predicted for the naphthacene/all-trans system. The corresponding rate constant for the Zn-Pc-(*t*-Bu)$_4$/all-trans system is not known but an upper limit for the back-transfer efficiency of 0.1 can be estimated by assuming a diffusion-controlled process. Thus, reversible triplet-energy transfer is significant for the endothermic triplet sensitizers and the changes in the $\Phi_{iso}^{app}(11\text{-cis}\rightarrow)/\Phi_{iso}^{app}(\text{trans}\rightarrow)$ ratio could be the result of relative changes in the back-transfer efficiencies of 11-cis and all-trans on going from H_2-TPP to naphthacene. Also, the changes in the photostationary states and in the primary product ratios observed with the endothermic sensitizers could partly reflect the onset of reversible energy transfer. However, we favor the explanation involving a "nonvertical" mechanism in these cases, as reversible energy transfer with back-transfer efficiencies of 0.1–0.5 cannot explain the high overall isomerization efficiencies.

Two-Bond Isomerization. The phenomenon of isomerization around two double bonds with only one excitation event has been considered theoretically in several cases.[90,92,105,106] Experimentally it is well-established in the sensitized photoisomerizations of 2,4-hexadiene[94] and alloocimene[95] whereas for retinals it has only been observed in the biacetyl-sensitized photoisomerization of 9,13-dicis[29] and in the direct photoisomerization of 9,13-*dicis*-rhodopsin.[29,107] Our data on the Zn-TPP-sensitized photoisomerization of 11-cis (Figure 4) strongly suggest that 11-cis can isomerize directly to 9-cis and 13-cis. A conservative comparison of the initial rates of formation of 9-cis and 13-cis starting from all-trans and 11-cis shows that only if the ratio of the rate constants for energy transfer from triplet Zn-TPP to 11-cis and all-trans, $k_{ET}^{\text{trans}}/k_{ET}^{11\text{-cis}}$, is >20 could the observed initial rates from 11-cis be explained by the consecutive processes

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$$\text{11-cis} \xrightarrow{h\nu} \text{all-trans} \xrightarrow{h\nu} \text{9-cis or 13-cis}$$

The measured rate constants (Table III), which are similar for all-trans and 11-cis, show conclusively that 11-cis undergoes one photon–two bond isomerization when sensitized by Zn-TPP. This conclusion relies, of course, on the quality of the rate constants, which we consider to be reliable for various reasons. First, their magnitudes are in the expected range (vide supra). Second, the rate constants for 11-cis and all-trans can, together with the relative quantum yields, account for the measured photostationary ratio $[\text{11-cis}]_{\text{PSS}}/[\text{all-trans}]_{\text{PSS}}$. Use of eq 4 predicts a ratio of 7.10×10^{-3}, which compares favorably with the measured ratio 7.25×10^{-3}. The data on the Zn-TPP sensitized photoisomerization of all-trans (Figure 3) similarly suggest that two-bond isomerization to 9,13-dicis occurs. Unfortunately, we do not have the rate constants necessary to support conclusions about this process. Moreover, the scatter in the data would probably not allow any final conclusions in this case.

Direct Photoisomerization. Interpretation of the observations made in connection with the direct illumination experiments on all-trans is complicated by the conflicting assignments of one of the HPLC peaks reported in the literature. Prolonged illumination of all-trans in acetonitrile affords a complicated mixture of isomers, most of which correspond to well-characterized isomers. This mixture, however, also contains an isomer which, depending on the composition of the eluent, can either appear as a shoulder in front of the 13-cis peak[4,34] or as a separate peak in front of 13-cis[108] or even elute together with 13-cis as indicated by our results. This peak was tentatively assigned to 7,13-dicis by Liu and co-workers[4,34] while Koyama et al.[108] assigned it to 11,13-dicis. The latter assignment was supported by NMR on the collected fraction. The absorption spectrum of 11,13-dicis has been reported by Knudsen et al.,[109] and it shows a very large blue-shift ($\lambda_{\text{max}} = 302$ nm) compared with all-trans. At 360 and 250 nm the extinction coefficients are ca. 1.2×10^4 and 1.1×10^4 M^{-1} cm^{-1}, respectively. Thermally 11,13-dicis is reported to be rather unstable as it rearranges cleanly to 13-cis.[109] From the known spectral data of 13-cis ($\epsilon_{360} = 3.8 \times 10^4$ M^{-1} cm^{-1} and $\epsilon_{250} = 1.0 \times 10^4$ M^{-1} cm^{-1}) this rearrangement should result in a considerable increase in absorption around 360 nm while the absorption at 250 nm should be essentially unchanged. Hence, we assign the HPLC peak appearing in front of the 13-cis peak to 11,13-dicis as this assignment can explain all the experimental observations. Similarly, the changes observed with the 9,13-dicis peak and the unknown peak at $k' = 2.05$ (9% diethyl ether/*n*-heptane) could suggest formation of the unstable isomer 9,11,13-tricis which has a spectrum similar to that of 11,13-dicis and forms 9,13-dicis upon rearrangement.[109] Unnoticed formation of 11,13-dicis in previous studies could eventually explain the large variations in the 13-cis/9-cis product ratios reported in the literature (see Introduction). The photostationary state obtained by direct irradiation of retinal in toluene (Table II) is noteworthy because it differs considerably from the triplet-induced photostationary states and because it contains a relatively large amount of 11-cis. Large amounts of 11-cis have previously only been observed upon direct illumination of retinal in polar solvents such as ethanol and acetonitrile.[31-33,47] That the formation of 11-cis is not solely due to the spectral distribution of the lamp used is shown by additional experiments in cyclohexane where the amount of 11-cis never exceeded 2% at the photostationary state.

Quantum Yields. The finding that biphenyl ($E_T = 275$ kJ/mol) and anthracene ($E_T = 178$ kJ/mol) have essentially identical efficiencies in sensitizing the isomerization of 11-cis is in conflict with the results of Rosenfeld et al.[41] By using the data of Rosenfeld et al.[41] and taking the triplet yields of biphenyl (0.84) and anthracene (0.71) into account the overall efficiency with biphenyl should be 6 times lower than with anthracene. We have no obvious explanation for this discrepancy, but it should be noticed that the analytical method employed in our work allows the isomeric purity of the samples to be measured throughout the experiment.

The quantum yield of triplet isomerization for 11-cis, $\Phi^{\text{T}}_{\text{iso}}(\text{11-cis}\rightarrow) = 1.0 \pm 0.2$, derived from the present experiments is in reasonable agreement with the limiting values 0.85–1.0 reported by Rosenfeld et al.[41] for low-energy sensitizers and with the value 0.75 reported by Raubach and Guzzo[28] for biacetyl sensitization. It is, however, considerably larger than the values 0.17 with biphenyl and 0.15 with biacetyl given by Rosenfeld et al.[10] as well as the value 0.17 with biacetyl given by Waddell et al.[29] The nearly constant ratio $\Phi^{\text{app}}_{\text{iso}}(\text{11-cis}\rightarrow)/\Phi^{\text{app}}_{\text{iso}}(\text{trans}\rightarrow)$ for the porphyrin sensitizers of highest triplet energy (Table III) justifies the evaluation of $\Phi^{\text{T}}_{\text{iso}}(\text{trans}\rightarrow) = 0.15 \pm 0.05$. This value is essentially identical with the value 0.17 (with biacetyl) obtained by Raubach and Guzzo,[28] but it is in striking conflict with the other values <0.002[10] and <0.003[29] found in the literature. Again, it is difficult to explain these large discrepancies, but analytical problems could have caused the earlier values to be too low. Raubach and Guzzo[28] as well as Rosenfeld et al.[10,41] used absorption spectroscopy with which it can be difficult to ensure the isomeric purity of the starting materials. Waddell et al.,[29] on the other hand, used HPLC as we did, but the solvent systems employed by Waddell et al.[29] necessitated considerable sample preparation before HPLC analysis, whereas we were able to analyze the samples directly. Moreover, we have been able to confirm the magnitude of $\Phi^{\text{T}}_{\text{iso}}(\text{all-trans}\rightarrow)$ by independent anthracene-sensitized isomerization experiments using γ-radiolysis (N.-H. Jensen, unpublished). Finally, our value is qualitatively supported by the fact that the sensitized photostationary states contain a considerable amount of cis isomers.

The quantum yield of direct isomerization of 11-cis at 254 nm, $\Phi^{\text{d}}_{\text{iso}}(\text{11-cis}\rightarrow) = 0.42 \pm 0.05$,[71a] has not been determined previously. All other reported values, which are in the range 0.12–0.25,[10,14,27,29] were obtained with excitation in the 350–360-nm range. Thus, our value could indicate a wavelength dependence of the direct photoisomerization yield. Such a wavelength dependence is conceivable as excitation at 254 nm might open new isomerization channels not accessible with excitation around 350 nm. It should, however, be noticed that Waddell and Hopkins[31] reported that the direct photoisomerization yield of all-trans (in hexane) is independent of wavelength between 430 and 270 nm. Moreover, there is a large scatter in the values of the direct photoisomerization yields of several of the isomers. Examples are the range given above for 11-cis, the range 0.04–0.12[10,14,29,31,35] for all-trans, and the values 0.21[29] and 0.32[35] for 13-cis. In all cases the solvents were hexane or 3-methylpentane with excitation around 350 nm. A wavelength-independent direct-photoisomerization yield of 0.42 ± 0.05 for 11-cis together with $\Phi^{\text{T}}_{\text{iso}}(\text{11-cis}\rightarrow) = 1.0 \pm 0.2$ and $\Phi_{\text{T}}(\text{11-cis}) = 0.5 \pm 0.1$[12,14] would be in gratifying agreement with eq 1 if $\Phi^{\text{S}}_{\text{iso}}(\text{11-cis}\rightarrow) = 0$, i.e. the direct photoisomerization of 11-cis entirely proceeds through the triplet state. Likewise, the value $\Phi^{\text{T}}_{\text{iso}}(\text{trans}\rightarrow) = 0.15 \pm 0.05$ together with $\Phi_{\text{T}}(\text{trans}) = 0.62$[14] can account for essentially all of the direct photoisomerization yield of all-trans. Consequently, these considerations strongly suggest a redetermination of the direct photoisomerization yields of the retinal isomers at wavelengths longer than 254 nm, as our results suggest that the singlet-state contribution to the direct photoisomerization is negligible for both 11-cis and all-trans.

Conclusions

The work reported here shows that all-trans and 11-cis undergo geometric isomerization upon sensitization with sensitizers which produce the retinal triplet states. The photostationary states and the distribution of the primary products are largely independent of the sensitizer triplet energy for energies above the vertical triplet energy of all-trans, but energy-dependent changes are observed at energies below the vertical triplet energy of all-trans. Unambiguous evidence for one photon–two bond sensitized photoisomerization of 11-cis has been obtained, whereas the evidence for a similar process in all-trans is less certain.

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The quantum yield for triplet isomerization of 11-cis, $\Phi^{T}_{iso}(11\text{-cis}\rightarrow) = 1.0 \pm 0.2$, is independent of the sensitizer triplet energy. The corresponding yield for all-trans, $\Phi^{T}_{iso}(\text{trans}\rightarrow) = 0.15 \pm 0.05$, derived from the relative isomerization efficiencies of 11-cis and all-trans, is substantially higher than the currently accepted values, but it agrees qualitatively with the cis-content in the photostationary states. The quantum yield of direct photoisomerization of 11-cis at 254 nm, $\Phi^{d}_{iso}(11\text{-cis}\rightarrow) = 0.42 \pm 0.05$,[71a] could indicate a wavelength dependence as previous measurements with excitation around 350 nm have given values around 0.25. The measured quantum yields suggest that the singlet contributions to the direct photoisomerization of all-trans and 11-cis are negligible. Additional experiments are needed to clarify this point. Photoisomerization of all-trans by direct excitation produces a thermally unstable isomer with λ_{max} = 302 nm. This isomer rearranges to 13-cis and we identify it with 11,13-dicis. On the basis of previous spectroscopic measurements and the present photoisomerization experiments a picture of the retinal triplet states as different mixtures of triplet species seems to be the best model. Within such a model the spectroscopic differences between triplet states obtained from different isomers and the sensitizer energy dependent changes in the primary product ratios can be explained by assuming the composition of the mixtures of triplet species to be dependent upon the starting isomer as well as the sensitizer triplet energy for energies below the vertical triplet energy of retinal.

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Lifetimes of Oxocarbenium Ions in Aqueous Solution from Common Ion Inhibition of the Solvolysis of α-Azido Ethers by Added Azide Ion[1]

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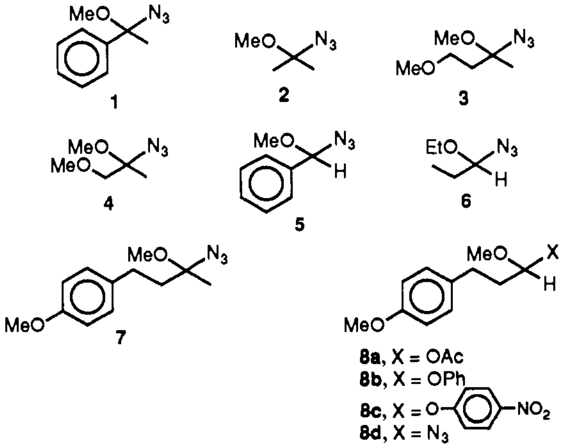
Abstract: Rate constants for hydration of the oxocarbenium ions derived from a series of carbonyl compounds have been determined from common ion inhibition of the solvolysis of the corresponding α-azido ethers by trapping of the oxocarbenium ion intermediate with added azide ion, assuming $k_{az} = 5 \times 10^9$ M^{-1} s^{-1}: acetophenone, $k_{HOH} = 5 \times 10^7$; acetone, 1×10^9; 4-methoxybutanone, 2×10^9; methoxyacetone, 4×10^9; benzaldehyde, 2×10^9; propionaldehyde, 2×10^{10} s^{-1}. Substitution on the reacting carbon atom affects log k_{HOH} 0.4 as much as log K_{eq}. Resonance effects are much larger than polar effects of substituents on k_{HOH}, compared with K_{eq}; this represents imbalance in the expression of these effects in the transition state. Use of these substituent effects to estimate the lifetime of glycosyl and methoxymethyl oxocarbenium ions gives values of $k_{HOH} \sim 10^{12}$ s^{-1} for the glycosyl cation and 10^{12}–10^{15} s^{-1} for the methoxymethyl cation. It is concluded that the glycosyl cation has a short but significant lifetime in aqueous solution and that there is little or no barrier for hydration of the methoxymethyl cation. The effects of substituents on the rate constants for addition to oxocarbenium ions are smaller than those for addition to the corresponding carbonyl compounds. The decrease in reactivity toward water of protonated acetone compared with the corresponding oxocarbenium ion by $\sim 10^5$ suggests that the proton occupies an intermediate position between the carbonyl group and water. The dependence of log k_{ROH} on pK_{ROH} for the addition of alcohols to oxocarbenium ions derived from derivatives of butanone and propionaldehyde in aqueous alcohol mixtures follows slopes of 0.5 and 0.1, respectively.

In recent years, the common belief that hydrolysis and substitution reactions of all acetals proceed through an oxocarbenium ion intermediate[2] has been called into question.[3,4] In particular, this mechanism will not be followed if the putative oxocarbenium ion intermediate has a lifetime that is shorter than a bond vibration ($\sim 10^{-13}$ s), because such an intermediate has no barrier to collapse.[5] Rate constants for hydration of the oxocarbenium ions derived from substituted acetophenone dimethyl acetals in the range $k_{HOH} = 7 \times 10^6$–4×10^8 s^{-1} were estimated from diffusion-controlled trapping of the intermediate with sulfite dianion[3] and very similar values were obtained from extrapolations of directly measured rate constants in strong acids.[6] A crude extrapolation of a linear free energy relationship between k_{HOH} for

Chart I



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