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Photochemical study of substituted *s*-triazines

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Abstract

A study of the photochemical behaviour of three substituted *s*-triazines with low photoreactivity has been carried out. The photoproducts formed via irradiation at $\lambda > 300$ nm of solutions of *s*-triazines substituted by 4-amino benzylidene camphor (TABC), 4-amino diisobutyl benzal malonate (TBMA) or 4-amino-2-ethyl hexyl benzoate (TPAB) in methanol under aerated conditions have been identified. In methanol the direct irreversible phototransformation quantum yields are very low (10^{-4} – 10^{-6}).

The irradiation of the compound TABC leads to an aldehyde function attached to a position para to the aromatic ring by oxidative scission of the conjugated ethylenic bond. In the case of the compound TPAB the scission of an NH- Φ bond gives a photoproduct with a primary amino group attached to the *s*-triazine. The irradiation of the compound TBMA provokes the scission of the conjugated ethylenic bond, leading to an aldehyde function. In this case a tautomeric form of the initial molecule has also been proposed.

Keywords: Substituted *s*-triazines; Photoreactivity; Irradiation

1. Introduction

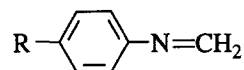
p-Amino benzoic acid (PABA) and benzylidene camphor have been widely used as active ingredients in commercially available sunscreens [1]. Benzylidene malonate derivatives are UV absorbers used in the photoprotection of automotive coatings [2]. Very few studies have attempted to characterize the photoproducts resulting from UV photolysis of these compounds in aqueous solution.

In 1985 Gasparro [3] suggested that *cis*- and *trans*-*p*, *p'*-azodibenzoic acid were formed as photoproducts upon irradiation of PABA in dilute aerated solution with 254 and 313 nm light. In 1991 Shaw et al. [4] identified a number of new photoproducts: in deoxygenated solutions between pH 7.5 and 11, 4-(4'-aminophenyl) aminobenzoic acid was detected, whereas in aerated solutions, 4-amino-3-hydroxybenzoic acid, 4-aminophenol and 4-(4'-hydroxyphenyl) aminobenzoic acid were found. The quantum yields of the formation of 4-(4'-aminophenyl) aminobenzoic acid were highly pH dependent ($\Phi \leq 10^{-4}$ at pH 7 and $\Phi > 10^{-3}$ at pH 11).

Upon light exposure, benzylidene malonate derivatives are known to dimerize into substituted cyclobutane derivatives [5].

The photoreaction products of benzylidene camphor derivatives have never been studied.

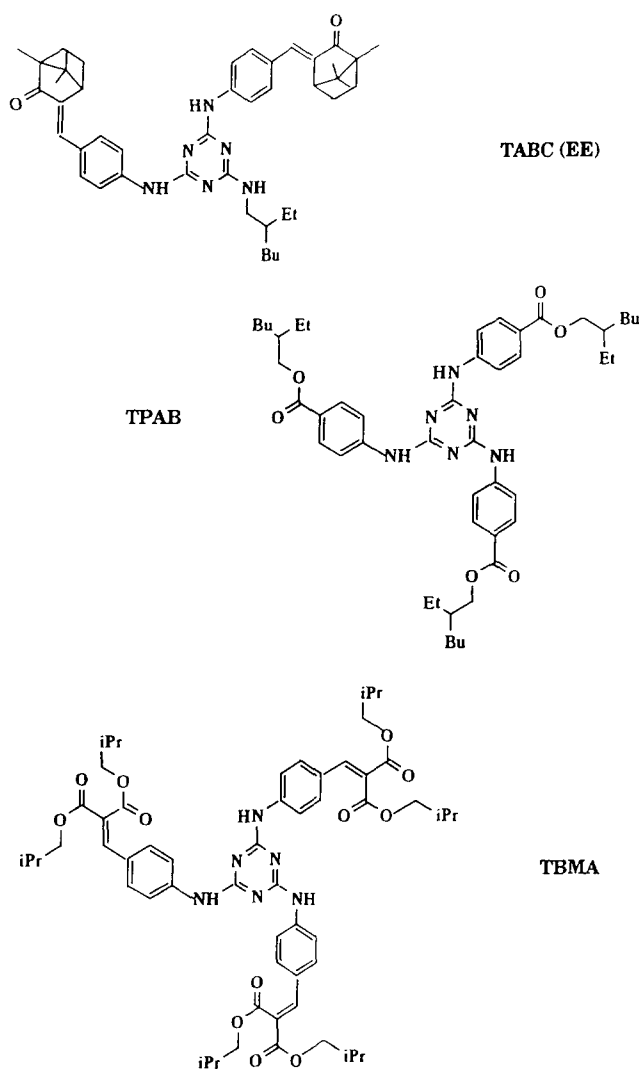
One major exception deals with the characterization of the photoproducts formed via irradiation at $\lambda > 300$ nm of aerated solutions of 4-amino benzylidene camphor, 4-amino diisobutyl benzal malonate and 4-amino-2-ethyl hexyl benzoate in methanol [6]; the three compounds have a similar photochemical behaviour leading to the formation of Schiff bases:



These photoproducts are rapidly transformed into initial compounds in an acidic environment or in aqueous solution. The formation of Schiff bases can be explained via successive reactions: a primary photoformation of a radical which attacks the methanol, leading, in the presence of oxygen, to the formation of methanal, followed by the condensation of this aldehyde with the initial primary amine.

New compounds have been developed for cosmetic applications which consist of *s*-triazine substituted by 4-amino benzylidene camphor (TABC), 4-amino diisobutyl benzal malonate (TBMA) or 4-amino-2-ethyl hexyl benzoate (TPAB) (see Scheme 1). These *s*-triazines possess a very high extinction coefficient at their UV absorption maximum, because electron delocalization is favoured.

Here we report the results of a study into the effects of UV light on these three substituted *s*-triazines in methanol. Photostability was estimated by investigation of the irreversible



phototransformation quantum yields under aerated conditions in methanol and a number of photoproducts have been identified in each case. The identification of these photoproducts was accomplished by investigation of their NMR, UV, IR and mass spectra.

2. Materials and methods

2.1. Chemicals

The compounds TABC and TBMA have been synthesized at L'Oréal Research Centre [7,8]; TABC included only two benzylidene camphor parts because of solubility considerations and was supplied in the EE form. TPAB [9] was purchased from BASF under the commercial name of Uvinul T 150.

2.2. Irradiations

Irreversible phototransformation quantum yields were determined at room temperature (20 ± 2 °C) using a high

pressure Osram 200 W mercury lamp coupled with a Bausch and Lomb monochromator. The light intensity was determined by actinometry based on the photoreduction of potassium ferrioxalate [10].

In order to isolate photoproducts, solutions in methanol (about 10^{-4} mol l⁻¹) of the various compounds were irradiated in different apparatus. TABC was irradiated at 365 nm using three MAW-Mazda 125 W lamps located at about 10 cm around the cylindrical reactor. Solutions of TPAB were irradiated using a cylindrical reflector with an elliptical base. Three tubes (Philips 15 W TLD) whose emission was centred at 310 nm were located along the first focal axis and the cylindrical reactor along the second focal axis. For exposure of the compound TBMA, irradiations were carried out in a photochemical reactor which consisted of a water-cooled polychromatic light source (Claude 250 W MFW) arranged at the centre of a Pyrex jacket containing the solution. Stirring was maintained during irradiation.

2.3. Chromatography

High performance liquid chromatography (HPLC) analyses were performed on a Waters 540 chromatograph equipped with a 990 photodiode array detector. The column used for analyses was an Interchrom Inertsil ODS-2 (250 mm × 4 mm) packed with particles of 5 μm diameter.

Photoproducts were purified using a Gilson HPLC system coupled to a model 115 UV detector. The column used for purifications was a Rainin Michrosorb C₁₈ (50 mm × 21 mm) semipreparative column packed with particles of 3 μm diameter.

2.4. Spectroscopy

Ultraviolet absorption measurements were obtained using a Cary 118C spectrophotometer.

Infrared spectra in CCl₄ were measured with an FTIR Nicolet 20 SX spectrophotometer.

Electron impact mass spectroscopy measurements were provided by the University of Orléans (France) operating in the normal scan mode at 70 eV.

¹H NMR data were obtained using a Bruker MSL AC 400 spectrometer. Spectra were recorded in CH₃OH-*d*₄ or CHCl₃-*d*.

2.5. Determination of irreversible phototransformation quantum yields

The irreversible phototransformation quantum yield is defined as the ratio of the number of molecules disappearing during a given time through the photochemical processes to the total number of photons absorbed during the same period of time.

The method of determination of quantum yields is based on HPLC measurements of the variation in the concentration of the compound with the exposure time.

The compound TABC presents a particular photochemical behaviour because of the possibility of a Z–E isomerization process. The presence in the molecule of two moieties with an ethylenic bond results in the existence of three photoisomers, i.e. EE, EZ and ZZ. The irradiation of a solution of EE isomer leads rapidly to a stationary mixture of the three forms which can be analysed by HPLC. The irreversible phototransformation of TABC can be studied only from the photostationary state obtained after a few minutes of irradiation. An approximation was necessary in order to determine the variation in the concentration by HPLC: the ZZ form must be neglected in the photostationary state. Thus it was possible to obtain the total concentration.

At $t=0$,

$$C_0 = [EE]_0$$

In the photostationary state,

$$C_\infty = [EE]_\infty + [EZ]_\infty + [ZZ]_\infty \approx [EE]_\infty + [EZ]_\infty$$

$[EE]_\infty$ can be calculated by HPLC measurements and $[EZ]_\infty \approx C_0 - [EE]_\infty$.

Thus, the variation in the total concentration can be estimated at each time.

3. Experimental results

3.1. UV spectra – isomerization quantum yields

In the TABC molecule, two isomeric forms (E and Z) can exist on each benzylidene camphor moiety because of the presence of unsaturation between the two cycles. Thus three isomers (EE, ZZ and EZ) should be considered for the whole TABC molecule.

The three isomers of the TABC molecule have been isolated by separation on a silica gel column and their UV spectra obtained. The values of λ_{\max} and ϵ for the various compounds are displayed in Table 1.

The study of the photoisomerization of TABC (EE) after short irradiation times, where only EE and EZ isomers were present in the solution at significant concentration, leads to the determination of the following initial quantum yields in methanol: $\Phi_{EE \rightarrow EZ}^0 = \Phi_{EZ \rightarrow EE}^0 = 0.2$.

Table 1
Extinction coefficient at maximum of absorption (accuracy $\pm 5\%$)

	λ_{\max} (nm)	ϵ ($\text{mol}^{-1} \text{l cm}^{-1}$)
TABC (EE)	351	73000
TABC (EZ)	355	60500
TABC (ZZ)	360	56000
TPAB	312	134000
TBMA	350	115000

Table 2
Irreversible phototransformation quantum yields determined by HPLC in methanol (accuracy $\pm 20\%$)

	λ_{irr} (nm)	$[]_0$ (mol l^{-1})	ϕ_d
TABC	365	1.10×10^{-5}	1×10^{-4}
TPAB	313	7.11×10^{-6}	7.5×10^{-5}
TBMA	365	5.98×10^{-6}	$< 10^{-6}$

3.2. Irreversible phototransformation quantum yields

The irreversible phototransformation quantum yields ϕ_d measured using the HPLC method described previously are reported in Table 2.

The results obtained prompt the following comments.

(1) The chromatogram of a solution of the compound TBMA irradiated for 500 h in methanol and the initial one were identical. If we consider that less than 10% of TBMA has disappeared (limit of detection of HPLC), an upper limit of the quantum yield of 10^{-6} can be determined.

(2) The three compounds TABC, TPAB and TBMA present high extinction coefficients and irreversible phototransformation quantum yields in methanol, which is consistent with the use of these molecules as UV filters in cosmetic applications.

3.3. Analysis of photoproducts

3.3.1. Compound TABC

The irradiated solution of TABC in methanol was analysed by HPLC: the three different undegraded forms of TABC (EE, EZ and ZZ) were eluted after various times (Fig. 1(a)). The photoproducts called P1 and P2 were initially formed. The photoproduct called X appeared after two days; P1 and P2 did not appear under degassed conditions. Very low amounts (less than 1 mg) of P1 and traces of P2 have been isolated for analysis. The formation and nature of compound X have not been studied, because this photoproduct appears only after a long irradiation time (2 days) in our experimental conditions. In outdoor conditions of sunscreen use (a few hours), X would not appear.

P1, eluted at lower time and identified as 1-(4'-amino benzylidene camphor)-3-(2-ethyl hexyl amino)-5-(4'-amino benzaldehyde)-s-triazine (E), was followed by P2, identified as 1-(4'-amino benzylidene camphor)-3-(2-ethyl hexyl amino)-5-(4'-amino benzaldehyde)-s-triazine (Z). The qualitative UV spectra of P1 and P2 were very similar to that of TABC (Fig. 1(b)).

The spectroscopic data obtained for P1 and P2, the main photoproducts detected in irradiated aerated solution, were completely consistent with the assigned structures (see Table 3).

3.3.1.1. Structural assignment of photoproduct P1

The three forms of TABC itself (EE, EZ and ZZ) gave ^1H NMR spectra with a characteristic ethylenic proton signal at 7.20 ppm for E positions and 6.55 ppm for Z positions.

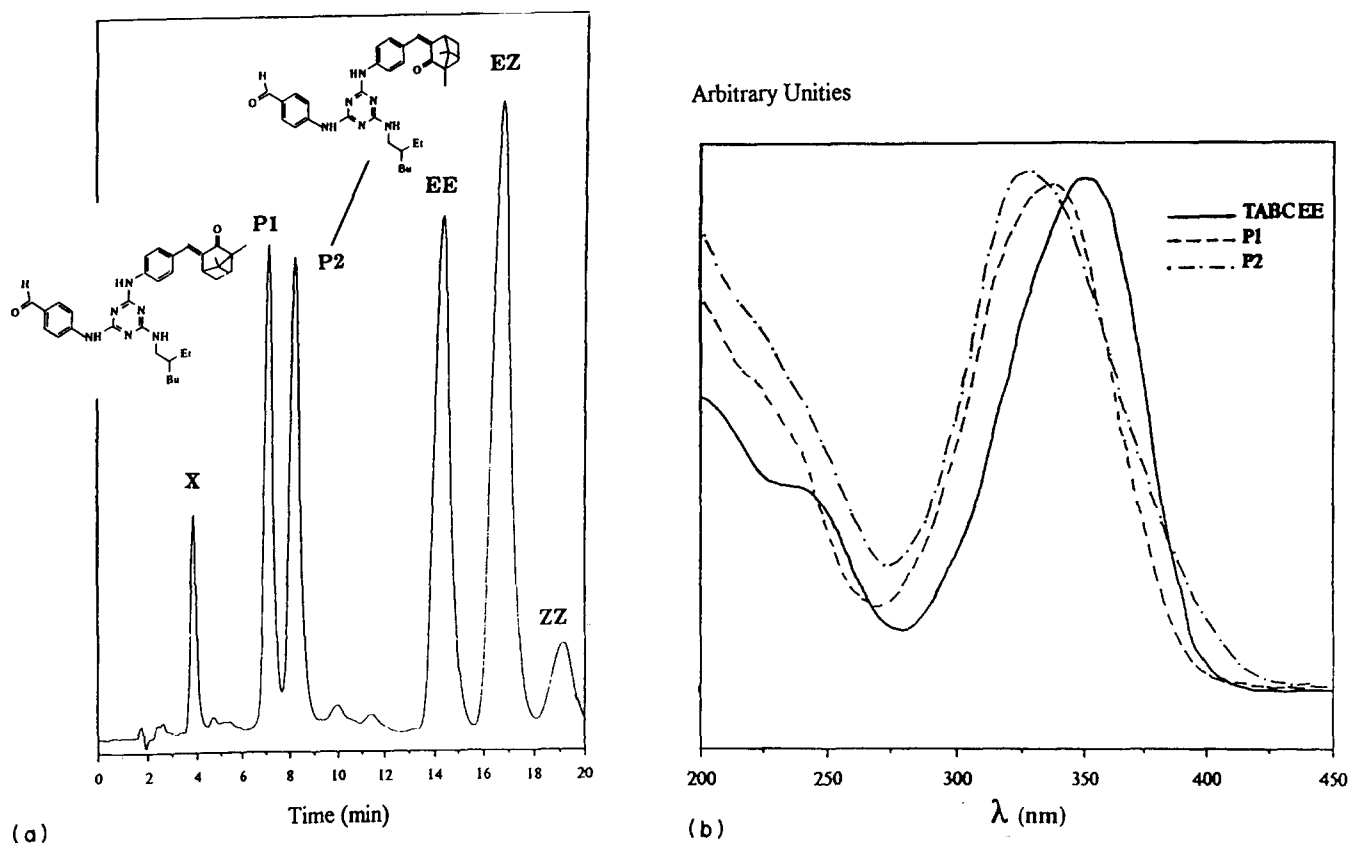


Fig. 1. (a) HPL chromatogram of irradiated solution of TABC in methanol. (b) Qualitative UV spectra of TABC, P1 and P2 compounds.

Table 3
Structural assignment of three isomer forms of TABC, P1 and P2

	NMR (CH ₃ OH- <i>d</i> ₄)		IR Carbonyl region $\bar{\nu}$ (cm ⁻¹)	Molecular mass (amu)
	Characteristic proton signal (ppm)	Number of protons		
TABC (EE)	7.20	2	1725	
TABC (EZ)	7.20	1		
	6.55	1		
TABC (ZZ)	6.55	2		
P1	7.20	1	1720	580
	9.80	1	1725	
P2				580

The ¹H NMR spectrum of the isolated photoproduct P1 showed such a proton signal at 7.20 ppm indicating the presence of one ethylenic proton (E). In addition, we detected one proton signal at 9.80 ppm confidently attributed to an aldehyde or carboxylic function. Between 0 and 5 ppm the ¹H NMR spectra recorded in CH₃OH-*d*₄ were very intricate and it was difficult to formulate any hypothesis from the investigation of this region.

The IR spectrum of P1 exhibited two bands in the carbonyl region at 1700 and 1725 cm⁻¹, whereas TABC itself presents a band at 1725 cm⁻¹ attributed to ketones on camphor. Thus, the band at 1700 cm⁻¹ may be consistent with the proposed

structure for P1: it could be attributed to a conjugated aldehyde function.

The high resolution EIM spectrum showed a molecular mass of 580 amu which was compatible with the suggested formula of P1.

3.3.1.2. Structural assignment of photoproduct P2

Traces of photoproduct P2 allowed us to obtain an EIM spectrum, but yields were not important enough to realize an IR or ¹H NMR spectrum.

The EIM spectrum showed a molecular mass of 580 amu corresponding to the same molecular mass as P1. This result

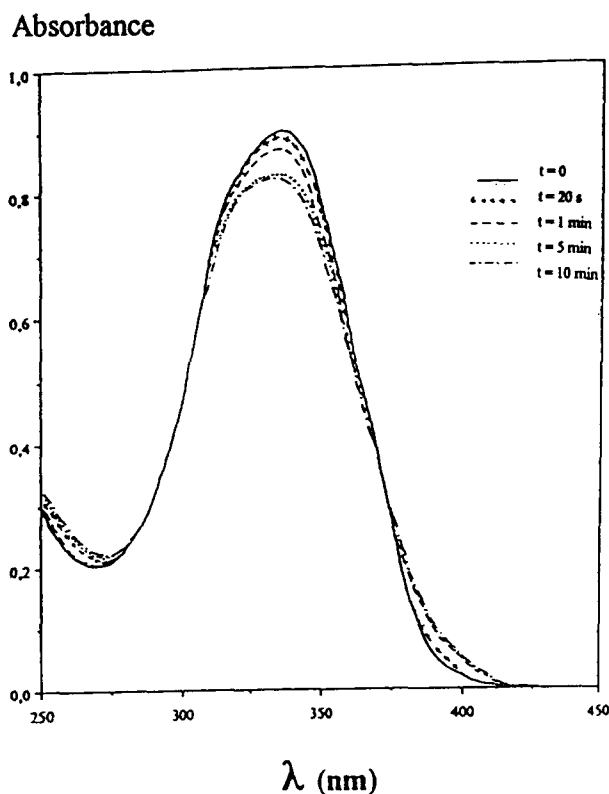


Fig. 2. Evolution of UV spectrum of photoproduct P1 during irradiation at 365 nm.

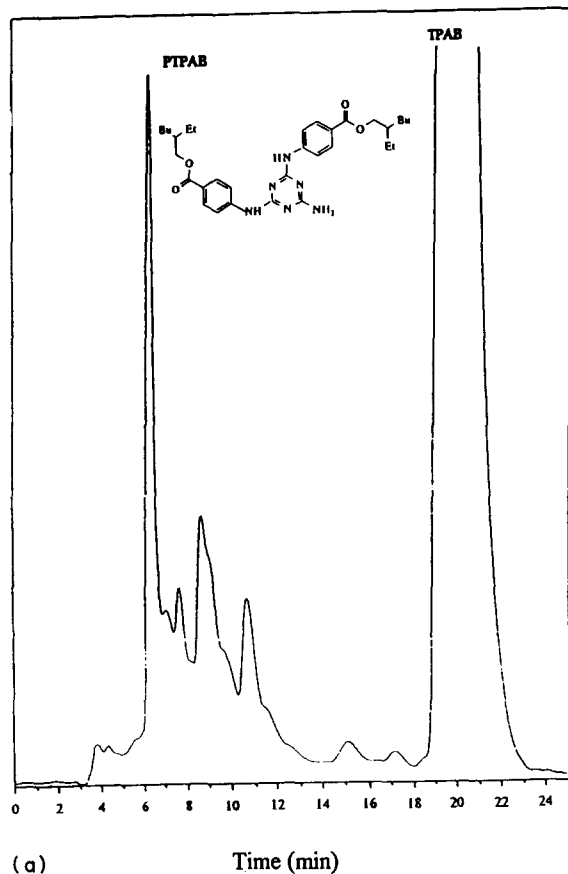
allowed us to think that P1 and P2 were the two isomers E and Z of the same molecule. In order to confirm this hypothesis, the isolated photoproduct P1 was irradiated at 365 nm using a monochromator; the UV spectrum evolution is reported in Fig. 2. The two isosbestic points and the photostationary state after 10 min of exposure were typical of a photoisomerization. Moreover, the photostationary state analysed by HPLC gave two peaks whose elution time and qualitative UV spectra were similar to those of P1 and P2.

3.3.2. Compound TPAB

The chromatogram of the irradiated solution of TPAB in methanol is displayed in Fig. 3(a). The undegraded TPAB was eluted after 21 min. Numerous photoproducts were detected between 3 and 18 min, but only the photoproduct called PTPAB could be isolated after two successive semi-preparative chromatographies. Yields were about 1 mg. PTPAB, eluted after 6.5 min, has been identified as 1,3-(*p*-(2-ethyl hexyl-1-yloxy carbonyl)-anilino)-5-(amino)-*s*-triazine. The qualitative UV spectrum of PTPAB was very similar to that of TPAB (Fig. 3(b)).

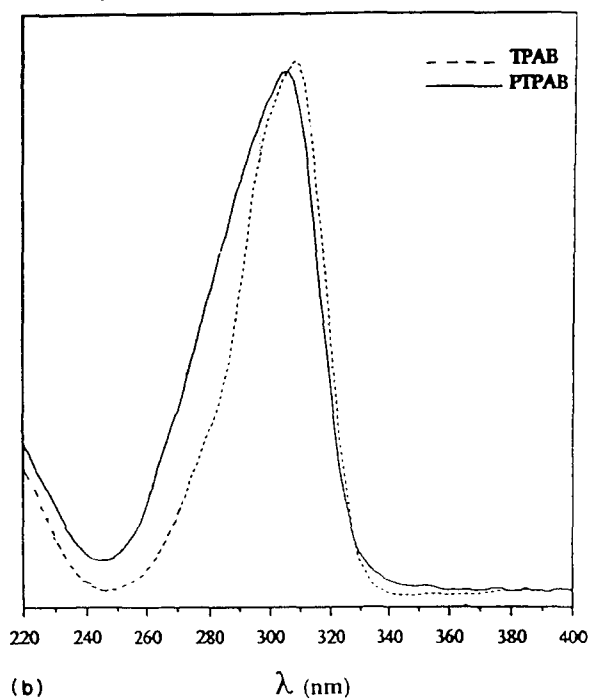
3.3.2.1. Structural assignment of photoproduct PTPAB (see Table 4)

TPAB itself gave a ^1H NMR spectrum with six protons whose chemical shifts were 4.25 ppm. This chemical shift was consistent with the six protons of the three CH_2 groups of the ester functions. The ^1H NMR spectrum of the isolated



(a)

Arbitrary Unities



(b)

Fig. 3. (a) HPL chromatogram of irradiated solution of TPAB in methanol. (b) Qualitative UV spectra of TPAB and PTPAB compounds.

Table 4
Structural assignment of TPAB and PTPAB

	NMR (CH ₃ OH- <i>d</i> ₄)		IR Characteristic bands $\bar{\nu}$ (cm ⁻¹)	Molecular mass (amu)
	Characteristic proton signal (ppm)	Number of protons		
TPAB	4.25	6	3435	
	7.9–8	12		
PTPAB	4.25	4	3435	590
	7.88	4	3553	
	7.94	4		

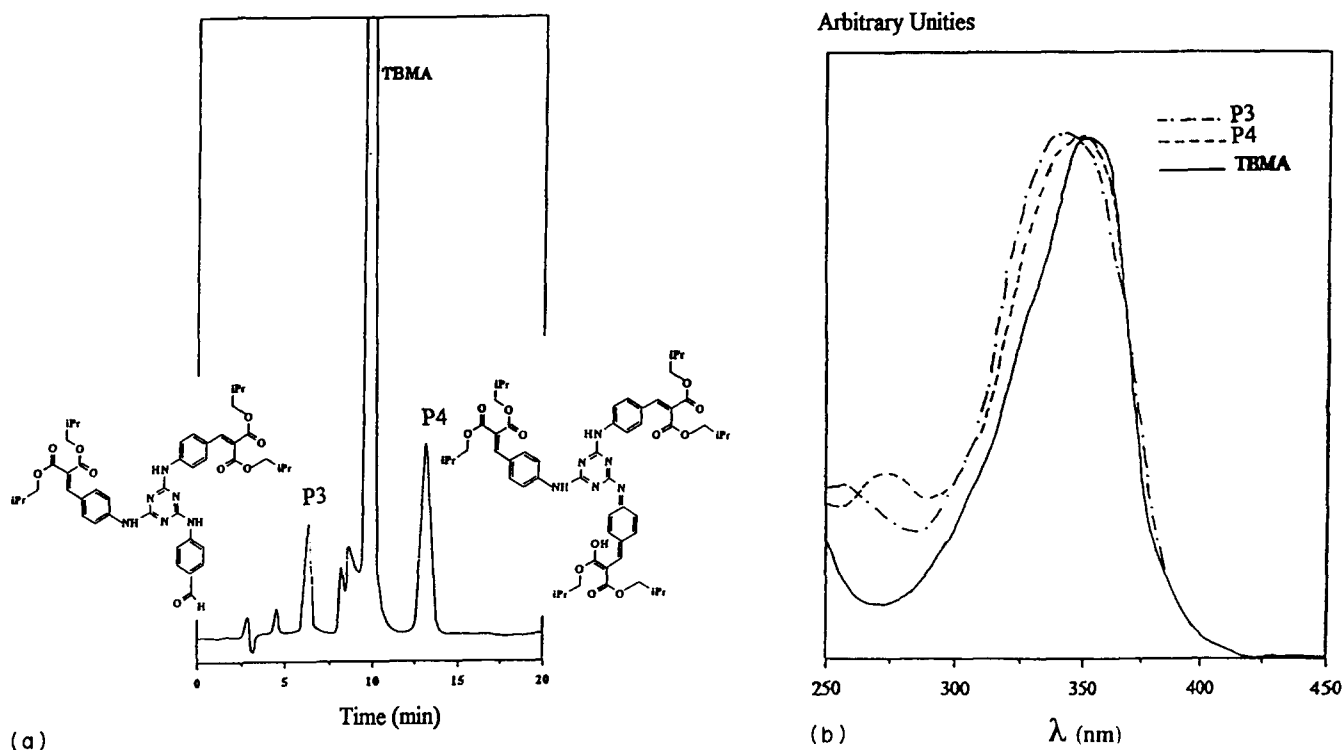


Fig. 4. (a) HPL chromatogram of irradiated solution of TBMA in methanol. (b) Qualitative UV spectra of TBMA, P3 and P4 compounds.

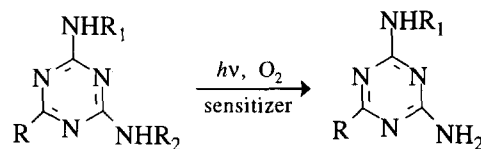
photoproduct showed such a signal at 4.25 ppm corresponding to only four protons, so this molecule had two ester functions. In the aromatic region, TPAB exhibited a badly resolved multiplet between 7.9 and 8 ppm corresponding to the 12 aromatic protons, whereas PTPAB presented two doublets at 7.88 ppm (four protons) and 7.94 ppm (four protons). This led us to conclude that the photoproduct had two aromatic rings.

The IR spectrum of TPAB showed a band of low intensity at 3435 cm⁻¹ attributed to the three secondary amine functions. In this region the photoproduct exhibited an additional band at 3553 cm⁻¹ which may correspond to a primary amine function.

In addition, the EIM spectrum gave a molecular mass of 590 amu which is consistent with the proposed structure.

Such products resulting from sensitized UV photolysis of substituted *s*-triazines in aerated solution have been described

in the literature, where R, R₁ and R₂ corresponded to alkyl groups [11–14]:



3.3.3. Compound TBMA

The irradiated solution of TBMA in methanol analysed by HPLC showed two well-defined photoproducts P3 and P4 (Fig. 4(a)).

The first photoproduct P3, eluted after 6 min, was followed by the undegraded TBMA (10 min) and by the second photoproduct P4 (13 min). P3 and P4 have been isolated and identified as 1,3-bis-(4'-amino diisobutyl malonate), 5-(4'-amino benzaldehyde)-*s*-triazine for P3 and a quinone imine

Table 5
Structural assignment of TBMA, P3 and P4

	NMR (CH ₃ OH- <i>d</i> ₄)		IR Characteristic bands $\bar{\nu}$ (cm ⁻¹)	Molecular mass (amu)
	Characteristic proton signal (ppm)	Number of protons		
TBMA	4.05	12	1727	
	7.50	6		
	7.65	6		
	7.75	3		
P3	4.05	8	1700–1710 1727	834
	7.50	4		
	7.65	4		
	7.75	2		
	7.80	2		
	9.90	1		
P4	3.50	4	1725 1734	1032
	4.05	8		
	5.70	1		
	7.20	2		
	7.45	4		
	7.70	4		
	7.85	4		

Table 6
Summary of proposed structures of analysed photoproducts

	Number of analysed photoproducts	Proposed structure of photoproducts
TABC	2 (E + Z)	Oxidative scission of the conjugated ethylenic bond ⇒ aldehyde attached to a position para to the aromatic ring
TPAB	1	Scission of an NH- Φ bond ⇒ primary amino group attached to the <i>s</i> -triazine
TBMA	2	(1) Oxidative scission of the conjugated ethylenic bond ⇒ aldehyde attached to a position para to the aromatic ring (2) Tautomeric form of the initial molecule ⇒ substituted quinone imine form attached to the <i>s</i> -triazine

form for P4. The qualitative UV spectra of P3 and P4 were very similar to that of TBMA (Fig. 4(b)).

The proposed structures accounted for the spectroscopic data obtained (see Table 5).

3.3.3.1. Structural assignment of photoproduct P3

The ¹H NMR spectrum of TBMA showed 12 protons whose chemical shifts were 4.05 ppm attributed to protons of the six CH₂ groups of the ester functions, whereas P3 had only eight protons corresponding to this chemical shift. In addition, the aromatic region of the spectra proved that only two *p*-substituted phenyl residues remained intact: P3 had eight aromatic protons and two ethylenic protons at 7.75 ppm. Moreover, P3 presented another substituent characterized by two doublets at 7.80 and 7.90 ppm and one proton at 9.9 ppm which may be attributed to an aldehyde function.

The IR spectrum of P3 exhibited two bands (1700–1710 and 1725 cm⁻¹), whereas TBMA possessed only one band at 1725 cm⁻¹ corresponding to the ester functions. The addi-

tional band found for P3 was consistent with the presence of a conjugated aldehyde function.

The proposed structure was compatible with the mass spectral evidence, the molecular mass being 834 amu. This information together with the IR and NMR spectra made the structural assignments of this compound unambiguous.

3.3.3.2. Structural assignment of photoproduct P4

This photoproduct gave a ¹H NMR spectrum exhibiting eight protons at 4.05 ppm typical of protons of the CH₂ groups of the ester functions. One proton was detectable at 5.70 ppm. Two aromatic rings remained intact (four protons detected at 7.45 and 7.85 ppm and two ethylenic protons detected at 7.70 ppm as a singlet). A third aromatic ring was characterized by four protons (7.20 and 7.70 ppm). This assignment was confirmed by the IR spectrum data.

TBMA gave an IR spectrum with a band at 1727 cm⁻¹ which may be attributed to the conjugated ester functions. P4 exhibited a band at 1733 cm⁻¹. This higher frequency may be explained by unconjugated ester functions.

In addition, the EIM spectrum gave a molecular mass of 1032 amu. This suggested that P4 was a tautomer form of TBMA.

We might speculate that P4 possessed a substituted quinone imine form which no longer contained a conjugated ethylenic bond. The enolic proton may be consistent with the signal detected at 5.70 ppm.

3.3.4. Summary

Various photoproducts have been isolated and characterized for the three compounds studied. Table 6 summarizes the identities of the analysed photoreaction products.

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