doublets centered at δ -9.45 with $^2J_{P(2)-H}$ = 51 and $^3J_{P(1)-H}$ = 4.0 Hz for FeH. The $^{31}P\{^1H\}$ NMR spectrum (THF, 42 °C) consists of two doublets at δ 172.3 and 37.4 (J_{P-P} = 24.4 Hz); the latter signal appears as a broad doublet ($^1J_{P(1)-H}$ = 380 Hz) in the proton-coupled ^{31}P NMR spectrum. The IR spectrum shows only terminal CO groups.[25] The corresponding **7**-d_2 was obtained similarly from Li$^+$**3**-d and excess CF_3COOD.[26] **7** may be the hydrogen analogue of a proposed intermediate in the methylation of **3** to **4**.

The aforementioned results demonstrate that **3** provides a general entry to new phosphido-bridged diiron complexes that differ from the complexes accessible from **2**.[4] We are currently investigating other reactions of **3**, including those that are directed at the synthesis of small metal clusters.

Parallel studies on reduction of $Fe_2(NO)_4(\mu-PPh_2)_2$[27] (**8**) indicate a behavior similar to that of **1**. Thus, respective reductions of **8** with $LiBEt_3H$ and Na/Hg afford solutions that show $^{31}P\{^1H\}$ NMR spectra very similar to those of **3** and **2**. Preliminary results point to new and rich chemistry of reduced **8**.[28]

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation through Grant CHE-7911882.

Registry No. 1, 19599-68-9; **2**, 72124-55-1; Li$^+$**3**, 86024-01-3; Na$^+$**3**, 86024-02-4; K$^+$**3**, 86024-03-5; **4**, 86024-04-6; **5**, 86024-05-7; **7**, 86024-06-8; **7**-d_2, 86024-07-9; $LiBEt_3H$, 22560-16-3; $NaBEt_3H$, 17979-81-6; $KBEt_3H$, 22560-21-0; $Fe_2(CO)_5(PPh_2Me)(\mu-PPh_2)_2$, 86024-08-0; CF_3COOH, 76-05-1; MeI, 74-88-4; EtI, 75-03-6; Fe, 7439-89-6.

Supplementary Material Available: Listings of final positional and thermal parameters and numbering scheme for **4** (8 pages). Ordering information is given on any current masthead page.

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[25] IR (THF) $\nu_{C\equiv O}$ 2057 (m), 2014 (s), 1995 (s), 1955 (sh) cm^{-1}.

[26] ^{31}P NMR (THF, ca. 30 °C) 172.9 (br), 38.5 (t, br, $^1J_{P-D}$ = 58.5 Hz).

[27] (a) Hieber, W.; Kummer, R. *Z. Anorg. Allgem. Chem.* **1966**, *344*, 292. (b) Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1979**, *112*, 1626.

[28] For example, reaction of $LiBEt_3H$-reduced **8** with CH_2I_2 affords $Fe_2(NO)_4(\mu-PPh_2)(\mu-PPh_2CH_2)$ and $Fe_2(NO)_4(\mu-CH_2)(\mu-Ph_2PPPh_2)$.

Transient Absorption and Two-Step Laser Excitation Fluorescence Spectra of the Excited-State and Ground-State Proton Transfer in 7-Hydroxyquinoline

Michiya Itoh,* Tomoko Adachi, and Kunihiro Tokumura

Faculty of Pharmaceutical Sciences, Kanazawa University
Takara-machi, Kanazawa 920, Japan

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The ring nitrogen of 6- and 7-hydroxyquinoline (6- and 7-HQ) is known to be more basic and the phenolic group more acidic in the excited state than in the ground state. Then, the excited-state proton transfer from the neutral form (N*) to the tautomer (T*, or zwitterion form) was reported in 6- and 7-HQ.[1] Recently, Thistlethwaite and Corkill[2] reported the nano- and picosecond fluorescnece study of the excited-state proton transfer in a methanol solution of 7-HQ. They suggested a mechanism of the proton transfer including that via the upper vibrational S_1 state. However, the transient absorption study that may provide us with valuable information on the existence of the ground-state tautomer (T) and on the proton transfer in the ground state (T → N) as well as in the excited state (N* ⇄ T*) has never been reported except for few recent papers,[3,4] though numerous investigations of the time-resolved fluorescence have been reported. Very recently, Itoh et al.[4] have reported the transient absorption spectroscopy of the excited-state and the ground-state proton transfer in the intramolecular hydrogen bonding system of 3-hydroxyflavone and 3-hydroxychromone.

The present paper describes the transient absorption kinetics of the ground-state tautomer (T) generated in the excited-state proton transfer followed by the fluorescent relaxation (N* → T* → T) of 7-HQ in the methanol solution. The recovery of the ground-state absorption bleaching of N was observed to be very consistent with the decay of the transient absorption. Furthermore, this paper demonstrates the first observation of the two-step laser excitation (TSLE) fluorescence of T*. The ground-state tautomer T generated in the excited-state proton transfer (N* → T* → T) by the first laser excitation and the second laser (dye) excitation of the T form absorption band (1-2 μs delayed from the first laser pulse) afford the TSLE fluorescence of T*.

The methanol solution of 7-HQ exhibits the dual fluorescence of N* (λ_{max} ~380 mn) and T* (λ_{max} ~530 nm) at room temperature, whose intensity ratio shows a considerable excitation energy dependence as pointed out by Thistlethwaite and Corkill.[2,5] The decay of the N* fluorescence is expressed by the double exponential (τ_1 = 2.1 ns, τ_2 = 0.20 ns) in the 340-nm excitation, while that of the T* fluorescence is expressed by the rise and decay (τ_1 = 3.0 ns, τ_2 = 0.30 ns).[6] These decay times are nearly same as those reported in the previous paper.[2] The transient absorption and bleaching of the ground-state absorption of this 7-HQ solution were measured by a conventional excitation laser and monitoring flash lamp system.[7] The considerably strong absorption spectrum was observed at λ_{max} 420 nm, as shown in Figure 1. The decay time of the absorption was determined to be 3.5 μs in the aerated solution. Since the decay time of 3.5 μs was invariant in deaeration and the lifetimes of N* and T* were as short as subnanoseconds, this transient absorption may be attributable to the ground-state tautomer T generated by the excited-state proton transfer and fluorescent relaxation. Further, the ground-state absorption bleaching and recovery were also observed. The recovery time was determined to be 3.6 μs, which is invariant in deaeration. These facts reveal the mechanism of the excited-state and also the ground-state proton transfer.

If the long-lived absorption band of T observed in this paper is exclusively excited within the lifetime by the second pulse (dye) laser at 1-2 μs delayed from the first laser excitation, the T* fluorescence (TSLE) decay and spectrum should be observed. A home-made N_2 laser (fwhm ~7 ns, peak power ~500 kW, and repetition rate ~1 Hz) was used as the first excitation laser. In order to remove the effect of a jitter of the first laser pulse, a pin photodiode and a delay circuit were used for the trigger signal to operate the second N_2 laser-pumped dye laser (Molectron UV-12 and DL-14). The ground state tautomer T of 7-HQ was generated by the first pulse and the transient absorption band of T was excited by the second dye laser pulse (420-450 nm) at 1.2 μs delayed from the first one. The fluorescence signal was detected by a monochromator-photomultiplier-oscilloscope system, where the oscilloscope was externally triggered by the second laser signal optically detected. This two-step laser excitation (TSLE) fluorescence spectrum of 7-HQ was measured as shown in Figure 1. The TSLE fluorescence spectrum is identical with the ordinary fluorescence spectrum observed in the excitation of the N form absorption band. The TSLE fluorescence excited at 440 nm was observed to exhibit a single-exponential decay (τ = ~3.0 ns) without fluorescence rise, while the ordinary fluorescence shows a rise (0.3 ns) and decay (3.0 ns) in the N form excitation mentioned above. These facts confirm that the transient absorption at 400-450 nm is attributable to T and demonstrate that the TSLE

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[1] Mason, S. F.; Philp, J.; Smith, P. E. *J. Chem. Soc. A* **1968**, 3051.

[2] Thistlethwaite, P. J.; Corkill, P. J. *Chem. Phys. Lett.* **1982**, *85*, 317.

[3] Huston, A. L.; Scott, G. W.; Gupta, A. J. *J. Chem. Phys.* **1982**, *76*, 4978.

[4] Itoh, M.; Tanimoto, Y.; Tokumura, K. *J. Am. Chem. Soc.* **1983**, *105*, 3339.

[5] They suggested several possibilities for the reason of the excitation-energy dependence of the fluorescence intensity ratio of N* and T* and of the controversy between the expected rapid proton transfer competing with the vibrational relaxation and the slow proton transfer (rise of T*) observed. However, the excitation-energy dependence is not properly interpreted at the present stage, though the predominant reaction scheme of the excited-state proton transfer and relaxation [1,2] may be correct.

[6] The fluorescence decay was determined by using a single-photon counting system (Ortec) and a nanosecond pulser (PRA 510). The data were obtained by a computer-simulated deconvolution.

[7] Tanimoto, Y.; Itoh, M. *Chem. Phys. Lett.* **1981**, *83*, 626.

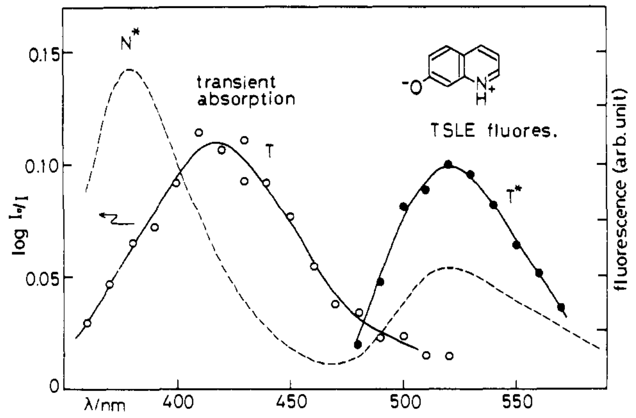

Figure 1. Transient absorption spectrum (○) of a methanol solution of 7-HQ (7×10^{-5} M) depicted at a 500-ns delay after a laser excitation. The light path length is 5 mm. The TSLE fluorescence spectrum (●) of a 7-HQ solution (4.3×10^{-4} M) was excited by 440-nm pulse at 1.2 μs delayed from the first 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.

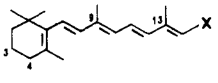
Medium- and Substituent-Directed Stereoselective Photoisomerization of Polyenes in the Vitamin A Series. Application of the Dellinger-Kasha Model[1]

R. S. H. Liu,* A. E. Asato, and M. Denny

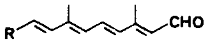
Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

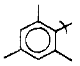
Received January 1, 1983

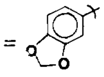
The solvent-dependent photoisomerization of retinal, **1a** by



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 =


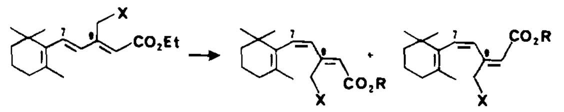
direct irradiation is a well-known phenomenon that has received considerable attention in terms of both its synthetic value[2] and mechanistic understanding.[3] On the other hand, very little attention has been paid to the regioselectivity of such reactions. For example, formation of isomers in hexane 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*

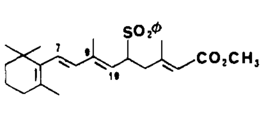
[a] In heptane. Data were those after 35–40% conversion. [b] Unpublished results of A. Singh and R. S. H. Liu. [c] This work.

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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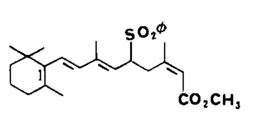

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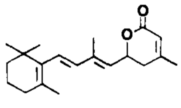

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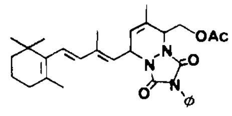

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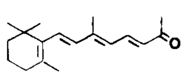

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[1] Photochemistry of Polyenes. 20. For the previous paper in the series, see ref 3c.

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