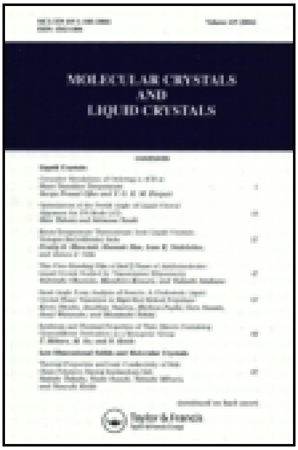

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromism Based on the Reversible Reaction of Singlet Oxygen With Aromatic Compounds

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Version of record first published: 24 Sep 2006.

To cite this article: Kurt Schaffner , Reinhard Schmidt & Hans-Dieter Brauer (1994): Photochromism Based on the Reversible Reaction of Singlet Oxygen With Aromatic Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 119-125

To link to this article: http://dx.doi.org/10.1080/10587259408037798

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 119–125
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Printed in the United States of America

PHOTOCHROMISM BASED ON THE REVERSIBLE REACTION OF SINGLET OXYGEN WITH AROMATIC COMPOUNDS

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Abstract The photolysis of the endoperoxides anthrabisbenzothiopyran (ABTPO) and of benzobisthioxanthene (BTXPO) has been studied in the wavelength range from 333 to 248 nm. At λ = 248 nm maximum quantum yields Q_C of 0.09 (ABTPO) and 0.10 (BTXPO) are found for the photocycloreversion reaction. Besides photocycloreversion a rearrangement reaction takes place with quantum yields $Q_R(248)$ of 0.013 for ABTPO and 0.018 for BTXPO. Furthermore the selfsensitized photooxygenation of ABT and BTX has been investigated in the concentration range from 10^{-5} to 10^{-4} M. The mean values of the quantum yield $\overline{Q}_P$ were found to be 0.02 (ABT) and 0.05 (BTX). The results indicate that ABT and BTX and their corresponding endoperoxides are components of highly reversible photochromic systems.

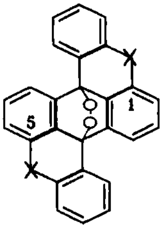
INTRODUCTION

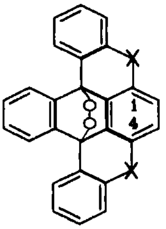
As we have demonstrated for the first time for the endoperoxide of heterocoerdianthrone (HECDPO), endoperoxides (ARPOs) of aromatic compounds (ARs) can be colourless components of highly reversible photochromic systems.[1] These systems operate via photoreversible photooxygenation of AR in which singlet oxygen ($^1O_2$, $^1\Delta_g$) is involved.[2]

$$\underset{\text{coloured}}{AR + O_2} \underset{h\nu', Q_C/\Delta}{\overset{h\nu, Q_P}{\rightleftharpoons}} \underset{\text{colourless}}{ARPO} \xrightarrow{h\nu', Q_R/\Delta} \text{rearrangement} \qquad (1)$$

ARPO may be split thermally as well as photochemically with quantum yield Q_C to give back the coloured AR and $^1O_2$, in competition to thermally or photochemically induced rearrangement.

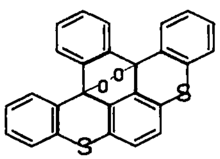
The quantum yield ratio Q_C/Q_R determines the degree of reversibility of the photochromic system (1), whereby Q_R strongly depends on the structure of ARPO. Very small Q_R values were found for ARPOs of the types illustrated below.



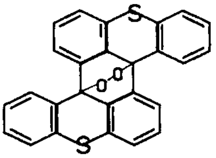


Formally these endoperoxides can be regarded as derivatives of 9,10-diphenylanthracene-endoperoxide (DPAPO) in which the two phenylsubstituents are connected by -X-bridges in 1.4 or in 1.5 position with the anthracene frame.[2] Suitable bridges X can be -CO-, -O-, arylic groups or -S-. HECDOP is one example. In this endoperoxide the two phenylsubstituents are connected by keto groups in 1.5 position with the anthracene frame.[1,2]

In this paper we report on photochemical porperties of the endoperoxides of anthra[1.9-bc:4,10-b'c']-bis[1]benzothiopyran (ABTPO) and benzo[1,2,3-kl:4,5,6-k'l']bisthioxanthene (BTXPO) being relevant for their photochromic behavior. Additionally results of the selfsensitized photooxygenation of the aromatic parent compounds are presented.



ABTPO



BTXPO

EXPERIMENTAL

ABT und BTX were prepared for the first time.[3] The syntheses was similar to procedures described in the literature.[4,5] Both compounds were purified by column chromatography in trichloroethylene using silica gel 60 (Merck). However, we did not succeed to obtain the substances free of chlorine. The "purified" compounds contained about 2.5 % of chlorine resulting from partial substitution of H by Cl. APTPO and BTXPO were prepared by selfsensitized photooxygenation of ABT and BTX, respectively, in oxygen saturated toluene. The solutions (ca. 0.3 mM) were placed behind a yellow filter and exposed to sunlight, being continuously stirred until decolorization occured. Then the solvent was evaporated at room temperature. The residues were dissolved in methanol. White crystals of endoperoxides were obtained.

The solvents toluene and CH_2Cl_2 (both from Merck, Uvasol) used for the photochemical measurements were not further purified.

Absorption spectra were recorded on a Perkin-Elmer 555 spectrophotometer. The apparatus for the determination of the photochemical quantum yields is described in detail in an earlier paper.[6]

RESULTS AND DISCUSSION

Spectra. The absorption spectra of ABT and ABTPO, and of BTX and BTXPO are shown in Figs. 1 and 2, respectively. As one can see from these, the absorption of the aromatic compounds shifts by more than 200 nm to the UV upon photooxygenation. Both endoperoxides show three absorption maxima. ABTPO has its first absorption maximum above 27800 cm^{-1} and BTXPO above 30000 cm^{-1}, respectively. For both endoperoxides the three maxima are attached to the $\pi\pi^*$-S_2, $\pi\pi^*$-S_3 and $\pi\pi^*$-S_4 states of the endoperoxides.

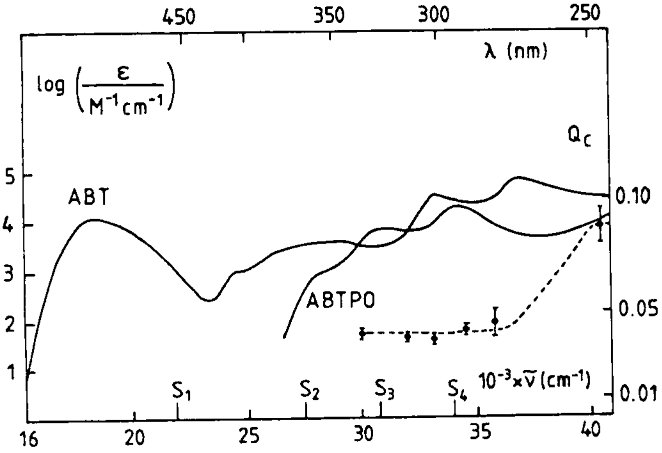


FIGURE 1 Absorption spectra of ABT and ABTPO, wavelength dependence of Q_C, solvent CH_2Cl_2.

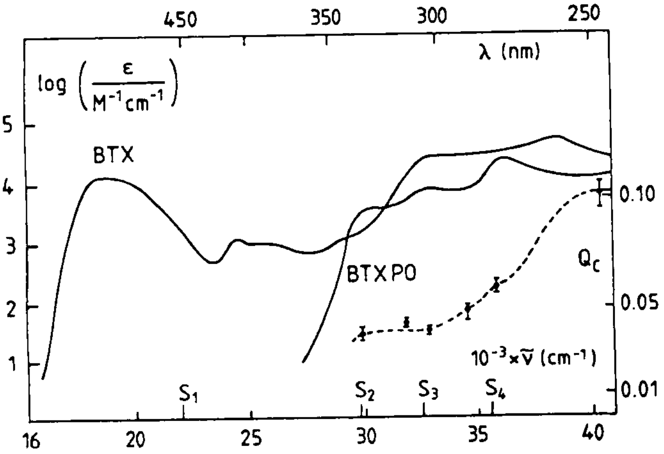


FIGURE 2 Absorption spectra of BTX and BTXPO, wavelength dependence of Q_C, solvent CH_2Cl_2.

Photooxygenation

Each of the reaction spectra (see Fig. 3 and 4) obtained for the selfsensitized photooxygenation of ABT and BTX in air saturated CH_2Cl_2 show two isobestic points: at 311 and 338 nm (ABT) and at 322 and 341 nm (BTX). The absorbance difference (AD) diagrams[7], which were obtained from the spectral changes, point out that these reactions are uniform.

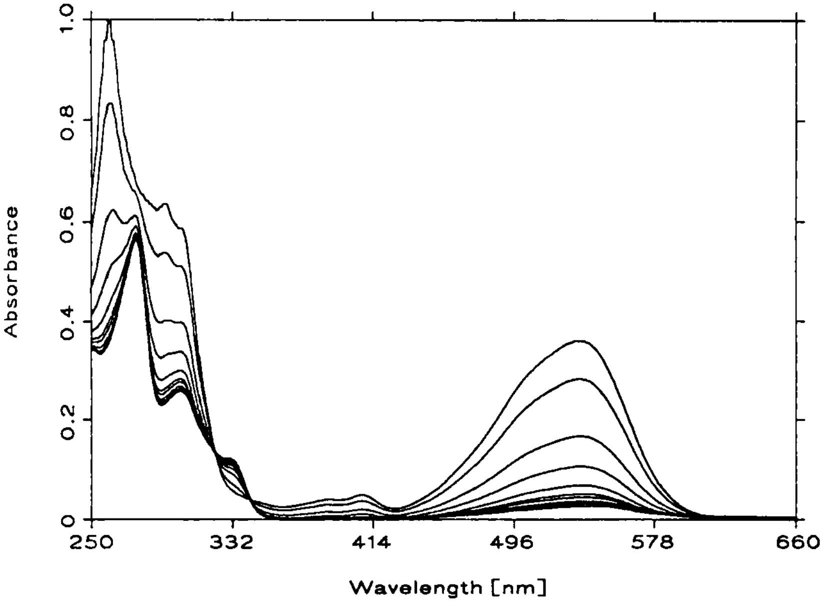


FIGURE 3 Reaction spectrum of the selfsensitized photooxygenation of BTX with two isobestic points at 322 and 341 nm, solvent CH_2Cl_2.

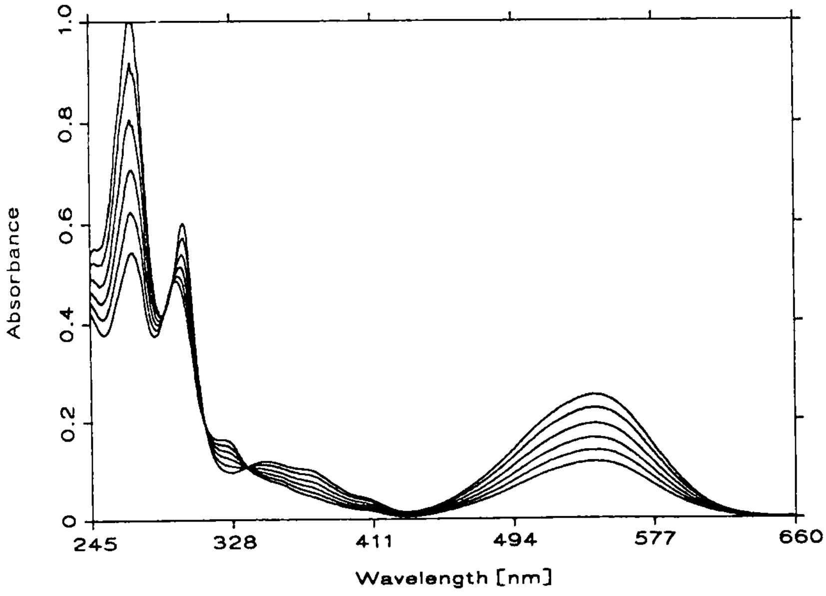


FIGURE 4 Reaction spectrum of the selfsensitized photooxygenation of ABT with two isobestic points at 311 and 338 nm, solvent CH_2Cl_2.

The mean quantum yields determined in air saturated toluene in the concentration range $3 \cdot 10^{-5}$ to $3 \cdot 10^{-4}$ M are $\overline{Q}_P(BTX) = 0.051 \pm 0.003$ and $\overline{Q}_P(ABT) = 0.020 \pm 0.001$. From the measurements of Q_P as a function of the aromatic compound concentration we determined the rate constant k of reaction with $^1O_2$ to be $k(BTX) = (6.9 \pm 0.5) \cdot 10^7$ M^{-1} s^{-1} and $k(ABT) = (1.7 \pm 0.6) \cdot 10^8$ M^{-1} s^{-1}.

Photocycloreversion and Rearrangement Reaction

In agreement with the predictions of the theory of Kearns and Khan[8] and the findings for many other endoperoxides[2] for both endoperoxides ABTPO and BTXPO two photochemical reaction pathways are observed. Photocycloreversion occurs from upper excited singlet states. Besides this reaction a rearrangement reaction is observed. As predicted by Kearns and Khan[8] and experimentally demonstrated for a series of endoperoxides[2] this reaction originates from the lowest excited $(\pi^*_{OO}\sigma^*_{OO})$ singlet state. As one can see from Figs. 1 and 2 the quantum yield Q_C of the photocycloreversion depends on photon energy. In the case of ABTPO Q_C remains constant in the range of $333 \text{ nm} > \lambda > 289$ nm and reaches a value of $Q_C = 0.09$ at $\lambda = 248$ nm. In contrast, for BTXPO already an increase of Q_P at $\lambda < 302$ nm is observed. At $\lambda = 248$ nm Q_C amounts to 0.10. Of course, the quantum yield Q_R of the photochemical rearrangement reaction also depends on wavelength,[2] but in moderate manner compared with Q_P. Upon irradiation at $\lambda = 248$ nm we found that $Q_R(BTXPO)$ to be 0.01_8 and $Q_R(ABTPO)$ to be 0.01_3, respectively.

As previously discussed in more detail, the ratio of $Q_C(\lambda)/Q_R(\lambda)$ is a measure of the reversibility of the photochromic system (1).[2] For the number n of photoreversible cycles until the photochromic material is decomposed to 1/e the following approximation holds:[2]

$$n \approx \frac{Q_C(\lambda)}{Q_R(\lambda) \cdot F}$$

where F denotes the fraction of ARPO which has been converted to AR per cycle. With F = 0.05 and the values of $Q_P(\lambda)$ and $Q_R(\lambda)$ found for ABTPO and BXTPO, respectively, the following numbers can be calculated: n(ABTPO) = 140 and n(BTXPO) = 110. Thus, both endoperoxides are components of highly reversible photochromic systems.

However, the number of possible photochromic cycles is for both still about one order of magnitude smaller than for endoperoxides of this type in which both bridges -S- are substituted by bridges -CO-.[2]

Acknowledgements. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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