

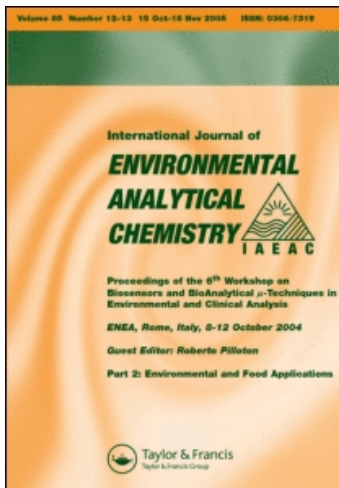
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# PHOTOOXIDATION OF 3,3'- AND 4,4'-DIMETHYLBIPHENYLS IN NATURAL SEAWATER

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Photochemical degradation of 3,3'- and 4,4'-dimethylbiphenyls was studied in natural seawater, without photosensitizer and under artificial UV irradiation. The photooxidation process takes place mainly on benzene ring side chains. Photoproduct analysis, carried out by GC-MS, FTIR and GC-FTIR confirm three successive oxidation states of methyl substituents : alcohol, aldehyde and carboxylic acids.

**KEY WORDS:** Photooxidation, PAH's, dimethyl biphenyls, seawater, GC-FTIR, FTIR, GC-MS.

## INTRODUCTION

As soon as hydrocarbons are introduced into the marine environment, they are subject to important abiotic and biological changes (solubilization, evaporation, photooxidation, biodegradation...). The intensities of these processes and their relative importance depend on the hydrocarbon family. For example, aromatic compounds are more sensitive to photooxidation than saturated hydrocarbons. Inversely, biodegradation of saturated hydrocarbons is usually easier than that of polycyclic aromatic derivatives.<sup>1</sup> Moreover, inside the same family of aromatic compounds, these evolutive phenomena can depend on the number and the position of alkyl substituents and lead to preferential degradations.<sup>2</sup> It can be described by many ratios or indices as "methyl naphthalene index" (MNI) or "methyl phenanthrene index" (MPI).<sup>3</sup> These index values are used to understand hydrocarbon origin and state of maturity, and to monitor their evolution. The aim of the present work is to contribute to the knowledge of mechanisms in petroleum PAH's photooxidation taking place in the marine environment.

We have specifically studied these phenomena in the case of alkylbiphenyls. Alkylbiphenyls are a class of aromatic compounds which often occur in similar concentrations to alkylnaphthalenes or alkylphenanthrenes in crude oil.<sup>4-6</sup> The most abundant alkylbiphenyls in petroleum are dimethyl derivatives and, among them, meta or para disubstituted compounds are predominant.<sup>7</sup>

Different authors have previously studied aromatic photooxidation pathways, but principally in the case of alkylbenzenes<sup>8-10</sup> or polycondensed aromatic rings.<sup>11-14</sup> On the other hand, only a few works concern biphenyl photooxidation.<sup>15</sup>

Therefore, we have studied the photooxidation of 3,3'-dimethylbiphenyl (3,3'-DMBP)

and 4,4'-dimethylbiphenyl (4,4'-DMBP). Photoproduct identifications have been done by gas chromatography coupled with mass spectroscopy (GC-MS) and FTIR spectroscopy (GC-FTIR). These two techniques are very complementary in the case of aromatic isomer structural determinations.<sup>16</sup>

## EXPERIMENTAL

### *Photooxidation experiments*

3,3'-DMBP and 4,4'-DMBP were Aldrich products with respective purities of 99% (612-75-9) and 97% (613-33-2). The natural seawater was taken in a Mediterranean coastal area (Carry-le-Rouet) and sterilized.

The compounds (50 mg) were irradiated in 200 ml of sterilized natural seawater during 24 days under magnetic stirring in 1 liter borosilicate round bottom flasks. The artificial UV irradiation was made using a Osram Ultravitalux (300 W) lamp sunlight. Flasks with identical contents (50 mg of DMBP in 200 ml of sterilized natural seawater) kept in the dark served to check for influences other than sunlight.

The irradiated solutions were first extracted with diethyl ether (3 x 25 ml). In this organic phase, a very light precipitate was progressively obtained (P1). The aqueous phase was acidified (HCl 3 N, pH = 1), then extracted a second time with CH<sub>2</sub>Cl<sub>2</sub>. A second precipitate (P2) was obtained in this phase. The combined organic extracts were dried on anhydrous MgSO<sub>4</sub>, filtered, concentrated with a Büchi Rotavapor® (35°C, light vacuum conditions) and then analysed by GC, GC-FTIR and GC-MS. The two precipitates were filtered with PTFE FH Millipore filters and analysed by FTIR.

### *Analysis*

Chromatographic separations (GC) of the photoproducts were achieved with a Vega 6000 Carlo Erba chromatograph and a CP SIL 8 CB (25 m x 0,32 mm x 0,25 µm) Chrompack column programmed from 70°C to 200°C at 3°C mn<sup>-1</sup>. An on column injector and helium carrier gas (2 ml.min<sup>-1</sup>) were used. For the hyphenated techniques, identical or equivalent columns and analog chromatographic conditions were used. The GC quantitative analysis of the residual compounds was made with biphenyl as internal standard.

GC-FTIR analysis were performed on a HRGC 5300 Mega Carlo Erba chromatograph (CP Sil 8 CB column as in GC) interfaced with a 20 SXB Nicolet FTIR spectrometer. The light-pipe and the transfer lines were maintained at 250°C. A liquid nitrogen cooled medium range MCT detector (4000-600 cm<sup>-1</sup>) was used. Sixteen data scans were collected and coadded per data file with a resolution of 8 cm<sup>-1</sup>.

Electron impact mass spectra (GC-EI MS) were obtained with an Unicam Automass spectrometer and a DI 200 Delsi chromatograph. Chromatographic conditions were different from GC-FTIR: the injection system was splitless, the temperature program 40 to 90°C at 30°C mn<sup>-1</sup> then 90 to 280°C at 5°C mn<sup>-1</sup>, and the pressure of carrier gas (helium) 40 kPa. For the spectrometer the temperatures were 200°C for the source and 240°C for the interface, and the ionisation energy was 70 eV.

Chemical ionisation mass spectroscopy (GC-CI MS) was performed with a 5989 A Hewlett Packard spectrometer interfaced with a 5890 chromatograph equipped with an

HP5-MS column (30 m x 0,25 mm x 0,25  $\mu\text{m}$ ) and a splitless injector. A constant flow of helium carrier gas was used (1 ml  $\text{mn}^{-1}$ ) and the temperature program was the same as that for GC-EI MS. For the mass spectrometer, source temperature was 240°C, interface temperature was 280°C; the reactant gas was methane (1 torr), and the ionisation energy was 230 eV.

FTIR analysis for solid products were achieved with a 20 SXB Nicolet spectrometer (KBr pellets, 128 scans, resolution of 4  $\text{cm}^{-1}$ ).

## RESULTS AND DISCUSSION

### 3,3'-DMBP photoproduct identification

GC analyses of dark controls showed no oxidation products. Conversely, GC analyses of organic fractions showed four principal compounds. The main peak corresponded to residual 3,3'-DMBP and was identified by GC-FTIR (spectral search versus vapour phase Aldrich library). The three other GC-FTIR spectra indicate that the compounds have the same aromatic skeleton as 3,3'-DMBP because numerous IR bands are common : 3038  $\pm$  2  $\text{cm}^{-1}$  (aromatic  $\nu$  CH) , 1604  $\pm$  1  $\text{cm}^{-1}$ , 1478  $\pm$  2  $\text{cm}^{-1}$  et 1438  $\pm$  2  $\text{cm}^{-1}$  (aromatic  $\nu$  C = C), 762  $\pm$  10  $\text{cm}^{-1}$  (out of plane  $\gamma$  CH), 698  $\pm$  1  $\text{cm}^{-1}$  (ring bending). The two last vibrations are characteristic of a meta disubstituted aromatic ring.

Moreover, the spectra of these compounds, following the elution order, show the characteristics of (i) an aldehyde ( $\nu$  CH 2808  $\text{cm}^{-1}$ ,  $2\delta$  CH 2718  $\text{cm}^{-1}$  and  $\nu$  C = O 1719  $\text{cm}^{-1}$ ), (ii) a primary alcohol ( $\nu$  O-H 3657  $\text{cm}^{-1}$  and  $\nu$  C-O 1028  $\text{cm}^{-1}$ ), (iii) a carboxylic acid ( $\nu$  O-H 3584  $\text{cm}^{-1}$ ,  $\nu$  C = O 1761  $\text{cm}^{-1}$ ,  $\delta$  OH 1342  $\text{cm}^{-1}$  and  $\nu$  C-O 1164  $\text{cm}^{-1}$ ).

The spectra also present two bands at 2933  $\pm$  2  $\text{cm}^{-1}$  and 2878  $\pm$  2  $\text{cm}^{-1}$  which confirm the presence of a methyl group. All these attributions are in good agreement with the interpretation of vapour phase IR spectra.<sup>17</sup> The GC-FTIR spectra of the three photoproducts are given in Figure 1.

Complementary GC-MS data allow us to determine exactly the structure of the photoproducts:

– In GC-EI MS, the classically described fragments are found (Figure 2)

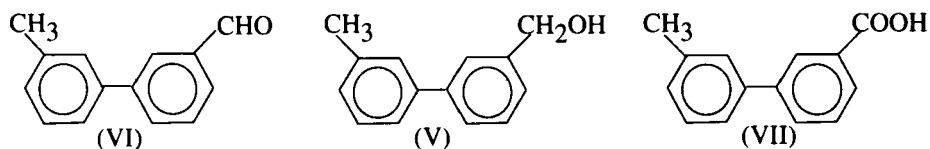
Aldehyde :  $m/z$  196 (M), 195 (M-1), 167, 165 et 152

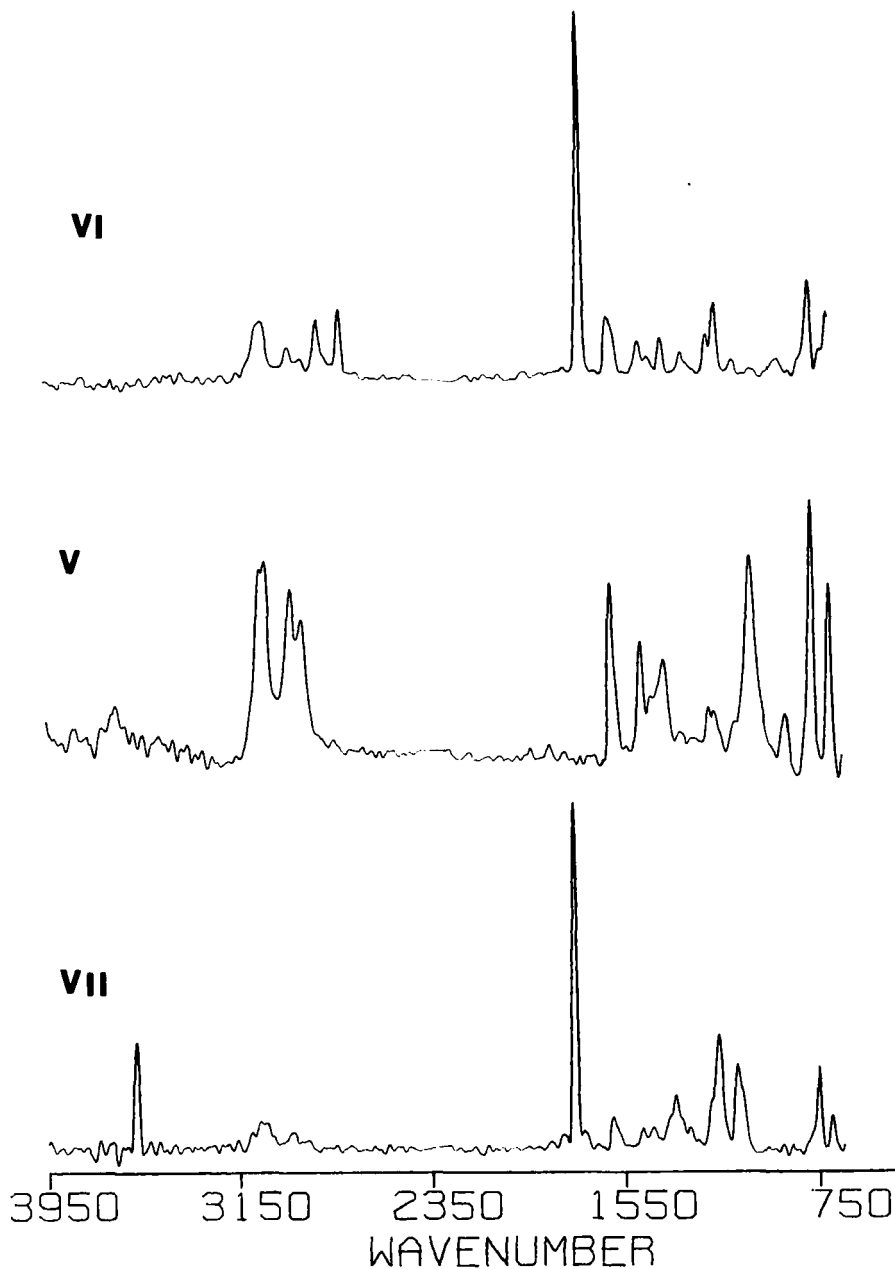
Alcohol :  $m/z$  198 (M), 183 (M-15), 180 (M-18), 167, 165 et 152

Acid :  $m/z$  212 (M), 195 (M-17), 167 (M-45), 165 et 152

– The GC-CI MS spectra systematically exhibit M+1 and M+28 peaks which confirm the molecular masses previously determined.

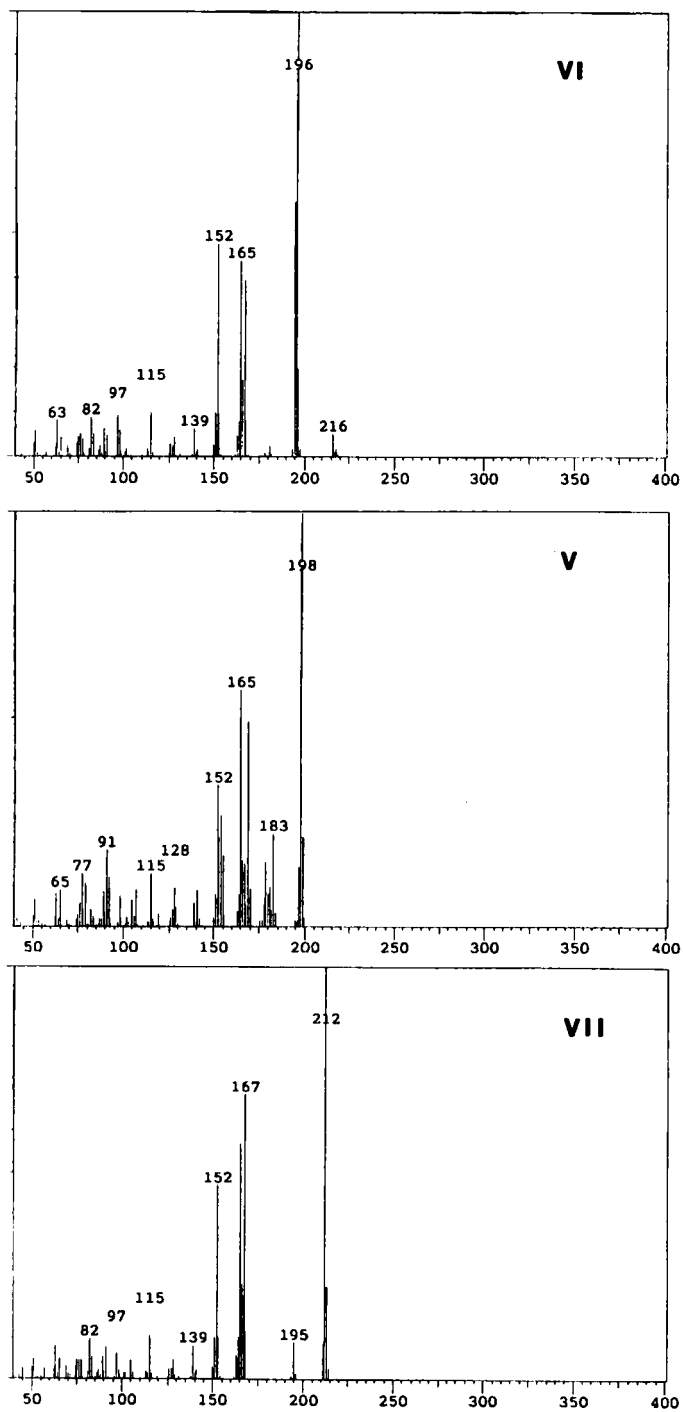
Consequently, the three following structures can be proposed: (VI) 3'-methyl-biphenyl-3-carbaldehyde, (V) 3'-methyl-biphenyl-3-methylene hydroxide and (VII) 3'-methyl-biphenyl-3-carboxylic acid



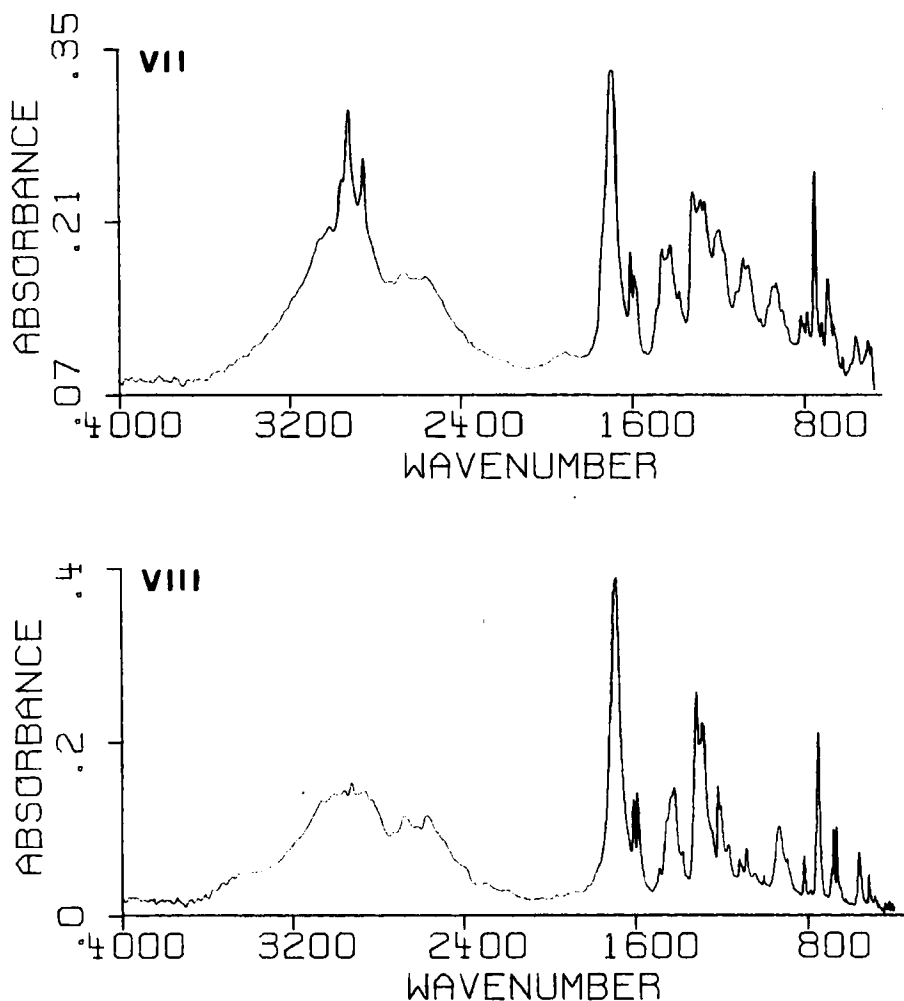


**Figure 1** GC-FTIR spectra of 3,3'-DMBP photoproducts (organic phase) (VI) : 3'-methyl-biphenyl-3-carbaldehyde, (V) : (3'-methyl-biphenyl-3)yl-methanol, (VII) : 3'-methyl-biphenyl-3-carboxylic acid.

The FTIR spectra of the two precipitates P1 and P2 exhibit carboxylic group bands: broad and complex bands between  $3500$  and  $2400\text{ cm}^{-1}$  ( $\nu$  O-H),  $1688\text{ cm}^{-1}$  ( $\nu$  C = O),  $1418 \pm 2$  and  $1312 \pm 1\text{ cm}^{-1}$  ( $\nu$  C-O +  $\delta$  OH),  $929 \pm 1\text{ cm}^{-1}$  ( $\gamma$  OH).



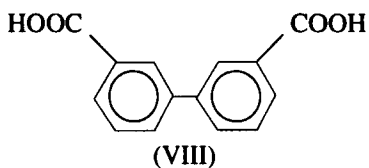
**Figure 2** GC-EI MS spectra of 3,3'-DMBP photoproducts (organic phase) (VI) : 3'-methyl-biphenyl-3-carbaldehyde, (V) : (3'-methyl-biphenyl-3)yl-methanol, (VII) : 3'-methyl-biphenyl-3-carboxylic acid.



**Figure 3** FTIR spectra of 3,3'-DMBP photoproducts (solid phase) (VII) : 3'-methyl-biphenyl-3-carboxylic acid, (VIII) : 3,3'-biphenyl dicarboxylic acid.

Moreover the two spectra show characteristic bands of a meta disubstituted aromatic ring (out of plane bending  $\gamma$ CH at  $748 \pm 1 \text{ cm}^{-1}$  and ring bending at  $688 \pm 1 \text{ cm}^{-1}$ ).<sup>18</sup> In addition, P1 spectra show  $\nu\text{CH}_3$  vibrations characteristic of methyl groups at 2954, 2923 and  $2853 \text{ cm}^{-1}$ , which are not seen in the P2 IR spectrum.

Consequently we can propose a diacid structure for P2 (VIII 3,3'-biphenyl dicarboxylic acid) and a monoacid structure for P1 (VII : 3'-methyl-biphenyl-3-carboxylic acid). This latter compound is the same than the one already found in the organic phase.



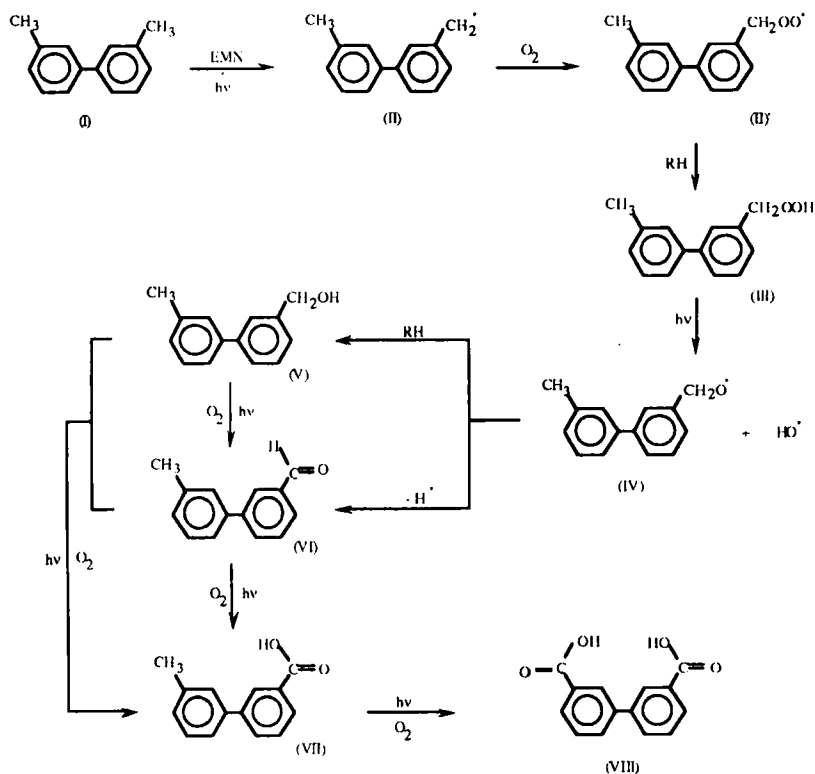


Figure 4 3,3'-DMBP photooxidation mechanisms.

#### 4,4'-DMBP photoproduct identification

In the organic phase, with the residual 4,4'-DMBP, only two photoproducts were detected. They were unequivocally identified by GC-EI MS and GC-CI MS as 4'-methyl-biphenyl-4-carbaldehyde and (4'-methyl-biphenyl-4)yl-methanol giving mass spectra which are closely related to those of homologous products derived from 3,3'-DMBP.

As for 3,3'-DMBP, we observe in the solid fraction the monocarboxylic and the dicarboxylic derivatives. The 4'-methyl-biphenyl-4-carboxylic acid exhibits the characteristic absorption bands of COOH and CH<sub>3</sub> groups.<sup>18</sup> The para disubstitution is confirmed by the out of plane bending  $\gamma$ CH band at 819 cm<sup>-1</sup>.

For the diacid derivative, the identification is completed by comparison with the FTIR spectra of the photoproduct obtained and the 4,4'-biphenyl dicarboxylic acid which is a commercial product (Aldrich 22-526-6).

#### Mechanisms

Momzikoff *et al.*,<sup>19</sup> measured the photo-sensitizing capacity of Mediterranean coastal waters and found far from negligible values. Consequently, it's reasonable to assume that seawater used in the experiment contained natural or man-made compounds which sensitized the photooxidation reactions. So the main rout of the photooxidation of 3,3'-



DMBP (I), is the abstraction of a hydrogen atom from the methyl group to occur the intermediate radical  $\text{ArCH}_2^\bullet$  (II). This radical can react with dissolved oxygen to yield the peroxy radical (II)' which abstract a hydrogen atom from RH to give the hydroperoxide (III) as a primary photoproduct.

This hydroperoxide (III) is homolytically split in a light induced reaction. The alkoxy radical (IV) is formed and can react either with an other aromatic molecule ( $\text{ArCH}_3$ ) producing an alcohol (V) and an aromatic radical, starting an autooxidation process by further reaction with oxygen, or by rapid hydrogen elimination forming the aldehyde (VI).

The acid (VII), may be obtained either by direct photooxidation of alcohol or aldehyde, or by reaction between the alcohol and the aldehyde. The dicarboxylic acid (VIII) may be formed directly by photooxidation of the monoacid.

If seawater didn't contain photosensitizers, the photooxidation mechanism can go directly via a light excited hydrocarbon-oxygen complex<sup>(15,20-22)</sup>. We assume, therefore, that the photodegradation of 4,4'-DMBP occurs in the same way as that of 3,3'-DMBP.

Moreover, we observe a significant difference in degradation ratios between 3,3'-DMBP and 4,4'-DMBP, respectively, 5,8% and 1,7%. Two explanations are possible.

First, by mesomeric effects. The radical  $\text{p-ArCH}_2^\bullet$  in the case of 4,4'-DMBP is more stabilized by resonance effect because the unpaired electron can be delocalized with the  $\Pi$  electrons of the two aromatic rings. On the other hand, for the  $\text{m-ArCH}_2^\bullet$  this delocalization occurs with only one ring.

The second explanation concerns the respective physical states of the two compounds. Indeed, the 3,3'-DMBP (melting point 5–7°C) leads to a micro-emulsion when stirred, leading to a better approach between dissolved oxygen and the reactant. On the opposite, the 4,4'-DMBP (melting point 118–120°C) remains solid and leads to a heterogeneous solution and thus a worse contact with oxygen which can explain a lower degradation yield.

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