

THE WAVELENGTH-DEPENDENT PHOTOCHEMISTRY OF THE ENDOPEROXIDE OF 1,4,9,10-TETRAPHENYLANTHRACENE: INDIRECT EVIDENCE FOR THE EXISTENCE OF SEVERAL REACTION CHANNELS LEADING TO CYCLOREVERSION

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Summary

The wavelength dependence of the quantum yield Q_1 for the cycloreversion of the endoperoxide of 1,4,9,10-tetraphenylanthracene (TPAPO) reveals that this reaction originates from the thermalized S_2 state, which is also the case for other anthracene endoperoxides. However, a second increase in Q_1 with decreasing wavelength is observed for an endoperoxide for the first time. This surprising result indicates the existence of several thermally equilibrated upper singlet states S_n ($n \geq 2$) leading to cycloreversion. A comparison of the Q_1 values for TPAPO and other related endoperoxides demonstrates that its magnitude for these compounds is determined essentially by internal conversion and hence by the energy gap $S_2 - S_1$.

The quantum yield Q_{dec} for the rearrangement of TPAPO was also determined. The influence on Q_{dec} of the type and position of the substituents on the anthracene moiety is discussed.

1. Introduction

Two reactions are generally observed in the photochemistry of endoperoxides.

(1) An irreversible rearrangement with quantum yield Q_{dec} occurs on excitation into the S_1 state [1].

(2) Cycloreversion leading to the regeneration of the parent hydrocarbon and oxygen occurs with quantum yield Q_1 . This reaction proceeds from an upper excited singlet state S_n ($n \geq 2$) and competes with internal conversion (IC) to S_1 [2].

The state selectivity of these reactions is revealed by the wavelength-dependent quantum yields [2, 3]. The reaction dominating the photochemistry of an endoperoxide cannot be predicted, since the factors that deter-

mine the magnitudes of Q_1 and Q_{dec} are not accurately known. Above all, steric effects appear to influence the rearrangement reaction [4]. In contrast, it is not known how the magnitude of Q_1 is related to the structure of the endoperoxide.

To understand these problems better we have extended our investigations to the endoperoxide of 1,4,9,10-tetraphenylanthracene (TPAPO). For comparison the photolysis of the endoperoxide of 9,10-diphenylanthracene (DPAPO) was measured in dichloromethane.

2. Experimental details

1,4,9,10-tetraphenylanthracene (TPA) was synthesized according to a procedure given by Weizman *et al.* [5]. TPA was purified by column chromatography. The spectral data are in agreement with those reported in the literature [6]. 9,10-diphenylanthracene (DPA) (Merck) was recrystallized from ethanol. TPAPO and DPAPO were synthesized from the parent hydrocarbons by photo-oxidation in CS_2 with polymer-bound rose bengal as sensitizer and were purified by column chromatography [7]. CH_2Cl_2 (Merck, spectroscopic grade) and *m*-xylene (Ega) were used as solvents in the quantitative experiments.

The electronic spectra were recorded on a Perkin-Elmer 555 spectrophotometer. All irradiations were performed in nitrogen-purged solutions at 22 ± 3 °C using the apparatus described in ref. 8. The absolute determination of the monochromatic quantum fluxes was performed using a calibrated photodiode and a recently developed reusable UV actinometer (Actinochrome R (248/334) from Amko, Tornesch) [9].

During the photolysis experiments the formation of TPA and DPA was monitored spectrophotometrically and was analysed as described in ref. 7 to calculate Q_1 . In the determination of Q_{dec} the irreversible consumption of TPAPO was measured directly by high pressure liquid chromatography (HPLC) and indirectly by spectrophotometric analysis of the TPA produced during subsequent thermolysis of irradiated and unirradiated solutions of equal initial TPAPO concentrations.

3. Results and discussion

3.1. Spectra

The electronic spectra of TPA and TPAPO are shown in Fig. 1. The absorption bands of both compounds are broad and show no vibrational structure. This indicates an acceleration of the thermal equilibration of the vibronically excited states caused by the four phenyl substituents.

The peroxide bridge may bind to the 1 and 4 or the 9 and 10 positions in the anthracene framework:

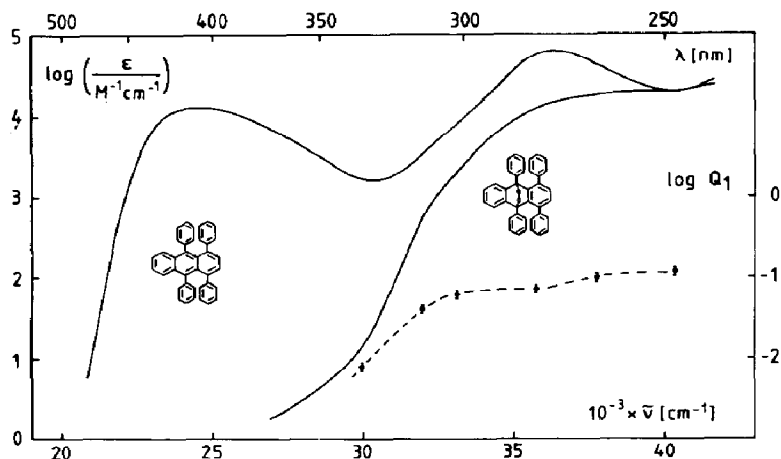
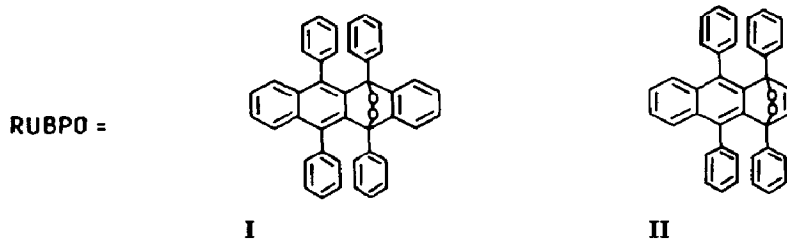


Fig. 1. Absorption spectra of TPA and TPAPO in dichloromethane. The quantum yield Q_1 is plotted as a function of the irradiation wavelength: Φ , experimental value with error limits.



In the 1,4-binding mode a strong similarity between the absorption spectra of TPAPO and the endoperoxide or rubrene (RUBPO (I)) is expected, since structures I and II have the same chromophores. However, this similarity does not exist. The onset of the $\pi_{CC}\pi_{CC}^*$ absorption occurs at $28\,500\text{ cm}^{-1}$ for RUBPO [10] but at $31\,000\text{ cm}^{-1}$ for TPAPO. It follows that the structure given in Fig. 1 with the peroxide bridge connecting the 9,10 positions is valid for TPAPO.

Therefore the steep slope of the long wavelength absorption of TPAPO at $31\,000\text{ cm}^{-1}$ must be due to the $S_0 \rightarrow S_2$, $\pi_{CC}\pi_{CC}^*$ (1L_a) transition in the *p*-terphenyl chromophore. In fact the onset of the 1L_a band of the unsubstituted *p*-terphenyl is found with comparable ϵ values at about $31\,500\text{ cm}^{-1}$ [11].

The flat tail of the absorption below $30\,000\text{ cm}^{-1}$ is ascribed to the $S_0 \rightarrow S_1$, $\pi_{OO}^*\sigma_{OO}^*$ transition in the peroxide chromophore. This absorption appears to extend into the visible range with very small extinction coefficients ($\epsilon < 1$) as is the case for the endoperoxide of anthracene (APO). The photochemical rearrangement reaction in APO, which has a very similar structure to TPAPO, can be induced by irradiation with $\lambda \geq 435\text{ nm}$ [1]. Therefore the S_1 ($\pi_{OO}^*\sigma_{OO}^*$) state of the endoperoxides of acenes must be localized at about $23\,000\text{ cm}^{-1}$ or less.

3.2. The photochemical cycloreversion

During short wavelength irradiation TPAPQ is split into its parent compounds TPA and oxygen. The quantum yield Q_1 is shown as a function of the irradiation wavelength in Fig. 1. It is only 0.008 in the overlapping region of the S_1 and S_2 bands and increases strongly with decreasing λ . Q_1 increases to an almost wavelength-independent region between 33 000 and 36 000 cm^{-1} with values ranging from 0.059 ± 0.004 to 0.072 ± 0.005 . After a further increase, a second plateau is reached between 37 500 and 40 500 cm^{-1} , where Q_1 ranges from 0.098 ± 0.006 to 0.118 ± 0.007 .

The wavelength dependence of Q_1 in the region from 30 000 to 36 000 cm^{-1} is as expected. Its asymptotic shape, which is the same as that observed for all endoperoxides investigated so far, results from the state selectivity of the cycloreversion which was predicted by Kearns and Khan [12] to proceed from an upper singlet state but not from the S_1 state. However, the second increase in Q_1 with decreasing λ has not previously been observed for other endoperoxides.

To exclude the possibility of an artefact in the experimental technique the photolysis of DPAPQ, which was investigated in an earlier study [3] using different methods, was re-investigated under experimental conditions identical with those described above. The spectrum of DPAPQ and Q_1 are shown as a function of λ in Fig. 2. Once again the typical wavelength dependence of Q_1 is obtained: a strong increase in the overlapping region of S_1 and S_2 and an asymptotic approach to a plateau in the region of the photochemically active band. As has already been found for the endoperoxide of 9,10-dimethylanthracene (DMAPO) and for APO, Q_1 decreases above 40 000 cm^{-1} , at the onset of the S_3 band, because new deactivation channels are

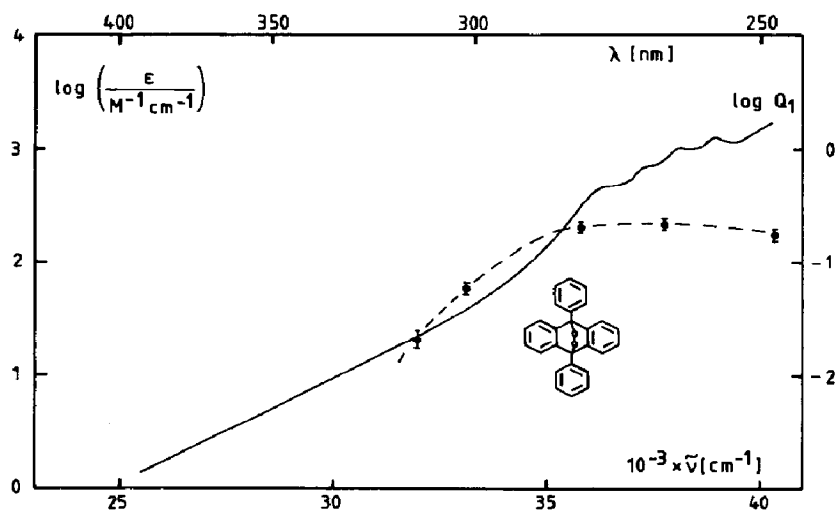


Fig. 2. Absorption spectrum of DPAPQ in dichloromethane. The quantum yield Q_1 is plotted as a function of irradiation wavelength: Φ , experimental value with error limits.

accessible [7]. It follows that the second increase in Q_1 found for TPAPO above $36\,000\text{ cm}^{-1}$ (Fig. 1) is real and significant.

The wavelength independence of Q_1 observed for DPAPPO in the region of the photochemically active S_2 band [3] suggests that the cycloreversion originates from a thermalized excited state. If this is also the case for TPAPO, then the second increase in Q_1 must be due to excitation of an upper singlet state which also results in oxygen release.

Unfortunately the spectrum of TPAPO does not indicate whether the $S_0 \rightarrow S_3$ transition occurs in the region from $36\,000$ to $37\,500\text{ cm}^{-1}$. As in *p*-terphenyl, which is the $\pi_{CC}\pi_{CC}^*$ chromophore of TPAPO, a completely unstructured spectrum is observed in this region. However, a comparison with spectral data for benzene and biphenyl shows that the energy of the 1L_b state of *p*-terphenyl is not much higher than that of the 1L_a state [13] (1L_a , $31\,500\text{ cm}^{-1}$; intersection of fluorescence and absorption [11]).

If it is assumed that the $S_0 \rightarrow S_3$ excitation of TPAPO occurs at about $37\,000\text{ cm}^{-1}$, the graduated wavelength dependence of Q_1 can be interpreted as follows: cycloreversion proceeds from S_3 with quantum yield $Q_1^{(3)}$, the competing IC to S_2 occurs with quantum yield $1 - Q_1^{(3)}$ and cycloreversion also originates from S_2 with quantum yield $Q_1^{(2)}$. The following equations then hold for the experimentally observed quantum yields for irradiation into the S_1 , S_2 and S_3 bands respectively:

$$Q_1^{S_1} = 0 \quad (1)$$

$$Q_1^{S_2} = Q_1^{(2)} \quad (2)$$

$$\begin{aligned} Q_1^{S_3} &= Q_1^{(3)} + (1 - Q_1^{(3)})Q_1^{(2)} \\ &= Q_1^{(2)} + Q_1^{(3)}(1 - Q_1^{(2)}) \end{aligned} \quad (3)$$

Thus the following behaviour is expected for the quantum yield: negligible values of Q_1 in the S_1 band, an increase in Q_1 in the region where S_1 and S_2 overlap, a wavelength-independent value of $Q_1^{(2)}$ throughout the S_2 band, a second increase in Q_1 in the region where S_2 and S_3 overlap and the appearance of a second plateau in the S_3 band.

It can be seen that the experimentally observed wavelength dependence of Q_1 is described qualitatively by the above model. This is a first strong indication that the cycloreversion of the endoperoxides may be due to several reaction channels originating from various thermalized upper excited singlet states S_n ($n \geq 2$).

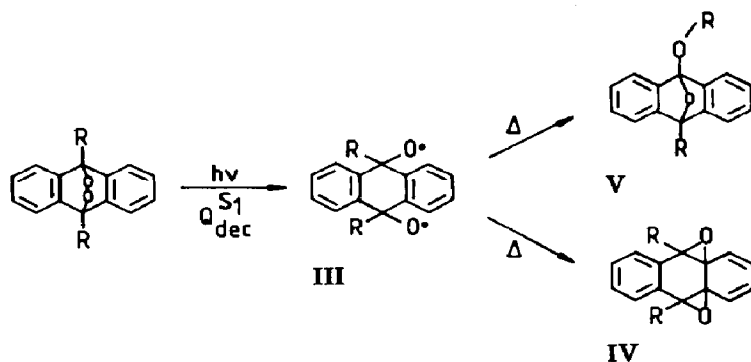
In seeking a relation between the magnitude of Q_1 and the structure of the endoperoxides it is necessary to compare Q_1 values of various compounds evaluated under similar experimental conditions. The maximum values of Q_1 found for TPAPO and DPAPPO on irradiation into the S_2 bands are 0.07 and 0.22 respectively. Maximum quantum yields of 0.22 and 0.35 have recently been reported [7] for APO and DMAPO respectively in dichloromethane. Hence the value measured for TPAPO is a factor of 3 - 5 smaller than the values obtained for the other three endoperoxides.

The graduation in the quantum yields appears to be a consequence of the presence of different $\pi_{CC}\pi_{CC}^*$ chromophores (*p*-terphenyl in TPAPO and *o*-xylene in APO, DMAPO and DPAPO) which lead to graduated energy gaps $S_2 - S_1$ in the endoperoxides.

Cycloreversion has to compete with the IC $S_2 \rightarrow S_1$, which slows down with increasing energy gap ΔE between S_2 and S_1 according to the Franck-Condon principle. Therefore IC in TPAPO, where $\Delta E \approx 8000 \text{ cm}^{-1}$, is presumably much faster than IC in DPAPO, DMAPO and APO, where $\Delta E \approx 12000 \text{ cm}^{-1}$. If it is assumed that the rate constants for cycloreversion are of the same order for similarly structured endoperoxides, $Q_1^{S_2}$ is expected to be of similar magnitude for DPAPO, DMAPO and APO but significantly smaller for TPAPO. This is in agreement with the experimental results.

3.3. The photochemical rearrangement reaction

On excitation into the S_1 ($\pi_{OO}^*\sigma_{OO}^*$) state a rearrangement of the endoperoxides of acenes initiated by the rupture of the peroxide bond is observed. As demonstrated by Rigaudy *et al.* [14] the intermediate biradical III rearranges in a secondary reaction to form mainly the diepoxide IV and to a lesser extent the cyclic ether V [14].



IV and V are converted into stable products in subsequent reactions.

$Q_{dec}^{S_1}$ is very sensitive to variations in the substituents in the 9,10 positions of the anthracene moiety. Presumably it is a steric substituent effect which acts mainly on the secondary reaction and to a lesser extent on the primary step. Thus a series of photochromic endoperoxides has been developed for which $Q_{dec}^{S_1} \leq 0.01$ [4]. In these compounds, which are endoperoxides of 9,10-diaryl-substituted anthracenes, the 1 and 4 or 1 and 5 positions of the anthracene moiety are connected by bridging groups $-X-$ with *ortho* positions of each aryl substituent. This arrangement prevents the formation of structures analogous to IV and V. In contrast with the low values found for photochromic endoperoxides, values of $Q_{dec}^{S_1} = 0.08$ for DPAPO [3] and even of $Q_{dec}^{S_1} = 1$ for APO [7] have been reported.

Now TPAPO offers the opportunity of studying for the first time the influence of additional independent substitution in the 1 and 4 positions on the photochemical rearrangement reaction.

Q_{dec} was determined by irradiating oxygen-free solutions of TPAPO in *m*-xylene at 302 nm until total conversions of about 35% were achieved. Under these conditions the number of light quanta absorbed by TPAPO can only be evaluated by simultaneously measuring the photolytically formed TPA as an internal standard. If $\Delta[\text{TPA}]$ and $\Delta[\text{TPAPO}] - \Delta[\text{TPA}]$ are the reversible and irreversible conversions of TPAPO respectively, the equation

$$Q_{\text{dec}}^{302} = \frac{\Delta[\text{TPAPO}] - \Delta[\text{TPA}]}{\Delta[\text{TPA}]} Q_1^{302} \quad (4)$$

holds for Q_{dec} .

The total conversion $\Delta[\text{TPAPO}]$ was investigated indirectly by thermolysis and directly by HPLC. Q_1^{302} was determined in independent experiments to be 0.091 in *m*-xylene. This result was substituted in eqn. (4) to give a mean value of 0.12 ± 0.01 for Q_{dec}^{302} . Since only IC to S_1 competes with the cycloreversion from S_2 $Q_{\text{dec}}^{S_1}$ can be calculated as follows:

$$Q_{\text{dec}}^{S_1} = \frac{Q_{\text{dec}}^{302}}{1 - Q_1^{302}} = 0.13 \pm 0.01 \quad (5)$$

Hence the value of $Q_{\text{dec}}^{S_1}$ found for TPAPO is only slightly larger than that obtained for DPAPPO.

Apparently it is the nature of the substituents at the carbon atoms connected by the peroxide bridge which is of decisive importance for the rearrangement reaction. In contrast, the additional substitution in the 1 and 4 positions is only of minor importance, at least as long as no connection between the substituents in the 1 and 9 positions and the 4 and 10 positions respectively is achieved, as is the case in the photochromic endoperoxides.

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