

FLASH PHOTOLYSIS STUDY OF TRIPHENYLMIDAZOLE

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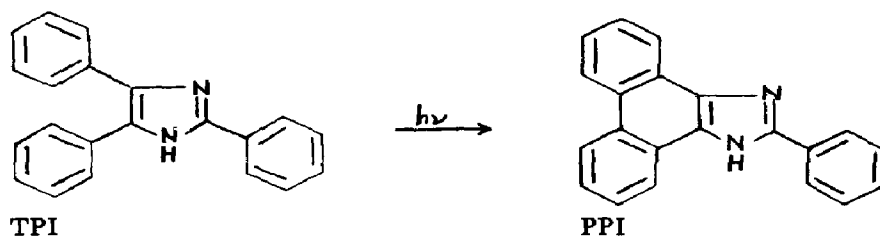
(Received July 22, 1986; in revised form September 18, 1986)

Summary

Flash excitation of triphenylimidazole in degassed isopropyl alcohol gives rise to a transient assigned as the dihydrophenanthroimidazole, which has a lifetime of 1.5 ms and exhibits absorption peaks at 350 and 550 nm. Variable temperature studies in the range 25 to -80°C indicate that the photocyclization occurs throughout this range; however, the lifetime of the dihydrophenanthroimidazole increases by a factor of 10 upon cooling. The dihydrophenanthrene from *cis*-stilbene in air-saturated isopropyl alcohol has a significantly longer lifetime of about 9 s. The relative insensitivity of the fluorescence yield of triphenylimidazole to solvent changes suggests that the photocyclization via the singlet state is unimolecular, does not involve hydrogen abstraction and does not require oxygen. The low photochemical quantum yield efficiency for conversion to 2-phenyl-9,10-phenanthroimidazole is believed to arise from the efficient reversion of the dihydrophenanthroimidazole back to the starting molecule.

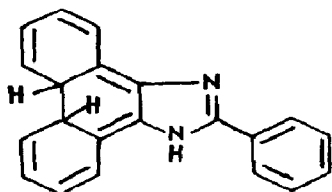
1. Introduction

In a previous study from this laboratory we demonstrated that the photocyclization of 2,4,5-triphenylimidazole (TPI) proceeds in degassed solutions to produce 2-phenyl-9,10-phenanthroimidazole (PPI) [1]



Since this process is related to the photocyclization of *cis*-stilbene to phenanthrene via *4a,4b*-dihydrophenanthrene [2, 3], and we were unable to observe the dihydrophenanthroimidazole (DHPI) with TPI, we initiated a flash photolysis study of this molecule in different solvents and at various

temperatures. Specifically, the aim was to search for the DHPI intermediate and to determine some of the factors controlling this photochemical process.



DHPI

The quantum yield for the photocyclization of TPI to PPI in degassed solvents is about 10^{-3} [1]. Since the reaction is known to proceed via the singlet state, the influence of solvent on the fluorescence of this molecule was also examined to see if its photochemistry involves bimolecular or charge transfer effects. It was recently shown that amines can lead to tautomerism of dihydrophenanthrenes [3, 4].

2. Experimental details

2.1. Materials

TPI obtained from Chemical Dynamics Corp. was recrystallized twice from ethyl alcohol to yield a colorless powder. 4,5-Diphenylimidazole was recrystallized from benzene and then ethyl alcohol to yield white needles. *cis*-Stilbene was obtained from Aldrich Chemical Co. and used without further purification. Spectrograde acetonitrile, isopropyl alcohol and ethyl ether were used as received.

2.2. Apparatus

A conventional 20 μ s xenon flash photolysis system operating at 180 J flash⁻¹, described elsewhere [5], was used in this study. Measurements in flash cells 10 cm long were made for air-saturated and vacuum-degassed solutions. Samples were degassed by four freeze-pump-thaw cycles at 2×10^{-4} Torr and then flame sealed from the vacuum line. UV absorption spectra were measured with a Cary Model 14 spectrophotometer and the fluorescence yields were measured relative to the value of 0.09 for D,L-tryptophan at pH 6.5 [6]. Variable temperature flash measurements were performed by cooling the sample, which was mounted in an optical Dewar, with liquid nitrogen and the temperature was monitored with an iron-constantan thermocouple.

3. Results

3.1. Room temperature flash studies

The flash photolysis of 6.0×10^{-5} M TPI in degassed acetonitrile gives rise to a transient absorption exhibiting peaks at 350 and 550 nm, with

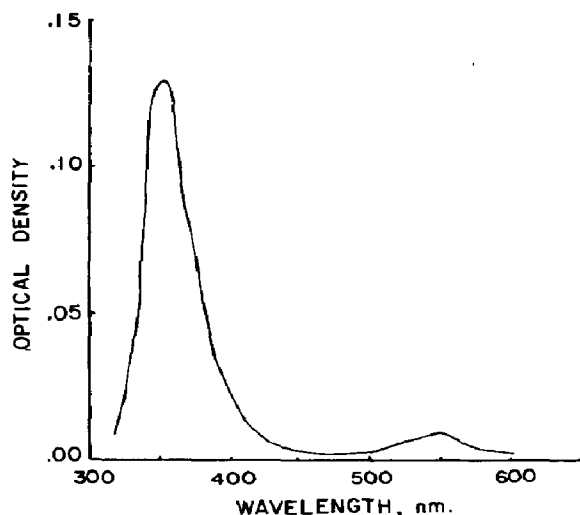


Fig. 1. Transient absorption with lifetime of 1.2 ms observed in the flash photolysis of 6.0×10^{-5} M TPI in degassed acetonitrile.

the optical density of the former significantly larger than that of the latter. The lifetime of the transient is 1.2 ms and follows first-order kinetics. The transient spectrum (Fig. 1) is also observed in isopropyl alcohol and ethyl ether. The lifetime is 1.5 ms in isopropyl alcohol.

Evidence for the aromatic photoproduct PPI is readily apparent from the absorption spectral changes following flashing. In Fig. 2 we see the disappearance of TPI in air-saturated isopropyl alcohol after 10 and 50 flashes, and the growing in of the PPI photoproduct absorbing at 254 nm. In order to relate the transient absorption in Fig. 1 to that of *4a,4b*-dihydrophenanthrene from *cis*-stilbene we also performed the flash photolysis of the latter. Flashing an air-saturated solution of 2.69×10^{-5} M *cis*-stilbene in isopropyl alcohol gives rise to a long-lived absorption at 450 nm with a

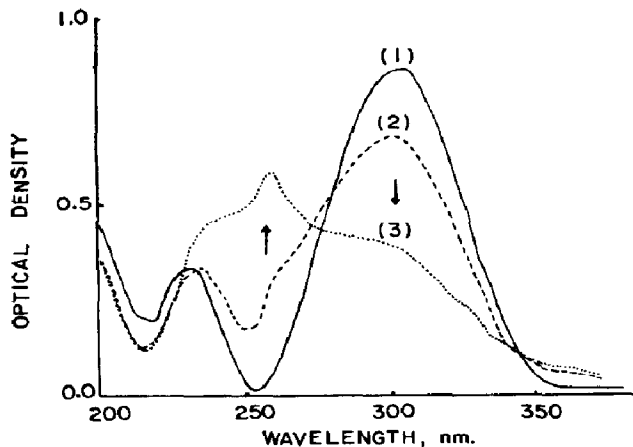


Fig. 2. UV absorption changes resulting from the flash photolysis of 4.0×10^{-5} M TPI in air-saturated isopropyl alcohol: (1) initial scan; (2) after 10 flashes; (3) after 50 flashes.

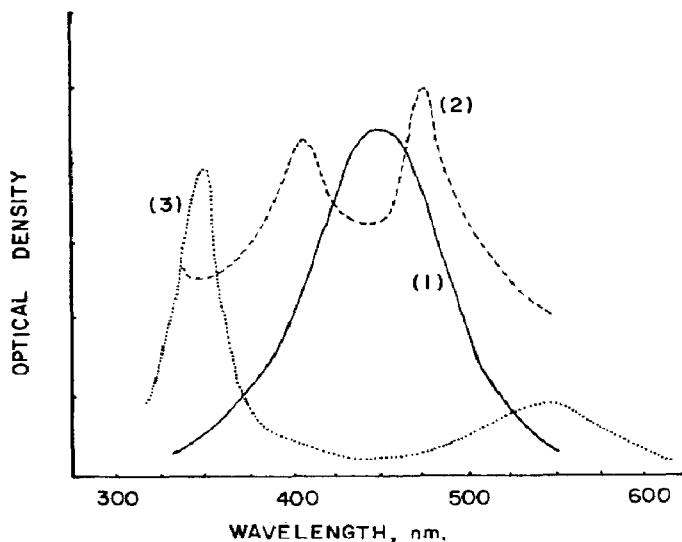


Fig. 3. Transient absorption spectra and lifetimes observed for flash photolysis in air-saturated isopropyl alcohol solutions: (1) *cis*-stilbene, $\tau = 9$ s; (2) DPI, $\tau = 1.2$ ms; (3) TPI, $\tau = 1.4$ ms.

lifetime of about 9 s, which is known to be that of the dihydrophenanthrene intermediate [7], which can oxidize further to phenanthrene. The corresponding DHPI transient observed in air-saturated 4,5-diphenylimidazole (DPI) in isopropyl alcohol has a lifetime of 1.2 ms, similar to that of TPI. The transient spectra observed for TPI, *cis*-stilbene and DPI are summarized in Fig. 3.

3.2. Variable temperature studies

The effect of temperature on the transient species from TPI was investigated in degassed isopropyl alcohol for the range +25 to -80 °C. As one might expect, the optical densities decrease and the lifetime increases in this range. At -80 °C the transient spectrum observed is the same as that shown in Fig. 1. The temperature dependence of the optical densities of the 350 and 550 nm transient bands is shown in Fig. 4, where it is seen that the photocyclization efficiency decreases with temperature and appears to level off at -40 °C. These results indicate that there are two paths for ring fission of the dihydrophenanthrene back to TPI: (1) thermal ring fission which becomes unimportant below -20 °C and (2) photochemical ring fission which still occurs below -40 °C. The temperature dependence of the rate constant for the transient disappearance is shown in Fig. 5, where the Arrhenius plot gives an activation energy of 2.6 kcal mol $^{-1}$ and a frequency factor of 5.9×10^4 s $^{-1}$.

3.3. Fluorescence behavior

The fluorescence yields of TPI measured in cyclohexane, ethyl ether and ethyl alcohol, using 285 nm excitation, are summarized in Table 1.

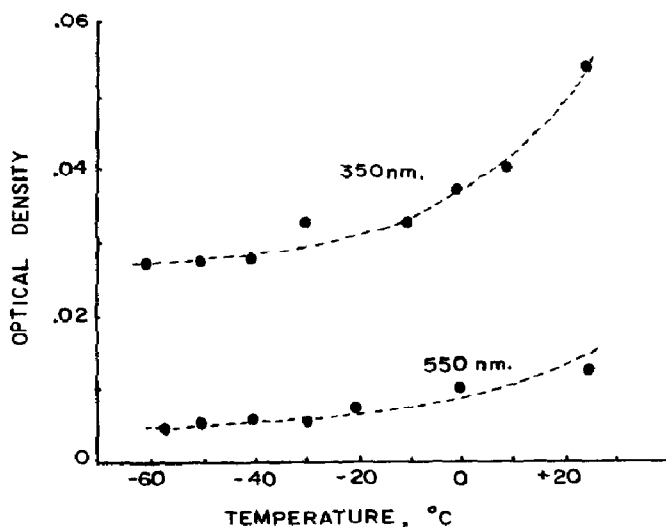


Fig. 4. Temperature dependence of the optical density at 350 and 550 nm from the DHPI intermediate in the flash photolysis of 4.0×10^{-5} M TPI in degassed isopropyl alcohol.

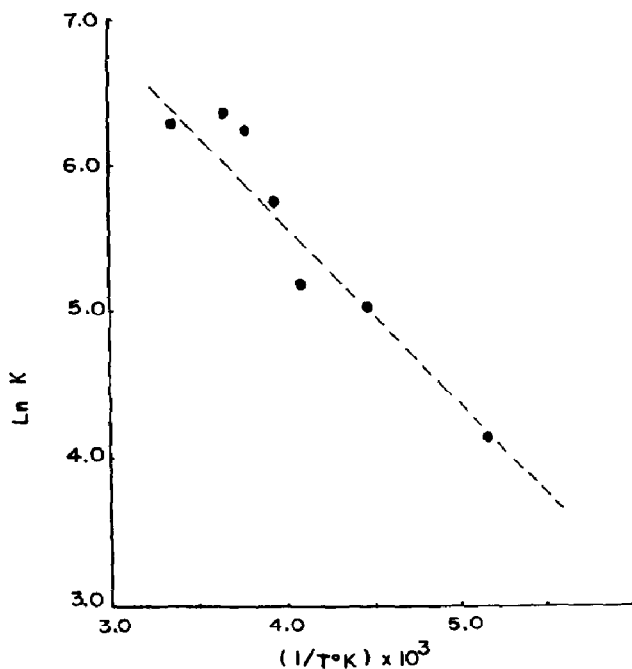


Fig. 5. Arrhenius plot of the decay rate constant for DHPI, measured at 350 nm, formed in the flash photolysis of TPI in degassed isopropyl alcohol.

The relative insensitivity of the fluorescence of TPI to the polarity of the solvent suggests that it does not play a major role in the photocyclization. The shift of the emitting singlet to higher energies in 0.1 M HCl is due to protonation of the pyridine-type lone pair in the heterocyclic ring.

TABLE 1

UV absorption and fluorescence of triphenylimidazole (285 nm excitation, air saturated)

	$\lambda_{\max}^{\text{abs}}$	$\epsilon \times 10^{-3}$	Φ_F^a	$\lambda_{\max}^{\text{fl}}$	$0-0$ ($\times 10^{-3} \text{ cm}^{-1}$)
Cyclohexane	308	27.4	0.22	380	29.2
Diethyl ether	308	28.3	0.22	379	29.1
Ethanol	304	27.4	0.19	380	29.4
0.1 M HCl	290	—	0.27	399	28.6

^a Φ_F values normalized to 0.09 for D,L-tryptophan at pH 6.5.

TABLE 2

Summary of absorption and fluorescence data for phenylimidazoles in ethyl alcohol

	λ_{\max} (nm)	$\epsilon_{\max} \times 10^{-3}$	Φ_F
2-Phenylimidazole	272	19.4	0.36
4,5-Diphenylimidazole	285	14.1	0.09
2,4,5-Triphenylimidazole	304	27.4	0.19

The absorption and fluorescence characteristics of substituted imidazoles show a dependence on the position and number of substituted phenyl rings. The data summarized in Table 2 for 2-phenylimidazole, 4,5-diphenylimidazole and TPI indicate a twofold increase in the extinction coefficient of TPI in its lowest excited singlet relative to the other two molecules, and a progressive shift to lower energies with phenyl substitution.

4. Discussion

The relative insensitivity of the transient absorption appearing at 350 and 550 nm for TPI in the three degassed solvents investigated suggests that the photocyclization is a relatively clean unimolecular process and that the transient is due to the DHPI intermediate. This assignment is further supported by the fact that DPI also gives the corresponding dihydrophenanthrene with a millisecond lifetime in air-saturated and vacuum-degassed isopropyl alcohol. Comparison of its absorption with that of the 4*a*,4*b*-dihydrophenanthrene, seen in the photocyclization of *cis*-stilbene or diphenylcyclopentene [7], indicates two significant differences. Noteworthy is that the decay of the dihydrophenanthrene in DPI and TPI is three to four orders of magnitude faster than the corresponding transient in the photocyclization of *cis*-stilbene. This dramatic change in lifetime may be due to the lone pair on the ring nitrogen which could induce proton transfers and tautomerism, or to a spontaneous loss of molecular hydrogen,

since the solutions are vacuum degassed and the transient lifetimes for vacuum-degassed and air-saturated solutions are similar. We believe that the reaction of DHPI with oxygen is slow compared with the more rapid loss of hydrogen and ring fission, *i.e.* the lifetime of the dihydrophenanthrene from TPI is not dominated by its reaction with oxygen as is the case with the dihydrophenanthrene from *cis*-stilbene. The band splitting of about 4000 cm^{-1} seen in the transient spectrum (Fig. 3) when comparing *4a,4b*-dihydrophenanthrene to the DHPI of DPI is presumably due to the energy splitting caused by the two ring nitrogens. An increased splitting is seen in the TPI transient spectrum, which is probably manifested by the phenyl ring in the 2-position of TPI.

The results of Figs. 4 and 5 indicate that the photocyclization of TPI to the DHPI still occurs at -80°C and its inefficiency is due to photochemical ring fission back to TPI, *i.e.*



Clearly the thermal ring-opening process is unimportant at low temperatures. The small frequency factor obtained from Fig. 5 is consistent with this scheme as is the larger negative activation entropy of $-39.4\text{ cal mol}^{-1}\text{ K}^{-1}$. For such a mechanism the quantum yield for photochemistry would be determined by the relationship

$$\Phi = \frac{k_p}{k_r + k_p} \frac{k_{cy}}{k_{isc} + k_{fl} + k_{cy} + k_{ds}}$$

i.e. the quantum yield is the product of the fraction of singlets which convert to DHPI with the fraction of DHPI which convert to the photoproduct PPI. Since the kinetic data indicate that the dominant process is ring opening, $k_r \gg k_p$, and the presence of air is not a major factor in determining the transient lifetime.

In summary, the absorption spectrum of the DHPI of TPI has been shown to have peaks at 350 and 550 nm. The fact that the lifetime is four orders of magnitude shorter than that of *4a,4b*-dihydrophenanthrene accounts for its absence in steady state photochemical experiments, and may explain the fact that in some photocyclizations the dihydrophenanthrene has not been reported. This study provides further support for the spontaneous loss of hydrogen from DHPI since we have not observed any other dihydrophenanthrene intermediates that may arise from tautomerism. Finally, since the photocyclization of TPI to the dihydrophenanthrene intermediate is known to proceed through the lowest excited singlet state, involves both a thermal and a photochemical contribution to the ring fission back to TPI, has a low frequency factor and large negative activation entropy and shows little solvent dependence of its fluorescence quantum yield, it proceeds in degassed solutions as a clean unimolecular event, whose rate is dominated by reversion of DHPI to TPI. The importance of this back reaction is well known [3]. Since some of the decay of DHPI results in PPI

we are forced to conclude that loss of hydrogen is occurring. Support for this view is the recent result [8] that the disappearance of the dihydrophenanthrene involves two routes: (1) a fast step involving loss of hydrogen and (2) a slow step involving reaction of the dihydrophenanthrene with oxygen. The direct conversion of dihydrophenanthrene to phenanthrene in the gas phase photocyclization of *cis*-stilbene is known [9].

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