SOLID STATE ACTINOMETERS BASED ON THE PHOTOREARRANGEMENT OF AROMATIC AZOXY COMPOUNDS IN POLY(METHYL METHACRYLATE)

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Summary

The relationship between product formation and photon dose in the title actinometers is found to be described better by a rectangular hyperbola than by the single exponential proposed previously.

Several methods have been investigated for decreasing the photosensitivity of azoxy compound–poly(methyl methacrylate) actinometers for use outdoors. The most successful method involves painting a UV-filtering substance directly onto the polymer surface.

The sensitivity of these actinometers has also been found to depend upon the spectral distribution of the source. As a result, it is necessary to calibrate the device before it is used for the first time with each radiation source.

1. Introduction

We recently reported a solid state actinometer system based on the photorearrangement of azoxybenzene (1a, see Fig. 1) in a medium of poly(methyl methacrylate) (PMMA) [1]. The attractive feature of this actinometer system was that clear pieces of PMMA–1a could be cut to a size which fitted the cuvette holder of a spectrophotometer, and the progress of the reaction could be followed by making a single absorbance measurement in the wavelength range where the product 2a absorbs. We gave a mathematical protocol for determining the photon dose incident upon the polymer sheet using the measured absorbance as the only input.

In this paper we report further investigations of the potential usefulness of azoxyarene–PMMA actinometers. We have made progress in improving the mathematical protocol for calculating the photon dose and in adjusting the light sensitivity of the actinometer system. We also report on the problems which arise when the solid state actinometer is used with sources of differing spectral composition.
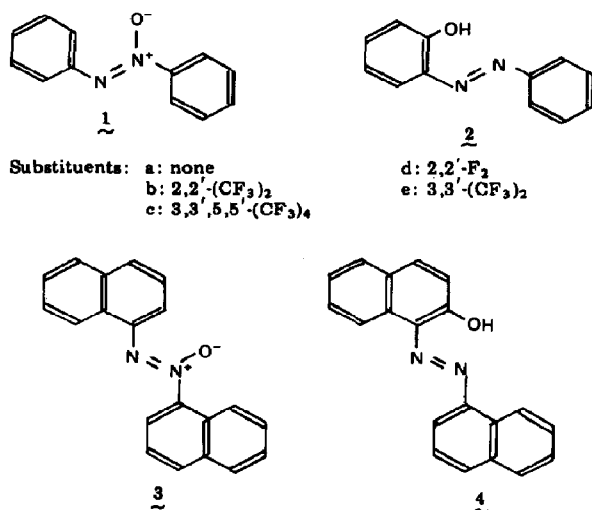
Fig. 1. Compounds 1 - 4.

2. Results and discussion

2.1. Mathematical protocol

The relationship between the absorbance and the total photon dose absorbed by the solid sample is a curve which rises steeply at first but rapidly levels off to a plateau that is well short of complete conversion of reactant into product. This behaviour was explained [1] as being due to competitive absorption of light by reactant and product; the layers of solid close to the irradiation source showed high conversion of reactant, but the interior of the polymer sample was not photolysed at all.

The empirical equation

$$I_0 = -p_\infty \phi^{-1} \ln\left(1 - \frac{A}{A_\infty}\right) \tag{1}$$

was found to be a reasonably good description of the dependence of the absorbance on the absorbed photon dose. In eqn. (1) I_0 is the absorbed photon dose, p_∞ is the limiting product concentration (called c in our previous paper), ϕ is the quantum yield and A and A_∞ are respectively the absorbances at the selected irradiation time and at the plateau. For convenience, I_0 and p_∞ are best given in units of moles per unit area of surface irradiated rather than in moles per litre.

Under the approximation that the reactant and product absorbed equally strongly at the wavelength of the irradiation source, the amount of product δP formed in an element at a depth l into the polymer is given by the equation

$$\delta P = R[1 - \exp\{-2.3\epsilon\phi I_0 \exp(-2.3\epsilon R l)\}] \tag{2}$$

where R is the concentration of reactant and ϵ is the molar absorptivity at the excitation wavelength. An equation similar in form to eqn. (2), only

more complex, was recently developed by Jackson and Lishan [2]. Their equation, which must be integrated numerically, explicitly considers the different absorptivities of reactants, products and inert light absorbers.

Equation (2) can be written in the logarithmic form

$$\ln\left(1 - \frac{\delta P}{R}\right) = -2.3\epsilon\phi I_0 \exp(-2.3\epsilon R l) \tag{3}$$

which appears to be similar to eqn. (1). However, eqns. (1) and (3) are not truly analogous. Firstly, the approximation $\epsilon_{reactant} = \epsilon_{product}$ is not exact. Secondly, the total product formed P in the polymer block is the sum of δP over all values of l; consequently, when δP in eqns. (2) and (3) is replaced by P the exponentials in these equations also appear as a sum and not as a single exponential.

Accordingly, when we examined the relationship between A and I_0 more closely, by taking a large number of data points of absorbance *versus* time, we found that eqn. (1) was not obeyed very closely (see Fig. 2). By trial and error, we found that the rectangular hyperbola

$$A = \frac{at}{1 + bt} \tag{4}$$
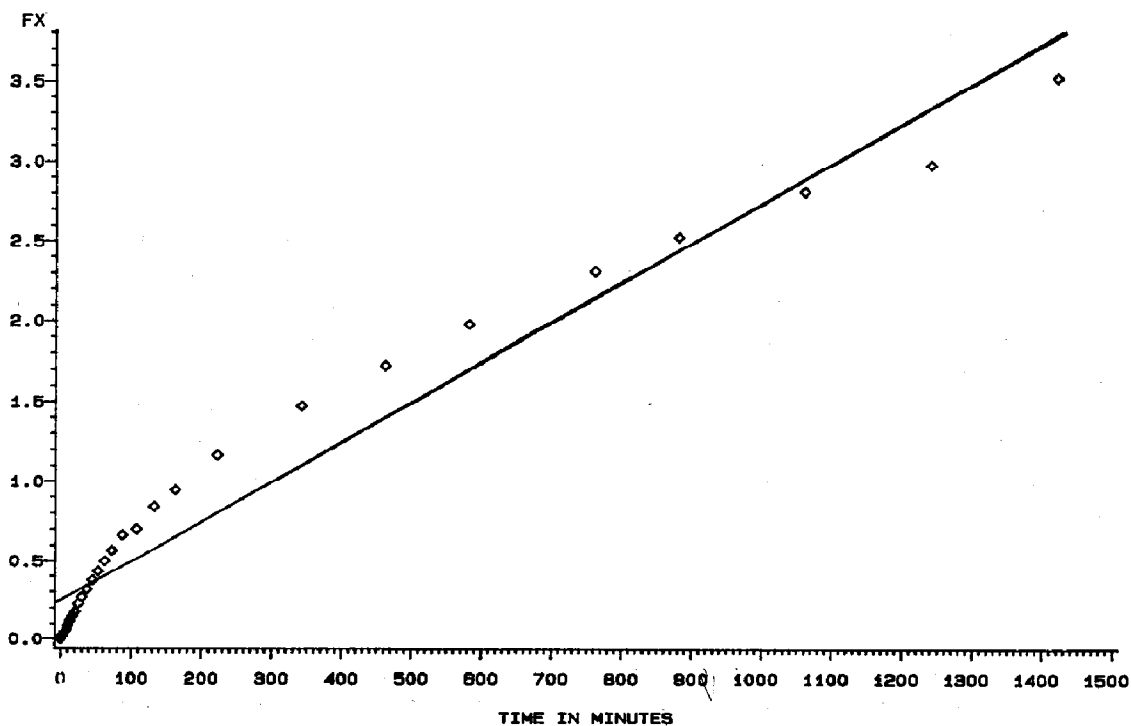
gave a better fit to the data (see Fig. 3).

Fig. 2. Plot of $-\ln(1 - A/A_\infty)$ *vs.* time for a 1 mg ml^{-1} solution of **1a** in PMMA. This is a plot of the second experiment in Table 1, with A_∞ set equal to 2.125 absorbance units.
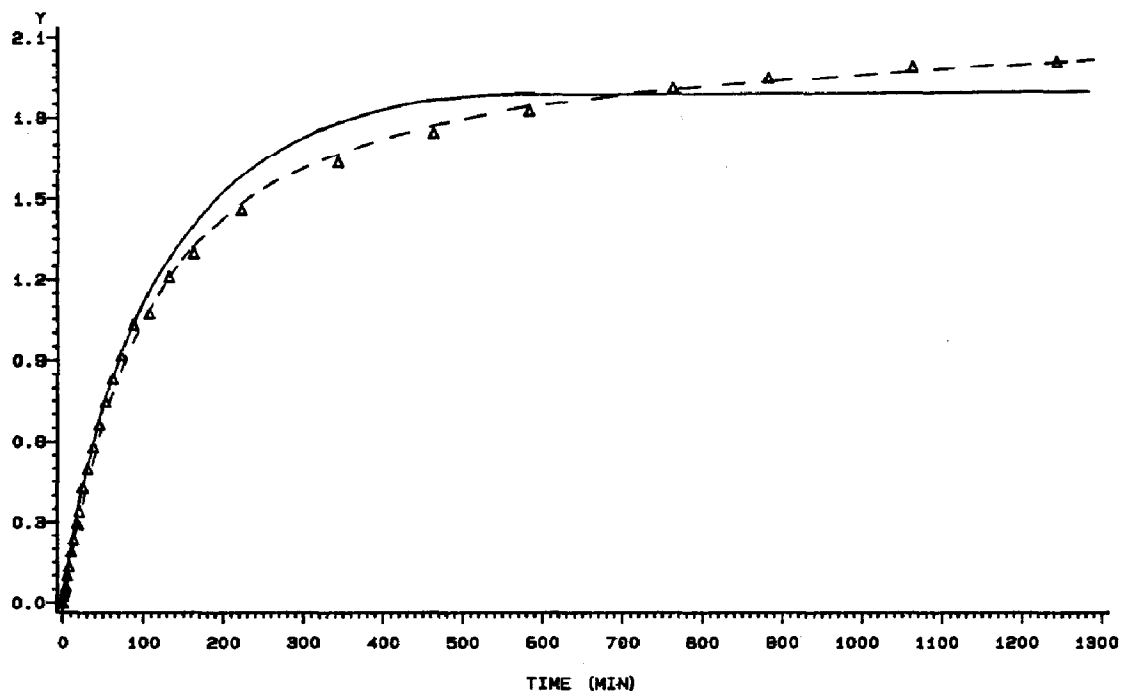
Fig. 3. Plot of absorbance *vs.* time for a 1 mg ml^{-1} solution of 1a in PMMA (same data as Fig. 2): Δ, experimental points; ———, best fit to eqn. (2a); — — —, best fit to eqn. (4).

In Table 1 are presented comparisons of the parameters a and b of eqn. (4) with those a' and b' from the equation

$$A = a'\{1 - \exp(-b't)\}$$ (2a)

when absorbance *versus* time data were fitted by multiple regression to the two mathematical models for three different azoxyarene–PMMA systems. The poorer fit of eqn. (2a) appears to be mainly concerned with the uncertainty in the value of the exponent b'. For the rectangular hyperbola, constants a and b do have experimental significance, even though the equation is empirical. Thus a, the limiting slope $I_0 \rightarrow 0$, represents the quantum yield of the reaction, while a/b corresponds to the plateau value A_∞ when the units are accounted for properly. Nevertheless, the reproducibility of the fitted parameters from run to run is less satisfactory than we had hoped for.

The protocol for calculating the photon dose from the absorbance is given by

$$I_0 = \frac{p_\infty}{\phi} \frac{A}{A_\infty - A}$$ (5)

I_0 is in moles per unit area when the plateau value A_∞ is also converted to p_∞ and expressed in these units. This expression loses precision as A approaches A_∞, and we have chosen $A \leqslant 0.7A_\infty$ as an arbitrary range over which we feel that eqn. (5) will be useful.

TABLE 1

Calculated and experimental parameters for absorbance *versus* time data

Solute	Concentration (mg ml^{-1})	Abs = $a'\{1 - \exp(-b't)\}$		Abs = $at/(1 + bt)$		a/b (absorbance units)	A_∞ (absorbance units)	$p_\infty \times 10^6$ (mol cm^{-2})	ϕ
		a'	$b' \times 10^3$	$a \times 10^2$	$b \times 10^3$				
1a[a]	1	1.94 ± 0.06	8.0 ± 0.8	2.08 ± 0.05	9.54 ± 0.25	2.18	2.13	0.64	8.4 × 10^{-4}
1a[a]	1	1.95 ± 0.06	6.7 ± 0.6	1.69 ± 0.11	7.56 ± 0.62	2.24	2.12	0.64	6.9 × 10^{-4}
1a[a]	1	2.03 ± 0.06	7.9 ± 0.8	2.31 ± 0.06	10.27 ± 0.31	2.25	2.20	0.66	9.1 × 10^{-4}
1b[b]	2	2.03 ± 0.12	5.1 ± 0.6	1.37 ± 0.46	6.02 ± 0.32	2.27	2.10	1.15	4.5 × 10^{-3}
1b[b]	4	2.31 ± 0.13	6.5 ± 0.1	2.09 ± 0.51	7.74 ± 2.5	2.70	2.18	1.25	4.7 × 10^{-3}
1b[b]	5	1.96 ± 0.10	7.8 ± 0.1	2.13 ± 1.62	9.41 ± 1.54	2.26	2.02	1.15	7.1 × 10^{-3}
3[a]	1	1.62 ± 0.09	6.1 ± 1.1	1.65 ± 0.21	9.88 ± 1.62	1.67	1.67	1.21	2.0 × 10^{-3}
3[a]	1	1.59 ± 0.14	6.8 ± 1.0	1.50 ± 0.23	8.38 ± 1.52	1.79	1.84	1.34	1.7 × 10^{-3}
3[a]	2	1.36 ± 0.14	10.7 ± 3.6	1.91 ± 0.39	12.13 ± 3.08	1.57	1.74	1.27	2.3 × 10^{-3}

Deviations are 95% confidence intervals.
[a]RPR photoreactor, 350 nm lamps.
[b]RUL photoreactor, 350 nm lamps.

2.2. Adjustment of light sensitivity

We wished to develop actinometers that would be useful for either high or low light intensities (high or low doses). One application foreseen was their use outdoors in environmental studies, where their simplicity and convenience of use would be especially advantageous. Taking the example of **1a** as the actinometer, and using the average value $\phi = 8.1 \times 10^{-4}$ from Table 1 (this value was obtained from the curve fitting, and differs from that reported in ref. 1 which was a "direct" determination, made under the approximation that product formation is initially linear with photon dose), we calculate from eqn. (5) that when $A = 0.7A_\infty$ the maximal photon dose that can be measured using the system **1a**–PMMA is 1.9×10^{-3} mol cm^{-2} at 350 nm. To put this into perspective we summed the I_0 values of Zepp and Cline [3] for latitude 40° N over the range 295 nm $\leqslant \lambda \leqslant$ 400 nm. Table 2 then shows estimates of the useful lifetime of the **1a**–PMMA actinometer out of doors.

TABLE 2

Effective lifetimes of the **1a**–PMMA actinometer outdoors at 40° N

	Summer at noon	Winter at noon
I_0 [a] (295 - 400 nm) (mol cm^{-2} s^{-1})	1.8×10^{-8}	7.1×10^{-9}
Photon dose[b] (mol cm^{-2})	1.9×10^{-3}	1.9×10^{-3}
Effective time (s)	1.1×10^5 (29 h)	2.7×10^5 (74 h)

[a]From Table 2 of ref. 3, taking $I_0 = W_\lambda/0.93$.
[b]See text.

Our goal was to decrease the light sensitivity of the actinometer to make it useful for longer term outdoor studies.

2.2.1. Variation of the azoxy compound

Derivatives of **1a** vary in their light sensitivity, but over a relatively narrow range [4]. Our requirements were for a substrate that could be prepared easily and cheaply, easy quantitation of the rearrangement product spectrophotometrically and the property of being "well behaved" in PMMA. By well behaved, we meant that the same value of A_∞ would be reached independently of the initial substrate concentration. Previous work [4] suggested fluorinated derivatives as candidate substrates.

2,2'-Difluoroazoxybenzene (**1d**) photorearranged normally, but with a quantum yield very similar to that of **1a**. It was therefore not studied in detail. Compounds **1c** and **1e** were not "well behaved" in PMMA. Upon irradiation, the main absorption band gradually decreased in intensity and a very weak absorption appeared near 450 nm. The value of A_{450} increased with the concentration of the substrate. It is likely that in PMMA (though not in solution, at least for **1c** [4]) the photochemistry involves a slow reduction rather than a photorearrangement.

The 2,2′-bis-trifluoromethyl derivative **1b** was well behaved and was studied in more detail (Table 1) but its quantum yield of rearrangement in PMMA was higher than that of **1a**. 1,1′-Azoxynaphthalene (**3**) was also well behaved, and while it also had a higher quantum yield it had two useful features. First, the absorption maximum (at about 500 nm) of its rearrangement product **4** is much better separated from the absorption band of **3**; second, the absorption is broad, and this allowed monitoring at the absorption maximum at low photon doses, and monitoring away from the maximum (at 575 nm) at higher photon doses, and hence higher conversions. In Section 2.4 we comment on the possible use of this substrate as a solution actinometer. To conclude this section, we were unsuccessful in finding azoxy compounds having a wide enough range of quantum yields of photore-arrangement to use this concept to develop a range of actinometers of different light sensitivities.

2.2.2. Incorporation of sunscreens into the actinometer formulation

The objective was to polymerize a mixture of PMMA, azoxy compound and an inert light absorber. Such UV filters are well known as polymer photostabilizers and as the sunscreens used in cosmetics. The substances selected for study were *p*-aminobenzoic acid, *o*-hydroxybenzophenone (HB) and pyrene (P). Of these, the first was unsuitable as a sunscreen, because it inhibited the polymerization of PMMA. Both HB and P were incorporated into the PMMA unchanged (in the absence of an azoxy compound), as shown by UV spectrophotometry.

Polymers were prepared containing either **1a** or **3** with a sunscreen, and these polymer samples were irradiated in parallel with control samples from which the sunscreen was omitted. The salient features of these experiments are given in Table 3. As seen in the last column, the sunscreen did increase the useful lifetime of the actinometer, but the additional filtering due to the sunscreen reduced the plateau value A_∞. This meant that the sunscreen could only be used at low concentrations, and under these conditions the extension of the useful "lifetime" of the actinometer was small.

2.2.3. Sunscreen coatings

This was our least desired option, because we felt that coating the polymer sample with a UV filter was more difficult to do reproducibly than preparing samples with either a different substrate or a sunscreen directly incorporated into the formulation. In the event, however, this was the only method which worked satisfactorily. The procedure involved dissolving the sunscreen in a commercial urethane-type floor varnish and painting the solution on the preprepared azoxy compound–PMMA sheet. The varnish was cured for 24 h before use. Table 4 shows some of the results.

Using coated actinometers, the same amount of product was formed as in the controls, and only the photon dose needed to form this much product was altered. This method was therefore more successful than incorporating the sunscreen into the actinometer formulation. However, because the sun-

TABLE 3

Effect of incorporating sunscreens into the polymer formulation[a]

Azoxy compound[b]	Sunscreen[c]	A_∞	Time to reach $0.7A_\infty$ (h)
1a	—	2.13[d]	4.0
1a	HB (1.0)	1.53	4.5
1a	HB (2.0)	1.24	6.7
1a	HB (4.0)	0.95	8.3
1a	—	2.20[d]	3.4
1a	P (1.0)	2.12	5.1
1a	P (2.0)	2.04	6.1
1a	P (4.0)	1.97	7.0
3	—	1.94[e]	8.2
3	HB (1.0)	1.20	7.6
3	HB (2.0)	0.91	8.3
3	HB (4.0)	0.74	9.5

[a]Using a Rayonet RUL photoreactor equipped with RUL 3500 lamps.
[b]Concentration, 1 mg ml^{-1}.
[c]Numeral in parentheses is amount in milligrams per millilitre.
[d]Monitored at 415 nm.
[e]Monitored at 575 nm.

TABLE 4

Effect of coating actinometer samples with a sunscreen in varnish[a]

Azoxy compound	Amount of sunscreen[b] (wt.%)	A_∞	Time to reach $0.7A_\infty$ (h)	ΔA_0[c]
1a	—	2.32	3.3	—
1a	1	2.50	13.3	0.26
3	—	2.40	18	—
3	0.1	2.61	19	0.07
3	0.5	2.59	33	0.07

[a]Using a Rayonnet RUL photoreactor equipped with RUL 3500 lamps.
[b]HB in varnish.
[c]Absorbance at $t = 0$, attributable to the coating.

screen is simply painted on, reproducibility of the thickness of the varnish coating is difficult to achieve without using special equipment. This latter refinement will be essential if coated solid state actinometers are to be introduced routinely.

2.3. Dependence of actinometer sensitivity on light source

We had been mystified by the observation that in this work both the absorbances of 1b corresponding to the same photon dose and the ultimate

absorbances A_∞ differed from those we had reported previously [1]. Eventually this was found to result from using different photoreactors in the two series of experiments. Table 5 shows how A_∞ changes with different radiation sources. This effect is ascribed to the different spectral distributions of different sources. This becomes relevant because the relative absorptivities $\epsilon_{reactant}$ and $\epsilon_{product}$ are both wavelength dependent. The total amount of product that is formed is a complicated function of the fraction of light absorbed by the reactant, as it is summed over all wavelengths.

This variation in photosensitivity with radiation source puts a limitation on the use of solid state actinometers. In the ideal situation, one would like to evaluate eqn. (5) in terms of universally applicable parameters p_∞ and ϕ, regardless of substrate concentration and light source. In practice, although a relationship of the algebraic form of eqn. (5) appears to hold whatever the radiation source, we now realize that it will be necessary to calibrate the actinometer before use with any given radiation source. Calibration will involve a determination of A at a series of I_0 values, so that the parameters a and b in eqn. (4) can be evaluated by multiple regression.

TABLE 5

Variation in A_∞ with light source

Radiation source [a]	A_∞	
	Compound 2a [b]	Compound 4 [c]
RPR-254	0.73	0.93
RUL-254	0.68	0.85
RPR-300	1.09	0.87
RUL-300	0.85	0.98
RPR-366	1.93	1.66
RUL-350	1.07	1.36
Direct daylight	2.20	1.40
Through glass	1.50	0.86
Fluorescent lights	0.20	0.50

[a] RPR and RUL are models of Rayonet reactor; the numerals are the nominal maximum outputs of the lamps in nanometres.
[b] Concentration of 1a, 1 mg ml^{-1}; 1b monitored at 425 nm.
[c] Concentration of 3, 1 mg ml^{-1} for excitation at 254 nm and about 350 nm; concentration of 3, 0.5 mg ml^{-1} for the other samples; 4 was monitored at 575 nm.

2.4. 1,1'-Azoxynaphthalene as a solution-phase actinometer

The spectral features which make 3 a desirable substrate in PMMA are equally useful when the compound is to be used as a conventional solution actinometer. We determined the quantum yield of photorearrangement at 350 nm in 95 vol.% ethanol and in ethyl acetate. The relevant parameters are given in Table 6.

TABLE 6

Quantum yield data for 3 in solution

Solvent	Monitoring wavelength (ϵ (l mol^{-1} cm^{-1}))	ϕ (350 nm)
95 vol.% ethanol	495[a] (17000) 575 (4000)	0.022
Ethyl acetate	495[a] (16000)	0.0034

[a]λ_{max}.

3. Experimental details

Procedures for purifying methyl methacrylate and for producing polymer sheets have been described previously [1]. With the exception of 1d, all the azoxy compounds were available from previous studies in our laboratory [4]. Sunscreens were commercial materials of reagent grade.

Curve fitting was done using a Statistical Analysis System (SAS) package on an IBM 4381 mainframe computer. The non-linear least-squares analysis, using a modified Gauss–Newton method, involved setting parameter limits for a model statement, whereupon the computer, through successive iterations, converged upon the values of the model's parameters which minimized the sum of the squares of the residuals as they correlated to the experimental data.

3.1. 2,2'-Difluoroazoxybenzene

This compound was made by oxidation of 2-fluoroaniline (10 ml) with H_2O_2 in glacial acetic acid (60 ml). A total of 60 ml H_2O_2 was added in portions over 4 days while the mixture was stirred at room temperature. The reaction mixture was poured onto ice, filtered and chromatographed on alumina. Elution with ligroin:benzene (9:1 by volume) changing gradually to benzene afforded fractions containing an orange and/or a yellow substance, as shown by thin-layer chromatography. The fractions containing the yellow substance were combined, evaporated and crystallized from aqueous ethanol, affording 1d (0.55 g; melting point, 36 - 37 °C; λ_{max}(EtOH) = 305 nm (ϵ = 11 640 l mol^{-1} cm^{-1})). Analysis gave the following result. Calculated for $C_{12}H_8F_2N_2O$: C, 61.39%; H, 3.43%; N, 11.93%; F, 16.18%. Found: C, 62.10%; H, 3.16%; N, 12.00%; F, 15.97%.

3.2. Photolysis of 2,2'-difluoroazoxybenzene
3.2.1. Semipreparation

The azoxy compound (0.45 g) was dissolved in 95 vol.% ethanol (350 ml) and irradiated for 2 h employing a 450 W medium pressure mercury arc, using a Pyrex immersion well photoreactor. The solvent was evaporated and

the residue was chromatographed over alumina. Elution with ligroin, gradually changing to ligroin:toluene (1:1 by volume) afforded, in addition to unreacted azoxy compound, 2-hydroxy-6,2'-difluoroazobenzene (0.10 g) which crystallized as red needles from ethanol (melting point, 118 - 119 °C; λ_{max}(alcoholic KOH) = 470 nm (ϵ = 5640 l mol^{-1} cm^{-1})). The following composition was found: C, 62.60%; H, 4.23%; N, 11.41%; F, 18.40% ($C_{12}H_8F_2N_2O$). The poor analysis appears to be due to an unaccountable tendency of the azo compound to decompose.

3.2.2. Quantum yield

Solutions of 1d in 95 vol.% ethanol and azoxybenzene in 95 vol.% ethanol were irradiated in Pyrex ampoules using a merry-go-round in a Rayonet model RPR photoreactor using 350 nm lamps. From the absorbances at 458 nm (KOH solutions) and knowing ϕ(azoxybenzene) = 0.017 [5], duplicate determinations afforded ϕ(2,2'-difluoroazoxybenzene) = 0.014 ± 0.003.

Acknowledgments

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