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PHOTOCHEMISTRY OF DI-α-METHYLENENAPHTHYLSULPHONE

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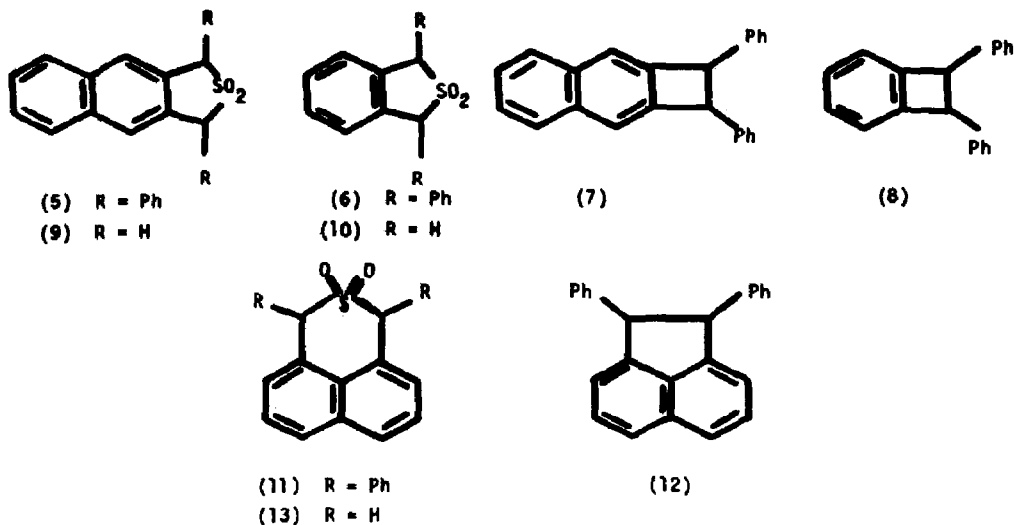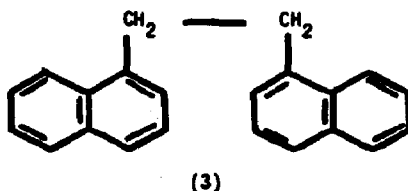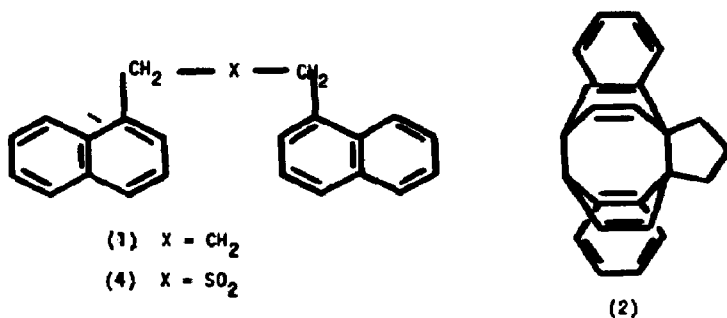*Department of Chemistry, The University, Southampton (Gt. Britain)*

Summary

Although fluorescence studies show that di-α-methylenenaphthylsulphone gives an intramolecular excimer, direct irradiation gives no products of internal cycloaddition but only 1,2-di-α-naphthylethane.

1. Introduction

A number of recent studies show that both intramolecular excimer formation [1, 2] and subsequent product formation by cycloaddition occur with substituted naphthalenes [3] and substituted anthracenes [4]. Excimer and cycloadduct formation are particularly favoured by a 1,3-disposition of the aromatic residues. Thus 1,3-di-α-naphthylpropane (1) shows excimer formation [2] and on irradiation gives (2) as a photoadduct. In contrast, owing to steric constraints 1,2-di-α-naphthylethane (3) gives neither an excimer nor a photoadduct. Our recent interest in the photochemistry of sulphones [5] has led us to examine the photochemistry of di-α-methylenenaphthylsulphone (4). In (4) it is expected that the sulphone chromophore (transparent above 220 nm) is insulated from the naphthyl residue. Hence in an excited state of the naphthyl chromophore analogy with (1) suggests that excimer and cycloadduct formation from (4) might occur. By contrast there is a precedent [6] for C—S bond cleavage with formation of SO_2 with certain substituted benzylsulphones. Here we describe our photochemical studies with compound (4) which show that although excimer formation is observed the sole photoproduct is derived from the loss of SO_2.

2. Experimental

Compound (4) was prepared following the method of Wellisch *et al.* [7]. α-Chloromethylnaphthalene (0.1 mol) and sodium dithionite (0.05 mol) were heated in dimethyl sulphoxide (100 ml) at 110 °C for 9 h. The cooled

(1) X = CH₂

(4) X = SO₂

(2)

(3)

(5) R = Ph
(9) R = H

(6) R = Ph
(10) R = H

(7)

(8)

(11) R = Ph
(13) R = H

(12)

solution was poured into ice-water, and the precipitate was collected and recrystallized from ethyl alcohol to give (4) (melting point, 209 - 211 °C (literature value, 218.5 - 219 °C [8]), λ_{max} = 225 and 287 nm, log ϵ = 4.69 and 3.82 respectively) in 18% yield.

2.1. Irradiation of di-α-methylenenaphthylsulphone

Compound (4) (0.5 g) was irradiated in benzene (300 ml) under nitrogen through quartz by a 400 W medium pressure lamp for 2 h. After irradiation the yellow solution was concentrated and the photoproducts were separated by preparative thin-layer chromatography. Elution with chloroform—cyclohexane (2:1) gave in addition to the polar unchanged starting material the non-polar (3) (0.2 g). Recrystallization from benzene—ethanol produced (3) (melting point, 156 - 158 °C (literature value 160 - 161 °C [9]).
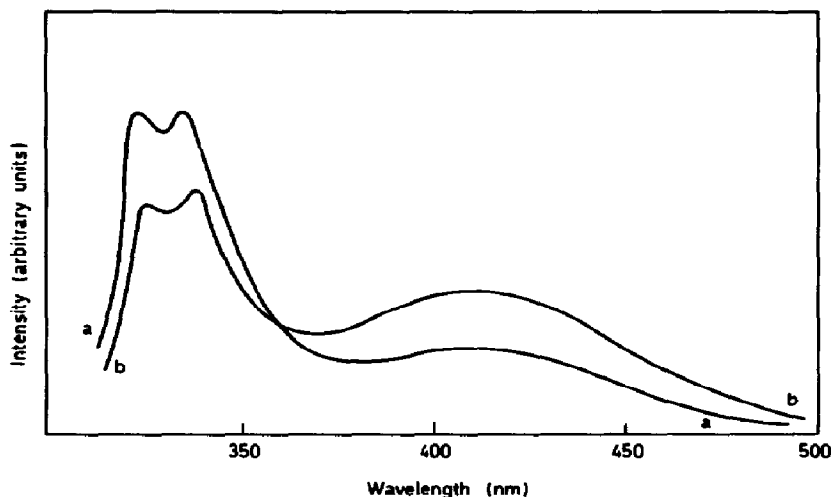
Fig. 1. Emission spectrum of di-α-methylenenaphthyl sulphone in cyclohexane (exciting wavelength 277 nm): (a) 0.5 × 10⁻⁴ M; (b) 1 × 10⁻⁴ M.

2.2. Spectroscopic studies

The absorption spectra were recorded using a Unicam SP800 spectrophotometer. The fluorescence spectra were recorded using a Farrand Mark 1 spectrofluorimeter. The spectra were recorded in cyclohexane or at 77 K in methylcyclohexane–isopentane (9:1). The fluorescence decay times were measured by the single photon counting technique as previously described [10].

Cyclohexane (Koch-Light spectroscopic grade) was further purified by passage through a column of silica gel (previously activated at 450 °C for 30 min). No solvent emission was observed at room temperature. Isopentane (BDH) and methylcyclohexane (BDH) were used directly without further purification and showed no observable emission.

The fluorescence spectra were recorded after repeated degassing by a freeze–thaw cycle.

3. Results and discussion

The fluorescence spectra of the solutions (0.498 × 10⁻⁴ mol l⁻¹ and 0.996 × 10⁻⁴ mol l⁻¹) of (4) in cyclohexane are shown in Fig. 1. Similarly fluorescence spectra of a solution (1.8 × 10⁻⁴ M) of (4) in a methylcyclohexane–isopentane glass (9:1) at 77 K were recorded and are shown in Fig. 2. Both series of spectra show two principal bands — a structural emission at about 340 nm and a broad structureless emission at about 410 nm. The higher energy band closely resembles the emission spectrum of simple alkylnaphthalenes. It is therefore assigned to fluorescence emission from uncomplexed naphthalene excited singlet states. The lower energy band is
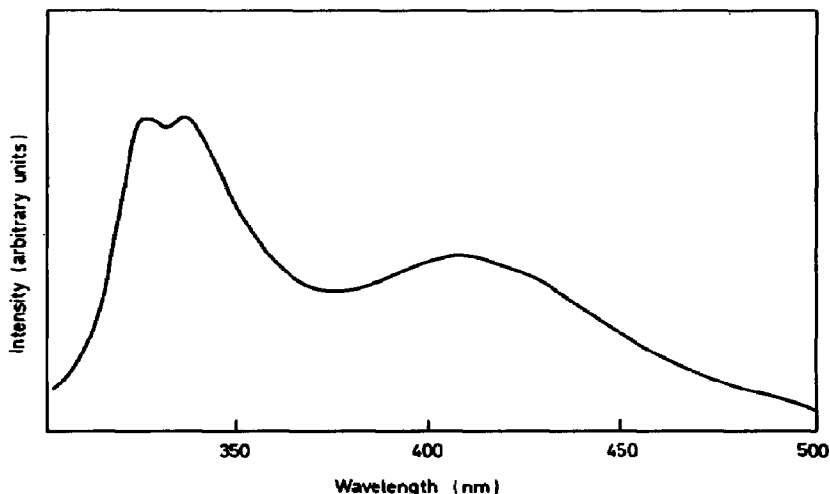
Fig. 2. Emission spectrum of di-α-methylenenaphthyl sulphone in methylcyclohexane–isopentane (9:1) at 77 K (exciting wavelength 277 nm, 1.15×10^{-4} M solution).

structureless, as expected of an excimer emission. Study of the emission intensities as a function of concentration gives further confirmation that this band arises from an excimer. In Fig. 1 it is seen that at increased concentrations of (4) the fluorescence intensity of the lower energy band increases relative to the high energy band. The influence of oxygen again suggests excimer formation. The possibility that an impurity accounts for one emission band is improbable. There is no change in the excitation spectrum on using different exciting wavelengths.

The evidence indicates that the sulphone (4) is emitting from an excimer. Such an excimer could either be an intramolecular or an intermolecular excimer. The results in the methylcyclohexane–isopentane glass, where diffusion at 77 K is prevented, show excimer formation. Hence in the glass and in part in the fluid solution intramolecular excimer formation occurs. In fluid solution the fluorescence intensity of uncomplexed (4) decreases with respect to the fluorescence intensity of complexed (4). This suggests that a component of the excimer emission originates from intermolecular complexes and that a further component originates from intramolecular complexes. The excited singlet state lifetimes of naphthalenes are short. Single photon counting indicates a lifetime of 4.26 ns for (4). Hence at low concentrations of (4) (10^{-4} M) the probability of intermolecular excimer formation as an effective dimer of (4) is unlikely unless complex formation already exists in the ground state. It is probable that this occurs but we can find no evidence for it. A plot of optical density *versus* concentration for (4) shows no deviation from the Beer–Lambert law. Hence it is established that (4) gives excimers in the same way as (1).

Irradiation of (1) gives the photoadduct (2). In contrast irradiation of (4) in benzene or cyclohexane gives (3) as the sole organic product and

SO_2. No evidence was found for cycloadduct formation. Even in diaryl sulphones [5] cleavage of the C—S bond to give aryl radicals is a facile photochemical process. In (4) formation of stabilized radicals on photolysis is overwhelmingly favoured by comparison with cycloadduct formation. This result, however, contrasts with some related photolyses of sulphones.

Whereas sulphones (5) and (6) undergo [6] photocleavage with formation of (7) and (8), the less substituted sulphones (9) and (10) were found to be photostable. Similarly although sulphone (11) gave (12), again the less substituted sulphone (13) was photostable. The relative photostability of (9), (10) and (13) must be explained by a preference for regeneration of starting sulphone in competition with loss of sulphur dioxide at the stage of an intermediate diradical. In contrast, cleavage of the C—S bond in (4) leads to two separated radicals. Recombination is less favoured and subsequent loss of SO_2 leads to (3) and to traces of 1-methylnaphthalene.

Thus although sulphone (4) forms an intramolecular exciplex, in contrast to (1), in the excited state interaction to give cycloadducts fails to compete with the more facile loss of SO_2.

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