# PRIMARY PHOTOCHEMICAL AND PHOTOPHYSICAL PROCESSES IN 2,2,4-TRIMETHYL-1,2-DIHYDROQUINOLINES

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## Summary

The quantum yield for the photodissociation of 2,2,4-trimethyl-1,2-dihydroquinolines in non-polar solvents increases from 0.01 - 0.04 (for excitation into the $S_1$ band) to 0.2 - 0.4 (for excitation into the $S_2$ band), while the quantum yield for fluorescence decreases. It is deduced that the photodissociation of 2,2,4-trimethyl-1,2-dihydroquinolines occurs from higher triplet states which are populated by intersystem crossing from the $S_2$ state.

## 1. Introduction

2,2,4-trimethyl-1,2-dihydroquinolines possess remarkable photochemical properties. On the one hand, photoirradiation of their solutions in $CHCl_3$ or $CCl_4$ results in a bright blue colour (Fig. 1) which disappears under the action of visible light. This effect may be due either to breakage of the C—N bond and formation of an *o*-quinonaldine structure [1, 2] which is responsible for the photochromic behaviour
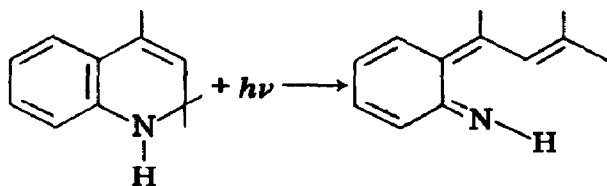


of these species or to a phototransfer of an electron from an excited dihydroquinoline molecule to $CHCl_3$, followed by radical chain addition of $\dot{C}Cl_3$ to positions 4, 6 or 8 with the formation of a conjugated chain, by a mechanism similar to that of photolysis of diphenylamines in $CCl_4$ [3].

The radical chain mechanism of the photocolouration of dihydroquinolines manifests itself in the observation that colouration continues for several minutes after illumination is stopped. This leads to the growth of the
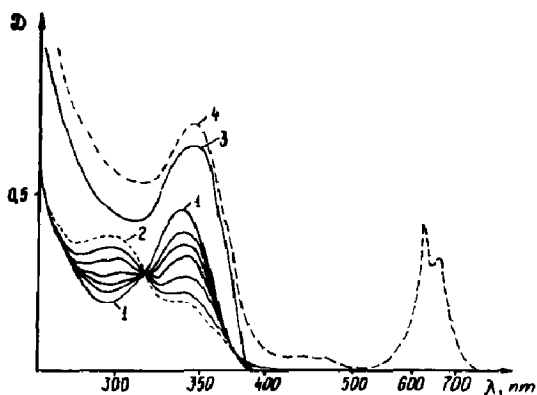
Fig. 1. Absorption spectra of 2,2,4-trimethyl-1,2-dihydroquinoline I in the absence of oxygen in heptane (concentration, $1.97 \times 10^{-4}$ M) before (curve 1) and after (curve 2) irradiation and in $CCl_4$ (concentration, $2.75 \times 10^{-4}$ M) before (curve 3) and after (curve 4) irradiation.

band in the visible region, which would not be observed for any non-chain reaction, including C—N bond cleavage. These observations support the radical chain mechanism [3].

On the other hand, we have found earlier [4 - 7] that photoirradiation of dihydroquinolines with low electron acceptor properties gives rise to dissociation of the N—H bond so that hydrogen atoms and aminyl radicals which are capable of dimerization to hydrazines are formed (Fig. 2).

It should be noted that the use of dihydroquinolines as antioxidants for unsaturated compounds [4] results from the formation of inactive aminyl radicals when a hydrogen atom is lost by the action of peroxide radicals.

In the present paper the mechanism of photodissociation of 2,2,4-trimethyl-1,2-dihydroquinolines I - V, the nature of their photochemically active excited state and the role of photodissociation in the system of radiative and non-radiative pathways of degradation of electronic excitation energy are considered.

Since photodissociation occurs according to a non-adiabatic mechanism, as a predissociation process, and the time of the elementary process is short (about $10^{-13}$ s) compared with the lifetime of the excited state, this reaction may be formally regarded as a means of degradation of the excited state energy [8]:

$$S_1 \longrightarrow S_0 \tag{1}$$

$$S_1 \longrightarrow S_0 + h\nu \tag{2}$$

$$S_1 \longrightarrow T_1 \tag{3}$$

$$S_1 \longrightarrow products \tag{4}$$

$$S_2 \longrightarrow S_1 \tag{5}$$

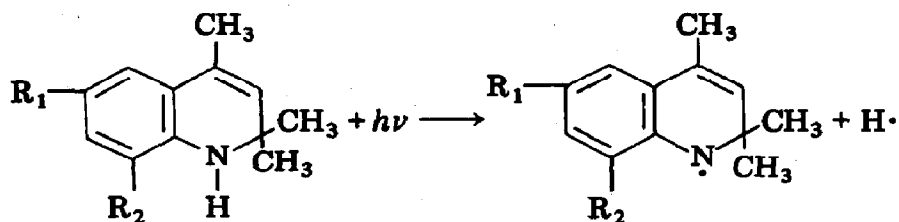$$S_2 \longrightarrow products \tag{6}$$

Fig. 2. Photodissociation of the dihydroquinolines (I, $R_1 \equiv H$, $R_2 \equiv H$; II, $R_1 \equiv C_2H_5O$, $R_2 \equiv H$; III, $R_1 \equiv OH$; $R_2 \equiv H$; IV, $R_1 \equiv CH_3$, $R_2 \equiv H$; V, $R_1 \equiv H$, $R_2 \equiv CH_3$).

$$S_2 \longrightarrow T_n \tag{7}$$

$$T_n \longrightarrow \text{products} \tag{8}$$

Then

$$\varphi_n{}^{S_1} = \frac{k_2}{k_1 + k_2 + k_3 + k_4}$$

$$\varphi_n{}^{S_2} = \frac{k_5}{k_5 + k_6 + k_7}\,\varphi_n{}^{S_1}$$

where $\varphi_n{}^{S_1}$ and $\varphi_n{}^{S_2}$ are the quantum yields for fluorescence on irradiation in the first and in the second absorption band respectively.

To establish all the pathways for radiative and radiationless deactivation of the excited states of organic molecules in solution, which obey Kasha's rule, it it necessary to determine the lifetimes of the lower excited singlet and triplet states as well as the quantum yields for the elementary processes taking place in these states such as fluorescence, intersystem crossing (ISC), internal conversion and photodissociation (or some other photochemical reaction).

With dihydroquinolines it is particularly difficult to determine the quantum yields of short-lived radicals, since data on the absorption coefficients for such radicals are usually not available. Hence our first concern was to find a means of determining the absorption coefficients of aminyl radicals, which enabled us to determine the quantum yields for photodissociation of the dihydroquinolines. Such findings regarding these species and amines in general have not been reported so far.

## 2. Experimental details

The absorption spectra and the decay kinetics of short-lived intermediates were investigated using a pulse photolysis instrument with a resolution time of 5 $\mu$s [9]. The lifetimes of the lowest singlet states were determined by means of single-photon counting [10]. The fluorescence spectra were recorded with an Aminco Bowman spectrofluorometer and the absorption spectra with a Specord UVIS spectrophotometer. The electron spin resonance

(ESR) signals were studied using an EPR-2 radiospectrometer. Stationary irradiation was performed using a DRSh mercury lamp.

The quantum yields for fluorescence of several dihydroquinoline derivatives in various solvents were inferred from the ratio of the lifetimes of the $S_1$ excited states, determined using pulse fluorometry, to the radiative lifetimes of these states, calculated from the Strickler−Berg formula [11] (Table 1).

The quantum yields for ISC were determined as in ref. 12 using a reference donor (carbazole [13]) and an acceptor of triplet energy (rubrene) (Fig. 3). Flash photolysis was used to obtain relative measurements of the concentration of rubrene triplet molecules and the decay kinetics of the triplet states of carbazole and the 1,2-dihydroquinolines during triplet-triplet energy transfer from these species to rubrene. Photoexcitation of the triplet energy donor was performed through a combination of filters (UFS-8 and SS-9) to avoid excitation of rubrene (Fig. 4).

$$\varphi_1 = \frac{\varphi_2[^3A_1]N_{D_2}\alpha_2}{[^3A_2]N_{D_1}\alpha_1}$$

where the subscripts 1 and 2 refer to the dihydroquinolines and carbazole respectively, $\varphi$ is the quantum yield for ISC, $[^3A]$ is the concentration of the acceptor (rubrene) triplet molecules, $N_D$ is the number of photons absorbed by the donor and $\alpha$ is the efficiency of the triplet-triplet energy transfer from the donor to the acceptor.

The following technique was employed for the determination of the absorption coefficients of short-lived radicals.

Photoirradiation of frozen solutions of 1,2-dihydroquinolines (at 77 K) results in aminyl radicals [4]. Their absorption spectra coincide with those of aminyl radicals obtained by flash photolysis in liquid solutions of 1,2-

TABLE 1

Radiative lifetimes $\tau_r$ and quantum yields $\varphi$ for fluorescence of the 2,2,4-trimethyl-1,2-dihydroquinolines

| Compound | Radiative lifetimes and quantum yields in the following solvents | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | Benzene | | Toluene | | Heptane | | |
| | $\tau_r$ (ns) | $\varphi$ [a] | $\varphi_r$ (ns) | $\varphi$ [a] | $\tau_r$ (ns) | $\varphi$ [a] | $\varphi$ [b] |
| I | 6.78 | 0.31 | — | — | 4.5 | 0.25 | 0.23 |
| II | 8.44 | 0.33 | 8.7 | 0.32 | 5.0 | 0.23 | 0.21 |
| III | 8.80 | 0.39 | — | — | 6.0 | 0.23 | — |
| IV | 7.62 | 0.35 | — | — | — | — | 0.205 |
| V | 7.62 | 0.24 | — | — | — | — | — |

$\lambda_{exc}$ = 365 nm.
[a] Calculated from $\varphi = \tau_{0m}/\tau_{0c}$, where $\tau_{0m}$ is the measured lifetime of the ground state and $\tau_{0c}$ is the lifetime calculated from the absorption spectra.
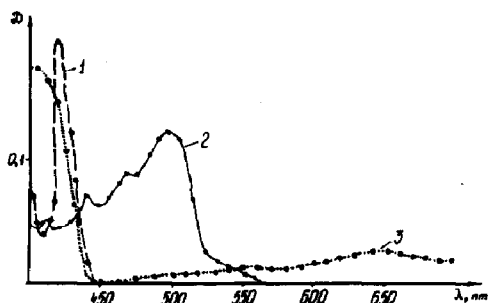[b] Determined by comparison with quinine bisulphate.

Fig. 3. Triplet–triplet absorption spectra of benzene solutions of carbazole (curve 1), rubrene (curve 2) and IV (curve 3).
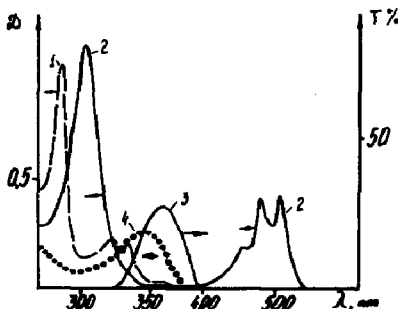
Fig. 4. Absorption spectra of solutions of carbazole ($1.2 \times 10^{-3}$ M) (curve 1), rubrene ($3.9 \times 10^{-5}$ M) (curve 2) and IV ($7.4 \times 10^{-5}$ M) (curve 4). The transmission spectrum of an UFS-8 + SS-9 filter combination is also shown (curve 3).
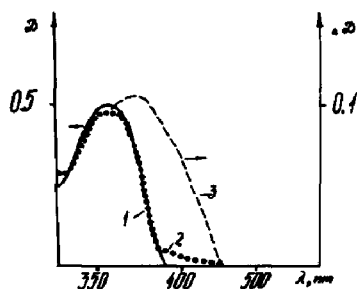


Fig. 5. Absorption spectra of IV (concentration, $4.1 \times 10^{-4}$ M) in methylcyclohexane before (curve 1) and after (curve 2) irradiation at 77 K and the spectrum of the short-lived intermediate (curve 3) in methylcyclohexane at 20 °C obtained by flash photolysis.

dihydroquinolines at 20 °C (Fig. 5). As shown by ESR, at 77 K aminyl radicals are virtually stable. On melting, the radicals decay and the initial absorption spectrum of the starting compound is restored.

By measuring the optical density of the samples at 77 K before and after irradiation and simultaneously determining the absolute concentration of aminyl radicals in the same cells by ESR it was possible to calculate the absorption coefficients of the aminyl radicals formed from the dihydroquinolines (Table 2).

TABLE 2

Absorption coefficients $\epsilon$ of aminyl radicals resulting from the photolysis of the 2,2,4-trimethyl-1,2-dihydroquinolines in methylcyclohexane at 77 K

| Compound | $\epsilon$ (M$^{-1}$ cm$^{-1}$) |
|---|---|
| I | 7500 |
| IV | 5000 |
| V | 3000 |

**TABLE 3**

Quantum yields for intersystem crossing, formation of aminyl radicals and disappearance of dihydroquinolines of the 2,2,4-trimethyl-1,2-dihydroquinolines on excitation in different absorption bands

| Compound | Quantum yields for excitation in the following regions | | | |
|---|---|---|---|---|
| | 340 - 360 nm | | | 200 - 280 nm |
| | $\varphi_{ISC}$ [a] | $\varphi_{radical}$ [a] | $\varphi_{dis}$ [b] | $\varphi_{dis}$ [b] |
| I | 0.02 | 0.011 | — | — |
| II | 0.014 | — | — | — |
| III | 0.017 | — | 0.023 | 0.42 |
| IV | 0.012 | 0.016 | 0.021 | 0.15 |
| V | — | 0.012 | 0.021 | 0.17 |

[a] In benzene.
[b] In heptane.

The quantum yields for the formation of the aminyl radicals were determined by pulse photolysis on the assumption that the absorption coefficients of the radicals obtained at 77 K change insignificantly as the temperature is increased to 293 K. A reference sample with a known quantum yield for photochemical conversion was a 6-nitroindolinespiropyran [14, 15]. Photoexcitation was performed at 365 nm through UFS—SS-9 filters. The optical density of the samples at this wavelength did not exceed 0.3. The results are presented in Table 3.

The quantum yields for the photodecomposition of the 1,2-dihydroquinolines were determined for irradiation in different absorption bands of these compound. The long wavelength band was isolated using a UFS-1—ZhS-2O filter and the short wavelength band was excited through a chlorine filter (length, 5 cm; pressure, 1 atm) (Fig. 6). In a preliminary study it was shown that the irreversible products of photolysis of 1,2-dihydroquinolines are the same whichever band is excited. The light intensity of the mercury lamp at the front and rear window of the sample cell was measured using a ferrioxalate actinometer [16]. The optical density at the irradiation wavelength was not higher than 0.3. The concentration of the dihydroquinolines was measured from the fluorescence intensity of the starting compounds, since the absorption spectra of the dihydroquinolines and the products of their photolysis overlap (Fig. 7).

The excitation anisotropy spectra were measured from 183 to 143 K in $n$-pentane using a multifunctional Jasny spectrofluorometer [17]. The relative fluorescence intensity $R$ at the wavelength corresponding to a maximum was determined. The instrumental polarization was eliminated by measuring the relative fluorescence at four orientations of the polarizer and the analyser. Thus
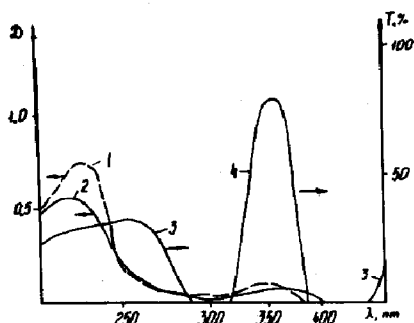
$$R = \frac{VV - VH \times HV/HH}{VV + 2VH \times HV/HH}$$

Fig. 6. Absorption spectra of **IV** (concentration, $6.1 \times 10^{-5}$ M) (curve 1) and **III** (concentration, $3.9 \times 10^{-5}$ M) (curve 2) and transmission spectra of a chlorine filter (length, 5 cm; pressure, 1 atm) (curve 3) and of a UFS-1–ZhS-2O combination of filters (curve 4).
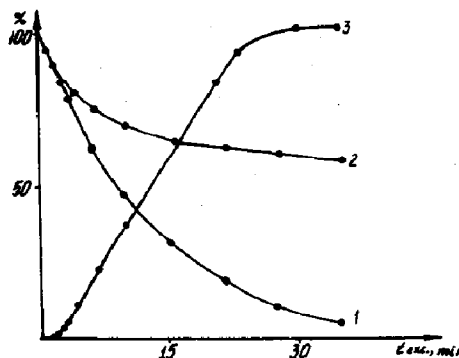
Fig. 7. Variations in the fluorescence (curve 1) and in the absorption of **I** in heptane at 340 nm (curve 2) and 390 nm (curve 3) under constant irradiation (filter, UFS-5).

where V represents a vertical orientation and H a horizontal orientation and the first letter of each of the pairs denotes the orientation of the polarizer and the second letter denotes the orientation of the analyser.

## 3. Results and discussion

As we demonstrated earlier, photoirradiation of solutions of the 1,2-dihydroquinolines I - V results in dissociation of the N—H bond and formation of aminyl radicals [4 - 7] which decay primarily by dimerization.

Oxygen does not affect the quantum yield for the formation of radicals. In its absence, however, dihydroquinolines display intense triplet–triplet absorption (Fig. 3). Obviously, the photodissociation does not proceed via the lowest triplet state.

On irradiation in the long wavelength absorption band the quantum yield for the formation of radicals is almost identical with that of photodecomposition of the dihydroquinolines. It appears therefore that the dihydroquinolines are consumed exclusively by conversion into radicals.

A most unexpected feature typically exhibited by all the dihydroquinolines studied was that on irradiation in the second absorption band the fluorescence quantum yield decreased by approximately a factor of 2 ($\varphi_{\mathrm{fl}}^{S_2}/\varphi_{\mathrm{fl}}^{S_1} = 0.55$ in 3-methylpentane; $\varphi_{\mathrm{fl}}^{S_2}/\varphi_{\mathrm{fl}}^{S_1} = 0.66$ in propanol), *i.e.* Kasha's rule was broken. This may be due to a photochemical reaction which is capable of competing with internal conversion into the $S_1$ state or due to ISC into a $T_n$ state (probably followed by a reaction from this or from a lower triplet state). The sharp increase (by a factor of 10 - 20) in the quantum yield for decomposition of the dihydroquinolines by irradiation in the second band and the concurrent decrease in the fluorescence intensity result from competition at the $S_2$ level between the photodissociation pathway and internal conversion to $S_1$.

The increase in the quantum yield for photodissociation with increasing excitation energy can by no means result from the increase in the kinetic energy of the hydrogen atoms since (i) no cage effect exists for hydrogen atoms [18] and (ii) calculations according to the Noyes formula for amines [19] show that the increase in the quantum yield for photodissociation as the excitation wavelength changes from 360 to 250 nm cannot exceed 50% (which is the value calculated for a diatomic molecule). (For polyatomic molecules 50% is the upper limit.)

Information on the excited states of aromatic amines including 1,2-dihydroquinolines is scarce. No convincing interpretation of the absorption spectra or of the nature of the luminescent state has been offered in this case, and the situation with indole is probably the best example.

The high absorption coefficients, the long natural fluorescence lifetimes (8 - 10 ns) and the bathochromic shifts in polar solvents suggest that the long wavelength absorption band of the dihydroquinolines belongs to the $1 \rightarrow a_\pi$ transition of an electron from the lone pair orbital of the nitrogen (which is already in the ground state and conjugated with the ring) to the $\pi^*$ orbital of the ring (the $^1L_b \leftarrow {}^1A_1$ transition in Platt notation). The dipole moment of a singlet $1 \rightarrow a_\pi$ transition always lies in the molecular plane. The fluorescence excitation polarization spectra indicate that the polarization of the long wavelength band of the dihydroquinolines is positive, and around the 0,0 transition it is near the limiting value, while the second absorption band is polarized negatively (Fig. 8). The second band is undoubtedly the $^1L_a \rightarrow {}^1A_1$ band of styrene which is of $\pi,\pi^*$ character, i.e. polarized in the molecular plane.

Clearly, excitation of the transition localized on the benzene ring cannot lead directly to rupture of the N—H bond, since excitation of the $^1L_b \leftarrow {}^1A_1$ transition of an aromatic system does not affect the bond lengths in the aromatic ring substituents [20].

Moreover, Plotnikov and Ovchinnikov [21] demonstrated that the repulsive term of the C—H bond (and, more generally, of any highly anharmonic X—H bond) is a triplet, so that a hydrogen atom should be lost primarily from the triplet state [22].



Fig. 8. Excitation anisotropy spectrum of an $n$-pentane solution of IV at 163 K.

We believe that, by excitation to the $S_2$ state, photodissociation of the N—H bond in dihydroquinolines occurs exclusively from a triplet non-bonding (Rydberg?) state achieved by ISC from the second excited singlet state since, judging by the energies of the Rydberg states in the gas phase, they are situated sufficiently high in energy and may only be efficiently populated from the second excited singlet state of 1,2-dihydroquinolines.

ISC from the second singlet state may successfully compete with the internal conversion $S_2 \leadsto S_1$ since even for molecules with a much smaller gap between the $S_2$ and the $S_1$ level (9,10-dibromoanthracene) internal conversion is slow enough to be dependent on the heavy atom [23].

The pattern of photodissociation of 1,2-dihydroquinolines from the upper excited triplet state is in good agreement with that of two-photon photodissociation of amines in frozen solutions at 77 K [24], where higher triplet states are also involved (in these experiments they were reached by absorption of a second photon in a long-lived $T_1$ state rather than by ISC from the $S_2$ state).

## 4. Conclusion

The photodissociation of the N—H bond in 1,2-dihydroquinolines, which results in hydrogen atoms and aminyl radicals, proceeds preferentially via higher triplet states.

## Acknowledgment

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