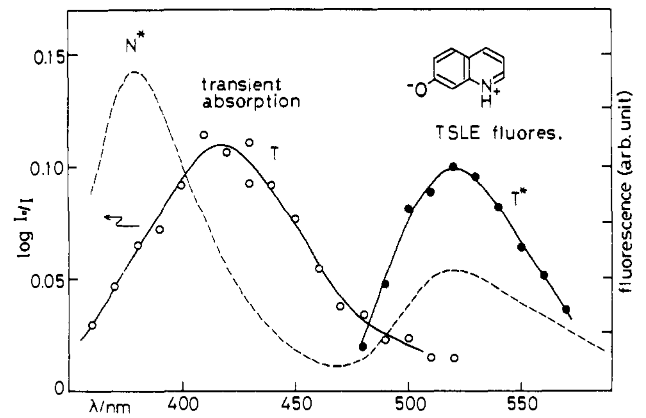

Figure 1. Transient absorption spectrum (○) of a methanol solution of 7-HQ (7×10^{-5} M) depicted at a 500-ns delay after a laser excitation. The light path length is 5 mm. The TSLE fluorescence spectrum (●) of a 7-HQ solution (4.3×10^{-4} M) was excited by 440-nm pulse at 1.2 μs delayed from the first N_2 laser pulse. The steady-state spectrum (– – –) as a comparison was measured in a methanol solution (1×10^{-4} M) in the excitation at 320 nm. All spectra were measured at room temperature.

fluorescence being in a mirror image with the transient absorption band is actually the direct excitation fluorescence of T* (T → T*). Further, if the reverse proton transfer in the excited state from T* to N* takes place, the TSLE fluorescence of N* may be observed in addition to the TSLE T* fluorescence. Unfortunately, no TSLE fluorescence of N* was observed, which suggests lack of the reverse proton transfer in the excited state. The TSLE fluorescence first reported here provides us with not only the important information on the mechanism of the excited-state and ground-state proton transfer but also a new spectroscopic technique for the study of unstable species including excited states in various photochemical processes, if the delay time between two pulses is variable to several tens of nanoseconds.[8]

Registry No. 7-Hydroxyquinoline, 580-20-1.

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(8) Recently, a similar TSLE technique was reported as a "two-color double resonance" in the multiphoton ionization spectroscopy. Ebata, T.; Imajo, T.; Mikami, N.; Ito, M. *Chem. Phy. Lett.* **1982**, *89*, 45. Ebata, T.; Mikami, N.; Ito, M. *J. Chem. Phys.* **1983**, *78*, 1132 and references therein.

Medium- and Substituent-Directed Stereoselective Photoisomerization of Polyenes in the Vitamin A Series. Application of the Dellinger–Kasha Model[1]

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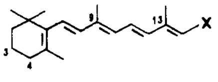
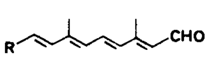
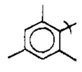
Received January 1, 1983

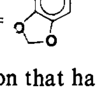
The solvent-dependent photoisomerization of retinal, **1a** by



1a, X = CHO
b, X = CO_2CH_3
c, 10F, X = CHO
d, 14F, X = CHO
e, 3-dehydro, X = CHO



2a, R =


b, R =


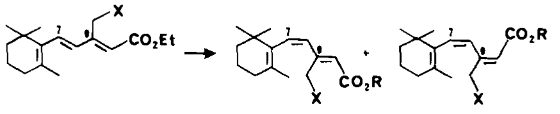
direct irradiation is a well-known phenomenon that has received considerable attention in terms of both its synthetic value[2] and mechanistic understanding.[3] On the other hand, very little attention has been paid to the regioselectivity of such reactions. For example, formation of isomers in hexane at the more crowded trisubstituted double bonds (9-cis and 13-cis) was rationalized in terms of high selectivity caused by the higher π-electron density of the polyenes in the n,π* state.[3c] But no explanation has been given to the general preference for the 13-cis isomers in retinal, substituted retinals,[3c] methyl retinoate (**1b**),[4] and aromatic retinoids[5] such as **2** (Table I).

Table I. Ratios of Primary Photoproducts from Direct Irradiation of Retinal and Related Compounds in Hexane as Solvent

compound	primary products	ratio	ref
retinal, 1a	13-cis:9-cis	3.6:1.00	2b
	13-cis:9-cis	4.0:1.00	3d
methyl retinoate, **1b**	13-cis:9-cis	6:1.00[a]	4
	13-cis:9-cis	13:1.00[b]	
10-fluororetinal, 1c	13-cis:9-cis	3.1:1.00	3b
14-fluororetinal, 1d	13-cis:9-cis:11-cis	2.3:1.00:0.26	3b
3-dehydroretinal, 1e	13-cis:9-cis	3.4:1	3b
mesitylretinal, **2a**	13-cis:9-cis	3.6:1	*c*
piperonylretinal, **2b**	13-cis:9-cis	2.3:1	*c*

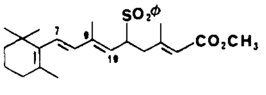
[a] In heptane. Data were those after 35–40% conversion. [b] Unpublished results of A. Singh and R. S. H. Liu. [c] This work.

High stereoselectivity has also been observed in our investigation of selective triplet-sensitized isomerization of trienes in the vitamin A series to the two 7-cis isomers.[6] The acetoxytriene ester **3a** (*t,t*) gave a final product mixture of the two 7-cis isomers in a ratio of 10:1 *in favor of the 7-cis,9-cis* (*3a* (*c,c*)) *isomer.*[7] On the other hand, the two C_{20}-sulfones (4 and **5**) gave mixtures containing 90% of respectively the 7-cis and the 7-cis,13-cis isomers.[8] No explanation could then be offered for these photo-



3 (t,t) 3 (c,t) 3 (c,c)

a, X = OAc; b, X = H



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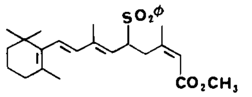

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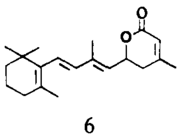

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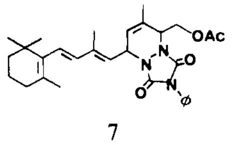

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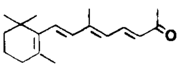

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(1) Photochemistry of Polyenes. 20. For the previous paper in the series, see ref 3c.

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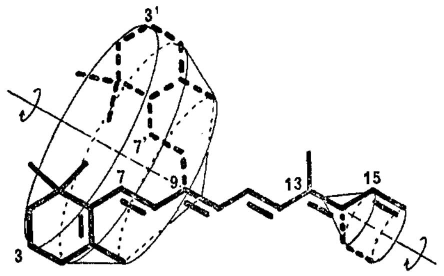

Figure 1. Different spatial requirements for the isomerization of an all-trans vitamin A derivative to 13-cis (right) and to 9-cis (left). For clarity the alternative process of rotating the right hand portion of the molecule for formation of the 9-cis isomer is not shown.

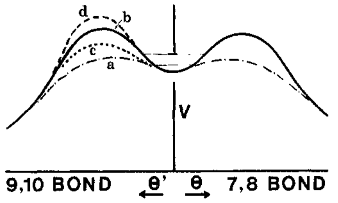

Figure 2. Medium and substituent effects on the portion of the torsional potential curve nearby planar all-trans triene triplets: (a) simple trienes (e.g., **3b**) in the absence of solvent cage induced barriers around the 9,10 (left) and the 7,8 bonds (right); (b) simple trienes with added solvent-induced barriers; (c) internally reduced barrier due to steric repulsions such as in 9-substituted triene **3a**; (d) externally increased barrier due to increased volume of activation in 10-substituted trienes **4**–**7**.

chemical results even though the observations were successfully incorporated into two stereoselective synthetic sequences for new geometric isomers of vitamin A. We have since encountered two more examples of stereoselective isomerization. Benzanthrone sensitization of compounds **6**[9] and **7**[10] gave exclusively the 7-cis isomers (by NMR).

We now believe that all these results are due to selective decay of the short-lived planar excited polyenes to different perpendicular species controlled by the medium and substituents. Medium effects on luminescent properties of compounds, including torsional barriers of the stilbenes, have been discussed by Kasha and coworkers.[11] The current discussion is in part a photochemical application of the Dellinger–Kasha model for medium effect on the excited state. In this model, viscous flow solvent cage effect is added to influence solute internal motions in the region where the potential barrier has zero slope.[11]

The relative amounts of the primary products of the 13-cis and 9-cis isomers in direct irradiation of the retinoids (Table I) are, to a large extent, a reflection of the relative ease of rotation of the 13,14 and the 9,10 "double" bonds of the planar pentaene in the excited singlet state. Rotation of the 13,14 bond requires only a small space for the relatively small end group at C-14 while rotation of the 9,10 bond requires a larger space for the much larger end groups (either end of the double bond). The two situations are depicted in Figure 1. Associated with the space requirement are the solvent induced barriers for rotation of magnitudes proportional to the number of solvent molecules to be displaced. That isomerization at the 9,10 bond should be competitively less favored appears to have been amply demonstrated by the data in Table I. The dramatic change of the 13-cis:9-cis ratio from 6.7 to 28 when irradiating *all-trans*-retinal in 3-methylpentane at 298 and 173 K reported by Waddell et al.[3e] is now accountable by the relative barrier heights for the two processes. It is also gratifying to find that for the chain-shortened C_{18}-ketone **8** the hindered 11-cis isomer is formed even in hexane (initial 11-cis:9-cis ratio = 1.5:1.00).[12] The smaller volume of activation associated with isomerization at the 11,12 bond in **8** makes rotation at the disubstituted double bond competitive with the more crowded trisubstituted 9,10 double bond.

The results for the trienes can be explained on similar grounds.[13] First, it should be mentioned that the simple triene ester **3b** (*t,t*), gave the two 7-cis isomers in a ratio only slightly in favor of the cis,cis isomer (1.9). For **2a**, while spatial requirement for rotation of the carbethoxy end group at C-10 remains unchanged, rotation at this center is facilitated by the increased steric crowding at the 9,10 bond. Since the environment around the 7,8 bond remains practically unchanged, the preferred direction of decay of the planar triplet becomes dominantly the 9,10-position. On the other hand for compounds **4**–**7**, which share the common feature of having the bulky substituent located on C-10, rotation of this reaction center now involves displacement of a larger number of solvent molecules, thus becoming relatively more difficult. Again, with no change at the alternate reaction site, the decay process now switches completely over to the 7,8 position. The observed opposite stereoselectivity is therefore quite understandable. These situations are made clear in a modified Dellinger–Kasha diagram[11b] for torsional potential curves of both double bonds (Figure 2).

While the notion of volume of activation has obvious general implication in being able to account for many results mentioned above and also other polyene systems in the literature (e.g., alloocimene,[14] 1,5-diphenylhexatrienes[15]), we hasten to add that other electronic or steric effects are also expected to have an effect on the directions of reaction of polyenes. With appropriate substituents, the latter could be more important. For example, the direction of isomerization of 1,6-diphenylhexatrienes[16] is more consistent with stability of different intermediates rather than the relatively small differences in volumes of activation. And the different ratios between retinoate ester and retinal cannot be accounted for by medium effect alone.

We might add that the motion of solvent-induced barriers of rotation has been used in discussions of photoisomerization of stilbene.[17] However, the concept has not previously been applied to account for the photochemical properties of polyenes.

Acknowledgment. We thank Professor M. Kasha for a stimulating discussion on medium effect on the excited states and in sharing his thoughts on torsional potentials. The work was supported by grants from the National Science Foundation (CHE-12686) and the U.S. Public Health Services (AM-17806). Gift samples of *all-trans*-retinal were generously supplied by Hoffmann-La Roche Inc.

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(9) Synthesized according to the procedure of Cainelli et al.: Cainelli, G.; Cardillo, G.; Contento, M.; Grasselli, P.; Umani Ronchi, A. *Gazz. Chim. Ital.* **1973**, *103*, 117–125.

(10) Prepared via Diels–Alder addition of vitamin A acetate with phenyltriazolinone.

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(12) Unpublished results of V. Ramamurthy and R. S. H. Liu; see also ref 3c.

(13) A referee expressed a legitimate concern of the applicability of such kinetic arguments to the longer lived triplets. We wish to add that while equilibration of isomeric triplets has been well established in linear dienes (Saltiel, J.; Rousseau, A. D.; Sykes, A. *J. Am. Chem. Soc.* **1972**, *94*, 5903–5905) and linear trienes,[14a] evidence does not support such a process in compounds in the vitamin A series. For example, two-bond isomerized products are generally of negligible importance (ref 12 and Waddell, W. H.; Crouch, R.; Nakanishi, K.; Turro, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 4189–4192). The absence of secondary quenching effect (Ramamurthy, V.; Liu, R. S. H. *J. Am. Chem. Soc.* **1976**, *98*, 2935–2942) further suggests that planar triplets are likely to be much higher in energy than the perpendicular triplets.

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