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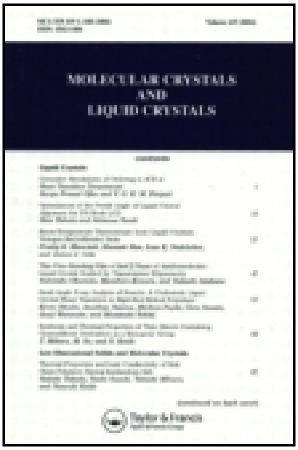

# Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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# Photochemical Properties of Spirooxazines

A. A. Firth [a] , D. J. McGarvey [a] & T. G. Truscott [a]

[a] Department of Chemistry, Keele University, Staffordshire, ST5 5BG, UK

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# PHOTOCHEMICAL PROPERTIES OF SPIROOXAZINES

A.A. FIRTH, D.J. McGARVEY AND T.G. TRUSCOTT
Department of Chemistry, Keele University, Staffordshire, ST5 5BG, UK.

Abstract The quenching of singlet oxygen ($O_2{}^1\Delta_g$) by the closed and open forms of various spiroindolinonaphthoxazines has been investigated by use of pulsed laser techniques. Significant variations in the quenching rate constants have been found depending on the molecular structures of the photochromic compounds. In addition, experiments which attempt to resolve the contributions to singlet oxygen quenching by the closed and open forms of the photochromics are discussed. It is demonstrated that the open form exhibits enhanced singlet oxygen quenching relative to the closed form.

## INTRODUCTION

Photochromism describes the reversible change of one chemical species to another on exposure to light. Under U.V. irradiation the C-O bond in spirooxazines breaks to form the coloured photomerocyanine:

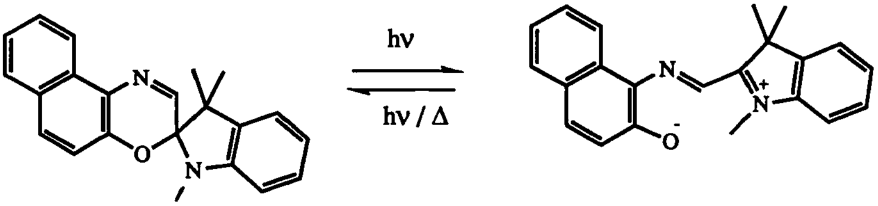
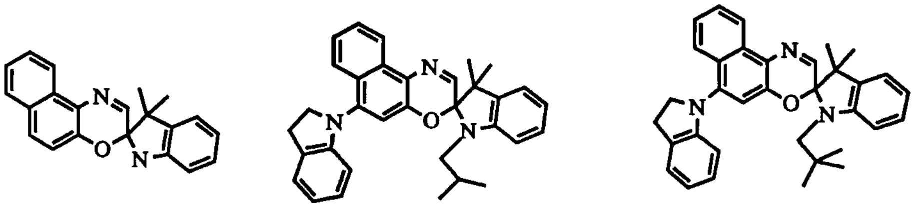


FIGURE 1 Photochromic reaction scheme.

Spirooxazines are of great commercial interest because of their potential use in glazing products for the motor-car and building industries. Unfortunately, these compounds are susceptible to photodegradation severely restricing their industrial use.

It is known that oxygen plays a major role in the photodegradation of many photochromic compounds. R. Gautron[2] who initiated degradation studies on spiropyrans in the 1960's, concluded that oxygen is involved in the degradation process. Recently, G. Baillet et al[3] have also shown that oxygen is involved in the photodegradation of spirooxazines and spiropyrans by carrying out photoproduct analysis. However, it is not yet known whether the degradation process takes place due to attack by singlet oxygen or radical species. We have therefore investigated the quenching of singlet oxygen by various spirooxazines in the closed and open forms using pulsed laser techniques in order to establish whether singlet oxygen may be important in the degradation process.



SO2 N-isobutyl PW8 N-neopentyl PW8

FIGURE 2 Photochromic compounds studied.

## EXPERIMENTAL

Singlet oxygen quenching rate constants for the closed forms ($10^{-3}$ - $10^{-5}$ M) in benzene were determined by a time-resolved germanium based near-infrared luminescence technique. This involved pulsed Nd/YAG (Spectron Laser Systems) excitation of a singlet oxygen sensitiser tetraphenylporphine, (TPP) at 532 nm (absorbance at 532 nm = 0.2). Singlet oxygen luminescence was detected at 1270 nm using a Judson germanium photodiode. Transients were captured on a Textronix digital oscilloscope (2432 A) and the kinetics of the transients were carried out by in-house software. The rate obtained was plotted against concentration and the bimolecular rate constant for the quenching of singlet oxygen was measured from the slope.

The open form of the spirooxazines was produced by continuous irradiation of the closed form (2 x $10^{-4}$ M in benzene) in the U.V. region using a 250 W Kratos xenon lamp (figure 3). A spectron dye laser at 650 nm pumped by the Nd/YAG laser was employed to excite a porphyrin, TPP (absorbance at 650 nm = 0.1). Detection of singlet oxygen and analysis of transients was carried out as outlined above. With TPP alone (in benzene) the singlet oxygen lifetime was not dependent on whether the sample was exposed to arc lamp irradiation or not.

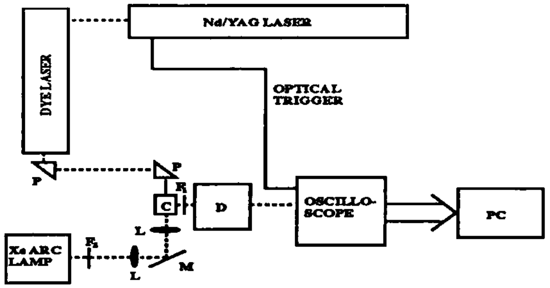


FIGURE 3 Experimental set-up to study the quenching of singlet oxygen by the open forms. (KEY: D = germanium detector).

## RESULTS

The results obtained for the quenching of singlet oxygen by the closed forms are given in table 1. The transients produced for the quenching of singlet oxygen by the closed and open form of N-neopentyl PW8 are shown in figure 4.

TABLE 1 Rate constants obtained for the quenching of singlet oxygen by the closed forms of the photochromics studied in benzene.

| Spirooxazine | Rate ($k_qM^{-1}s^{-1}$) ± 0.4 |
|---|---|
| SO2 | $4.4 \times 10^5$ |
| N-isobutyl PW8 | $4.1 \times 10^6$ |
| N-neopentyl PW8 | $4.5 \times 10^6$ |

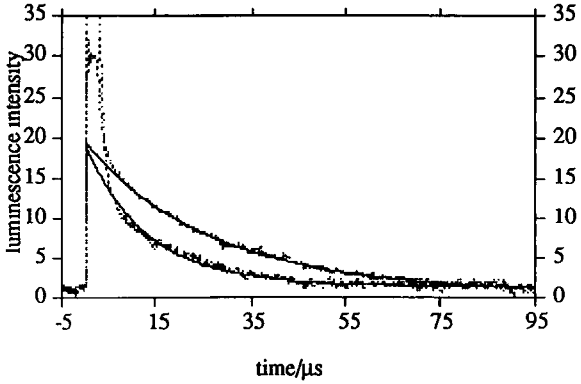


FIGURE 4 Quenching of singlet oxygen by the closed and open forms of N-neopentyl pw8 in benzene (faster decay - open form).

## DISCUSSION

All three photochromics quench singlet oxygen in the closed form, but the rate constant for SO2 is an order of magnitude lower than the others (see table 1). As can be seen from the structures, SO2 has the 'simplest' structure suggesting that the increased rate of reaction of the other two compounds is due to the presence of additional side groups on the oxazine part of the molecule.

The open form of N-neopentyl PW8 quenches singlet oxygen more efficiently than its closed form (see figure 4). The increased quenching of singlet oxygen may suggest that this is the less stable form of the photochromic and photodegradation may take place in this form. The open form of N-isobutyl PW8 showed similar behaviour, although an insufficient steady-state concentration of the SO2 open form could be produced to detect singlet oxygen quenching.

It is not clear whether spirooxazines quench singlet oxygen by a chemical or physical process (or both). However, the presence of amine groups should enhance the physical quenching of singlet oxygen due to the participation of change transfer interaction.[4]

There is still no direct evidence from our experiments or in the literature that singlet oxygen is involved in the degradation process. Nevertheless, it may be possible for singlet oxygen to react with the various diene systems present in both the closed and open forms of these molecules. Further studies are in progress to establish the contribution of chemical quenching to the total quenching of singlet oxygen by spirooxazines.

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