

# Mechanism of photocyclization of substituted phenylbenzoquinones

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## Abstract

The mechanism of the photocyclization of phenylbenzoquinones substituted in *meta* position on the phenyl to 2-hydroxydibenzofuran derivatives was investigated by combined laser flash photolysis (LFP) and continuous irradiation measurements in various solvents. In any type of solvent, the triplet state of the quinone is converted by a thermally activated process to a cyclized intermediate **X** which, in polar and/or acidified solvents, rearranges to the final product by a sequence protonation/deprotonation, whereas in non-polar solvents, it reopens to the starting material. The triplet state of the quinone responsible for the cyclization is an  $n\pi^*$  state located, depending on the substituent, a few kilojoules per mole above or below the  $\pi\pi^*$  triplet state involved in dimerization but the rate of cyclization is not determined by the nature of the lowest triplet state because the energy splitting between the  $n\pi^*$  and  $\pi\pi^*$  triplet states is much smaller than the activation energy of the cyclization reaction. The *meta* methoxy substituted compound gives rise, in the excited singlet state, to an intramolecular charge transfer state stabilized by polar solvents so that the yield of formation of the triplet and, consequently, the cyclization quantum yield strongly decrease in these solvents. The two rotamers of this compound have, in their triplet state, quite different reactivities so that the cyclization is regiospecific. Substitution by an electron withdrawing group such as  $\text{CF}_3$  has two major effects: (i) it raises the energy level of the  $\pi\pi^*$  states so that the lowest triplet state becomes  $n\pi^*$  and H-abstraction to alkanes and alcohols becomes an important reaction pathway and (ii) it makes possible an electron transfer from solvents with a low oxidation potential to the quinone triplet state, reducing strongly the triplet lifetime and, consequently, the quantum yield of cyclization. Thus, many factors influence the cyclization quantum yield measured under continuous irradiation as well as the competition between the various reaction pathways. That is why previous mechanistic studies based on measurements of this type on a series of compounds in various solvents are largely erroneous. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Photocyclization; Phenylbenzoquinones; Triplet state

## 1. Introduction

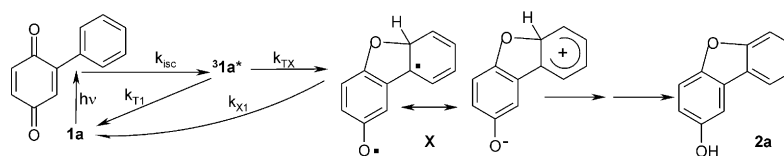
Phenylbenzoquinones undergo a rapid and efficient cyclization reaction to give dibenzofuran derivatives: the conversion of 2,6-diphenylbenzoquinone in 3-phenyl-2-hydroxydibenzofuran was reported by Hageman and Huysmans [1], 30 years ago, and phenylbenzoquinone [2] as well as 4,4'-dimethoxybiphenyl-2,5,2',5'-bisquinone [3] also yields hydroxydibenzofuran derivatives. From the first studies of the mechanism of this photocyclization reaction, by microsecond-flash photolysis and CIDNP [4,5] techniques, it was concluded that the reaction involves hydrogen or electron abstraction from the solvent by the triplet state of the quinone, followed by the attack of the resulting semiquinone radical on one of the phenyl substituents. Many years later, a study of the photorearrangement of phenylbenzoquinone (**1a**) in hydroxydibenzofuran (**2a**) by

combined laser flash photolysis (LFP) and continuous irradiation techniques allowed us to propose a completely different mechanism, shown in Scheme 1 [6].

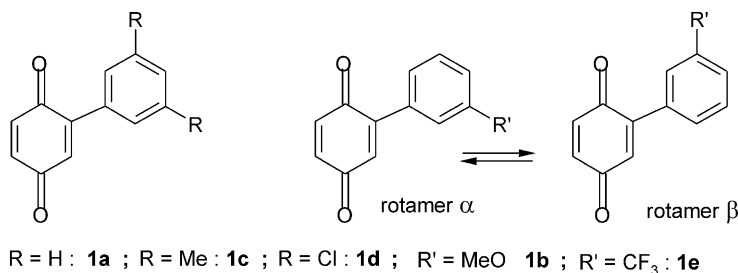
The cyclized intermediate **X**, a biradical or a zwitterion, was not observed during this study because it never accumulates in the solution at a concentration sufficient for spectroscopic observation, its rate of decay being larger than its rate of formation from the triplet species,  $^3\mathbf{1a}$ .

More recently, Hageman and Verhoeven [7] interpreted the effects of substituents and solvents on the yields of dimerization and cyclization by a changing nature of the lowest triplet state: an  $n\pi^*$  triplet for the molecules distorted out of planarity by steric effect of substituents, yielding hydroxydibenzofuran in any type of solvent and a  $\pi\pi^*$  triplet for the planar ones, yielding a dimer which, in polar solvents, would be converted to hydroxydibenzofuran by a secondary photolysis. Although the authors stated that their mechanism and ours are “*in agreement... as far as the cyclization steps are concerned*”, their mechanism clearly disagrees with some of our results such as, e.g., the

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Scheme 1.



Scheme 2.

experimental facts that: (i) in diluted solutions, **1a** gives **2a** with a quantum yield close to 0.5 in benzene containing 0.1 M acetic acid (not a very polar solvent mixture!); (ii) in polar solvents as well as in acidified non-polar solvents, the growth of **2a** and the decay of  $^3\mathbf{1a}$  follow first order kinetics with lifetimes  $\approx 1 \mu\text{s}$  indistinguishable in LFP experiments, indicating that any intermediate species has a lifetime shorter than 100 ns; (iii) the secondary photolysis of a dimer intermediate is strictly impossible in our LFP conditions (single shot experiments with a 200 ps excitation laser pulse) because the amount of dimer formed before the end of the 200 ps laser pulse is negligible<sup>1</sup> since the rate of formation of the dimer cannot be larger than  $10^6 \text{ s}^{-1}$  in the diluted solutions ( $[\mathbf{1a}] \approx 0.5 \text{ mM}$ ) that we studied.

We report here on studies of several phenylbenzoquinones substituted on the phenyl in 3 or 3,5 positions by methoxy, methyl, chloro and trifluoromethyl groups. Substitution by a methoxy group in the 4-position does not stabilize the **X** intermediate sufficiently to make it observable but this lowers a CT state of the singlet manifold so that the quantum yield of intersystem crossing and, consequently, the yield of photocyclization decrease drastically as the polarity of the solvent increases [8]. Simple mesomeric considerations predicts that if the structure postulated for **X** is correct, substituent(s) in the 3 or 3,5 positions should stabilize this species much more efficiently than in the 4-position so that this intermediate may become observable by LFP. Furthermore, the effect of substituent may provide information on the details of the mechanism which will be compared with the Hageman's one and the comparison between the 3,5- and the 3-substituted compounds will allow to tackle the problem of rotamers which only exist in the latter ones.

<sup>1</sup> The calculated concentration of the dimer at the end of the laser pulse is  $\approx 10^{-8} \text{ M}$  or less.

## 2. Materials and methods

The 3-methoxy-phenylbenzoquinone (**1b**), 3,5-dimethyl-phenylbenzoquinone (**1c**), 3,5-dichloro-phenylbenzoquinone (**1d**) and 3-CF<sub>3</sub>-phenylbenzoquinone (**1e**), were synthesized by arylation of the *p*-benzoquinone with the corresponding diazotized aniline according to the method described by Kögl et al. [9] and Kvalnes [10] (Scheme 2).

Continuous irradiation were made using a medium pressure Hg-lamp (HPK 125) with a set of glass filters (Schott glasses UG5 and WG345) to isolate the 366 nm Hg-line or a 2 kW xenon-arc lamp coupled with a Jobin–Yvon monochromator set at  $365 \pm 5 \text{ nm}$  (10 nm irradiation bandwidth). After determination of the absorption coefficients of the phenylbenzoquinones **1b–1e** and of the dibenzofurans **2b–2e** and measurement of the irradiation photon flux by actinometry using a solution of Aberchrome 540 in toluene, the quantum yields of disappearance of **1** and/or those of formation **2** were determined by UV spectroscopy, with a procedure taking into account the decrease of the fraction of light absorbed by **1** as the reaction progresses.

Phosphorescence emission spectra and phosphorescence lifetime were obtained with a Spex Fluorolog apparatus equipped with a 1934D Phosphorimeter accessory.

The LFP apparatus used a frequenced tripled Nd-Yag laser (200 ps, 10–20 mJ at 355 nm) for excitation and a pulsed 75 W Xe-arc, a monochromator, a photomultiplier (Hamamatsu IP28 or R446) and a 7912 AD transient digitizer or a TDS 620B digital oscilloscope (Tektronix) for the analysis which is performed at right angle to the excitation (crossed beams arrangement). The response time of the system is less than 5 ns. The temperature of the sample was controlled by Pelletier elements in the range +0 to +65°C and, for lower temperatures, the sample cell was placed in a clear Dewar flask and cooled by a flow of N<sub>2</sub> gas refrigerated by liquid N<sub>2</sub>.

Table 1

Quantum yields of photocyclization of **1b** and **1c** in various N<sub>2</sub>-flushed solvents and the effect of acetic acid

	Solvent										
	MeOH	EtOH	C <sub>6</sub> H <sub>12</sub>	CH <sub>3</sub> CN	C <sub>6</sub> H <sub>6</sub> + acetic acid (in mM)						
[AcOH]	0	0	0	0	0	0.12	0.24	0.45	1.2	2.4	13
$\phi$ ( <b>1b–2b</b> )	0.16	0.21	<0.14 <sup>a</sup>	0.19	<0.03	0.27	0.42	0.53	0.74	0.84	0.92
$\phi$ ( <b>1c–2c</b> )	0.87	–	<0.06 <sup>a</sup>	0.95	0.02	0.11	0.20	0.32	0.54	0.64	0.88

<sup>a</sup> Some reduction products (hydroquinone) formed.

Table 2

Quantum yields of photocyclization of **1b** and **1c** in N<sub>2</sub>-flushed benzene with added methanol

	MeOH (M)									
	0.011	0.013	0.016	0.022	0.065	0.074	0.14	0.25	0.54	25
$\phi$ ( <b>1b–2b</b> )	0.25	0.35	0.46	0.62	0.87	0.93	0.90	0.84	0.75	0.16
$\phi$ ( <b>1c–2c</b> )	0.12	0.20	0.31	0.39	0.91	0.95	–	–	–	0.87

Chromatographies were made on silica gel columns with a mixture of dichloromethane and light petroleum (50:50) as eluent. NMR spectra were recorded on a Bruker DPX400 (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C).

### 3. Results

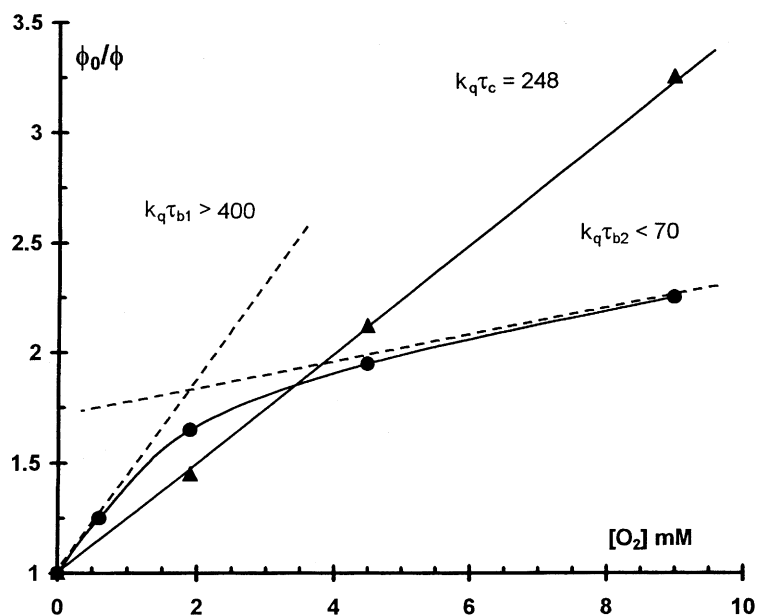
#### 3.1. Under continuous irradiation

The values of the quantum yield of the cyclization reaction in various N<sub>2</sub>-flushed solvents are given in Table 1 for **1b** and **1c**. This value is negligible in neat benzene but increases rapidly upon addition of small amounts of acetic

acid ([AcOH] < 10<sup>-3</sup> M) and reaches its maximum value for [AcOH] ≈ 10<sup>-2</sup> M.

Addition of methanol in benzene increases the quantum yield which reaches a maximum value for [MeOH] ≈ 0.1 M and then, as shown in Table 2, it slowly decreases for higher [MeOH] values, specially in the case of **1b**, where  $\phi = 0.16$  in neat methanol, a low value which does not increase upon addition of millimolar amounts of acetic acid.

The quantum yield was measured in benzene + 10 mM acetic acid, after flushing the solution with N<sub>2</sub>:O<sub>2</sub> mixtures containing various amounts of oxygen. The result indicates a quenching of the reaction by oxygen but whereas the plot of  $\phi_0/\phi$  vs. [O<sub>2</sub>], shown in Fig. 1, is linear for **1c** and yields  $k_q\tau \approx 250 \text{ M}^{-1}$ , this plot is non-linear for **1b** and can be

Fig. 1. Stern–Volmer plots for the quenching by O<sub>2</sub> of the photocyclization of **1b** (●) and **1c** (▲) in acidified benzene.

interpreted as the result of an efficient quenching ( $k_q\tau > 400 \text{ M}^{-1}$ ) for the low values of  $[\text{O}_2]$  and a poorly efficient one ( $k_q\tau \approx 70 \text{ M}^{-1}$ ) in the range of large  $[\text{O}_2]$ .

From these measurements, the quantum yield of conversion **1b**  $\rightarrow$  **2b** is optimal in  $\text{N}_2$ -flushed solvents of low polarity slightly acidified. The 300 mg of **1b** in 100 ml of  $\text{N}_2$ -flushed  $\text{CH}_2\text{Cl}_2$  containing 10 mM AcOH were photolyzed by a 500 W medium pressure Hg-lamp through a 1 cm thick filter solution (3 M  $\text{KNO}_3/\text{water}$ ) which cuts wavelengths shorter than 330 nm. After partial evaporation of the solvent, column chromatography of the reaction mixture gave us small amounts of anisyl-hydroquinone and polymeric materials, including dimer and 240 mg of **2b** (80% chemical yield) which were analyzed by NMR. This analysis revealed that both isomers  $\alpha$  and  $\beta$  of **2b** are formed but the ratio  $\alpha/\beta$  is about 98/2, as determined by integration of the  $^1\text{H}$  signals of the methoxy group, identified by HMQC ( $^1\text{H}$ -detected multiple quantum coherence) and HMBC ( $^1\text{H}$ -detected multiple bond heteronuclear multiple quantum coherence) comparison.

As shown in Table 3, the quantum yields of cyclization of **1d** and **1e** are small or negligible in polar and non-polar solvents as long as no acid is added to the solution. The efficiency of acetic acid to trigger the cyclization reaction is considerably less than for **1c**. To get similar values of the quantum yield, the amount of acetic acid to be added in benzene is about  $10^3$  times larger for **1d** than for **1c**. The ratio intercept/slope of the linear plots of  $1/\phi$  vs.  $1/[\text{AcOH}]$  gives the value of the product " $k_{\text{AcOH}} \times \tau$ ", where  $k_{\text{AcOH}}$  is the rate constant for the reaction of an intermediate with AcOH and  $\tau$  the lifetime of this intermediate. This ratio is

Table 3  
 $\phi_{\text{cycl}}$  for **1d** and **1e** in various solvents

Solvent	[AcOH] (M)	$\phi(\mathbf{1d-2d})$	$\phi(\mathbf{1e-2e})$
MeOH	0	a	b
$\text{C}_6\text{H}_{12}$	0	c	c
$\text{CCl}_4$	0	–	$\approx 0$
	1.0	–	$< 0.5$
$\text{CH}_3\text{CN}$	0	$\approx 0$	$\approx 0$
	1.3	0.19	$< 0.15$
$\text{C}_6\text{H}_6$	0	$\approx 0$	$\approx 0$
	0.038	0.149	–
	0.07	0.257	–
	0.17	0.355	–
	0.28	0.473	–
	0.7	0.552	–
$\text{C}_6\text{H}_6$	1.3	–	0.08
	[TFA] (M)	$\phi(\mathbf{1d-2d})$	$\phi(\mathbf{1e-2e})$
	0.005	–	0.09
	0.01	–	0.13
	0.02	–	0.16
	0.03	–	0.18

<sup>a</sup> Photocyclization occurs but a thermal reaction yields hydroquinone.

<sup>b</sup> Photolysis gives some hydroxydibenzofuran and, mainly, reduction to hydroquinone; a thermal reaction gives hydroquinone only.

<sup>c</sup> Photoreduction to hydroquinone, no hydroxydibenzofuran formed.

equal to  $8 \text{ M}^{-1}$  in the case of **1d**, whereas it is around 1400 and  $3660 \text{ M}^{-1}$  for **1c** and **1b**, respectively. The quantum yield of cyclization of **1e** in benzene is less than 10% even in the presence of molar amounts of acetic acid and it is less than 50% in  $\text{CCl}_4 + \text{AcOH}$  (1 M).

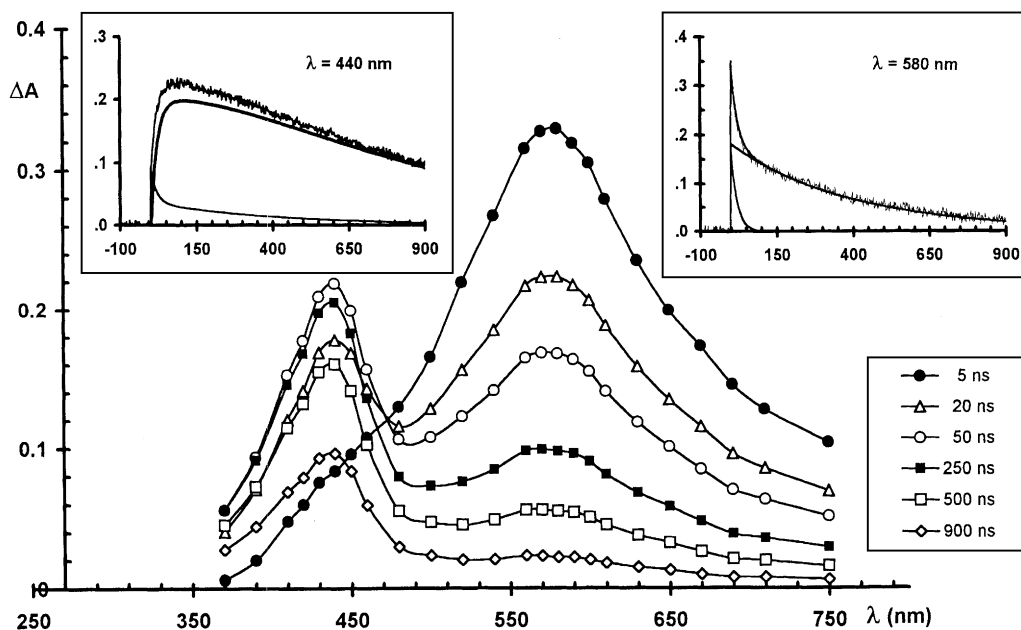


Fig. 2. Transient absorption spectra recorded for **1b** in benzene. Insets: kinetic traces,  $\Delta A$  vs. time, analyzed as the sum of the absorptions of: (1) two triplet rotamers at 580 nm, (2) the two triplet rotamers plus the **X** species at 440 nm.

### 3.2. Laser flash photolysis measurements

#### 3.2.1. Measurements on **1b**

The LFP of a solution of **1b** in N<sub>2</sub>-flushed benzene reveals the existence of three transient species. Immediately after excitation, a broad absorption band extends over the 370–750 nm spectral region with a maximum around 590 nm (see Fig. 2). During 70–80 ns, this absorption rapidly decays to about 40% of its initial value, with a lifetime  $\approx 20$  ns. During this decay, a new absorption band with a maximum around 440 nm grows up with a 18 ns risetime, identical within experimental errors to the decaytime of the absorption at 590 nm. Then, the absorption at 440 nm decays with a 700–750 ns lifetime, whereas at 590 nm the remaining absorption decays with a 400 ns lifetime (see insets in Fig. 2).

The 18–20 ns lifetime associated to the initial decay of the 590 nm absorption and to the growth of the 440 nm band, decreases to 16–18 ns in aerated solutions and to 13–15 ns in an O<sub>2</sub>-flushed solution so that the species responsible for the fast initial decay at 590 nm is quenched by O<sub>2</sub> with a rate constant around  $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The 400 ns lifetime associated to the late part of the decay of the 590 nm absorption also decreases in aerated (170 ns) and O<sub>2</sub>-flushed solution (50 ns) so that the rate constant for the quenching by O<sub>2</sub> of the species responsible for the “slow” decay at 590 nm is around  $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . In contrast, the lifetime of the species absorbing at 440 nm is not affected by O<sub>2</sub> (750, 700 and 720 ns in N<sub>2</sub>-flushed, aerated and O<sub>2</sub>-flushed solutions: changes are within experimental incertitude).

The addition of acetic acid induces a clear reduction of the lifetime of the “440 nm transient”, whereas it does not affect the 20 and 400 ns lifetimes of the species absorbing at 590 nm. From the data shown in Table 4, the “440 nm transient” reacts (or is quenched) by AcOH with a rate constant =  $4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

The amplitude of the transient absorption measured at 590 nm decreases as the polarity of the solvent increases (see Table 5) and the 440 nm transient is not observed in MeOH or MeCN.

The temperature dependence of the lifetime of the three transient species was studied between +22 and –75°C in N<sub>2</sub>-flushed CH<sub>2</sub>Cl<sub>2</sub> for the two “590 nm transients” and from +2 to +62°C, in N<sub>2</sub>-flushed CCl<sub>4</sub>, for the “440 nm transient”. The linear plot of  $\ln(1/\tau)$  vs.  $1/T$  yields the following kinetic parameters for the “440 nm transient”:  $A = (3.5 \pm 1.5) \times 10^{13} \text{ s}^{-1}$  and  $\Delta E = 38.5 \text{ kJ/mol}$ . In contrast,

Table 4  
Effect of acetic acid added in benzene on the lifetime of the transient species

	AcOH (mM)				
	0	0.4	1.2	4	12
$\tau$ (440 nm) (ns)	700	310	160	70	40
$\tau$ (600 nm) (ns)	400	400	370	430	–

Table 5  
Amplitude of the transient absorption at 590 nm for **1b** in various solvents

	Solvent					
	CCl <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>6</sub> Cl	CH <sub>2</sub> Cl <sub>2</sub>	MeCN	MeOH
$\Delta A_{590}$	0.30	0.35	0.33	0.132	0.07	0.06

the same Arrhenius plots for the short-lived and long-lived “590 nm transients” are curved, especially in the latter case, indicating that these species decay via (at least) two deactivation processes, one being (nearly) independent of temperature with a rate constant  $k_0$ , and the other thermally activated with a rate constant  $k_d = A \exp(-\Delta E/RT)$ . Non-linear curve fitting of the data points with the function  $1/\tau = k_0 + A \exp(-\Delta E/RT)$  gave  $k_0 \approx 2.5 \times 10^5 \text{ s}^{-1}$  for both “590 nm transients”,  $A \approx 5 \times 10^{11} \text{ s}^{-1}$  and  $\Delta E = 22.6 \text{ kJ/mol}$  for the short-lived one and  $A \approx 2 \times 10^{12} \text{ s}^{-1}$  and  $\Delta E = 33.4 \text{ kJ/mol}$  for the long-lived one.

#### 3.2.2. Measurements on **1c**

The LFP of a solution of **1c** in N<sub>2</sub>-flushed benzene reveals the existence of two transient species. Immediately after excitation a first transient absorption, with a maximum around 580 nm, is observed over the 400–750 nm wavelength range and its decay at 620 nm can be analyzed as a single first order process with a 180 ns. The transient absorption spectra recorded at 80 or 250 ns after the excitation reveal the existence of a second transient species absorbing in the 400–550 nm region with a maximum around 450 nm (see Fig. 3).

The evolution of the transient absorption at 460 nm as a function of time can be analyzed as the sum of the absorptions of two species: one formed within the time resolution of our system and decaying by a first order process,  $A_t = A_0 \exp(-t/\tau_1)$ , where  $\tau_1 \approx 180$  ns, the other one, **B**, being

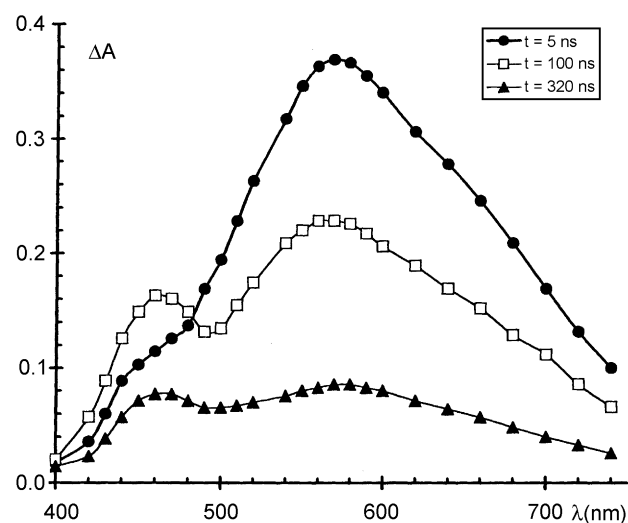


Fig. 3. Transient absorption spectra recorded at various delay times after excitation of **1c** in N<sub>2</sub>-flushed benzene.

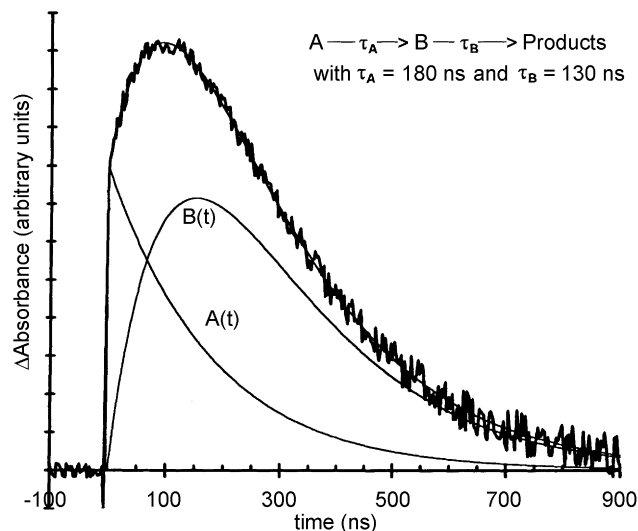


Fig. 4. Kinetic trace  $\Delta A$  vs. time recorded for **1c** at 460 nm in  $N_2$ -flushed benzene, analyzed as the sum of the absorptions of two species: **A** (triplet state of **1c**) and **B** (**X** species).

formed from the **A** species and decaying with a lifetime  $\tau_2 \approx 130$  ns. For such a system, simple mathematics give  $B_t = \alpha A_0 [\exp(-t/\tau_1) - \exp(-t/\tau_2)]$  with  $\alpha = \tau_2/(\tau_1 - \tau_2)$  if **A** decays only by conversion into **B**, and  $B_t$  reaches its maximum value at time  $t_{\max} = \ln(\tau_1/\tau_2)\tau_1\tau_2/(\tau_1 - \tau_2)$ , around 150 ns in this case. At this time  $t_{\max}$ ,  $B_t = 0.30A_0$  and  $A_t = 0.43A_0$ . Therefore, although  $\tau_1 > \tau_2$ , there will be a growth of the absorbance at wavelengths where  $0.30\varepsilon_B$  is larger than  $(1 - 0.43)\varepsilon_A$ , i.e.  $\varepsilon_B > 2\varepsilon_A$ . This is the case at 460 nm as shown in Fig. 4.

The lifetime of the **A** species measured at 620 nm in benzene flushed with  $N_2$ , air, a 1:1 mixture of  $O_2/N_2$  and with  $O_2$ , decreases from 185 to 116, 75 and 44 ns, respectively, yielding a quenching rate constant  $k_q \approx 1.8 \times 10^9 M^{-1} s^{-1}$ .

### 3.2.3. Measurements on **1d** and **1e**

LFP of these compounds in  $N_2$ -flushed benzene or acetonitrile reveals only one transient species, with a maximum absorption at 540 nm for **1d** and 520 nm for **1e** as shown in Fig. 5. This transient is clearly the same kind of species as those observed with **1b**, **1c** and **1a**, absorbing in the same region with a maximum at 590, 580 and 530 nm, respectively. The presence of a second transient species with a maximum absorption around 440–450 nm, may be suspected when looking at the evolution of the transient absorption spectrum of **1e** in acetonitrile as a function of time: the shoulder around 400 nm is more pronounced in the spectra recorded at 60 or 170 ns after excitation than in the spectrum recorded immediately after excitation.

When monitored at the wavelength of their maximum absorption, the transient species of **1d** and **1e** decay according to a first order kinetics, with a lifetime depending strongly on the solvent for **1e**, as shown in Table 6, and around 140 ns for **1d** in  $N_2$ -flushed benzene. This lifetime is poorly affected

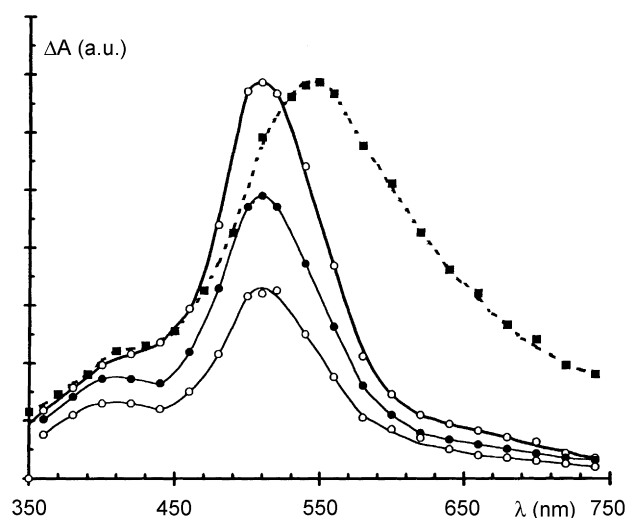


Fig. 5. Transient absorption spectra for **1d** (■) at 0 ns delay and for **1e** at 0 ns (○), 63 ns (●) and 170 ns (◊) delay after excitation in  $N_2$ -flushed benzene.

Table 6

Lifetime of the transient species for **1e** in various  $N_2$ -flushed solvents

Solvent	$\tau$ (ns)
$C_6H_5-Cl$	$520 \pm 10$
$C_6H_6$	$220 \pm 20$
$C_6H_5-CH_3$	$51 \pm 5$
$C_6H_5-OCH_3$	$8 \pm 5$
$CCl_4$	$1300 \pm 100$
$CH_3CN$	$1000 \pm 100$
$CH_2Cl_2$	$570 \pm 10$
$C_6H_{12}$	$30 \pm 2$
MeOH	$180 \pm 10$
EtOH	$54 \pm 5$
<i>i</i> -PrOH	$30 \pm 2$

by the addition of acetic acid in the solution ( $\tau \approx 120$  ns for **1d** in  $N_2$ -flushed benzene with  $[AcOH] = 0.28$  M), but is strongly reduced by the presence of  $O_2$  in the solution, the quenching rate constant of these species by  $O_2$  being equal to  $1.5 \times 10^9$  and  $1.6 \times 10^9 M^{-1} s^{-1}$  for **1d** and **1e** in benzene and to  $2.2 \times 10^9 M^{-1} s^{-1}$  for **1e** in acetonitrile (see Table 7).

### 3.3. Phosphorescence measurements

The emission and excitation spectra of **1a** and **1e** have been recorded in methylcyclohexane glasses at 77 K and

Table 7

Effect of  $O_2$  (%) on the lifetime of the transient species for **1d** and **1e**

	$\tau$ (ns)				$k_q$ ( $M^{-1} s^{-1}$ )
	0	21	50	100	
<b>1d</b> in $C_6H_6$	140	107	72	49	$1.41 \times 10^9$
<b>1e</b> in $C_6H_6$	220	135	83	52	$1.64 \times 10^9$
<b>1e</b> in $CH_3CN$	950	170	85	42	$2.16 \times 10^9$

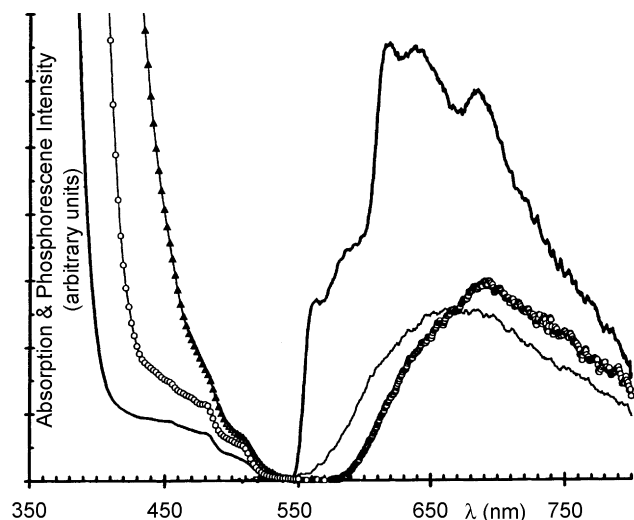


Fig. 6. Tail of the absorption spectra of **1e** (—), **1a** (-o-) and **1b** (-▲-) and phosphorescence spectra of **1e** (—) and **1a** (o) in an MCH glass and of **1e** (—) in an ethanol glass.

have been corrected for the background emission of the solvent, for the response of the system (emission spectra) and for the emission of the excitation source (excitation spectra). The emission of **1a**, shown in Fig. 6, extends from 580 to >800 nm with a maximum around 695 nm and does not present any structure. In contrast, the emission of **1e** presents a clear structure with maxima at 564, 585, 621, 643 and 690 nm. The excitation spectra recorded with observation at 585 and 620 nm reproduce exactly the absorption spectrum of **1e** indicating that this structure is not due to the structured emission of a strongly emissive impurity. The emission of **1e** in an ethanol glass, at 77 K, also shown in Fig. 6, appears in the same spectral region but does not present any structure.

## 4. Interpretation

### 4.1. Identification of the observed transient species

The broad absorption band in 400–700 nm region with a maximum at 590, 580, 540 and 520 nm for **1b**, **1c**, **1d** and **1e**, respectively, resembles the T–T absorptions of the phenylbenzoquinone **1a** ( $\lambda_{\max} = 530$  nm) [6] and of the *p*-anisyl-benzoquinone ( $\lambda_{\max} = 620$  nm) with a clear relation between the wavelength of maximum absorption and the electronic effect of the substituent(s). This spectral “signature” and the facts that the species responsible for these absorptions are formed within less than 5 ns and quenched by O<sub>2</sub> with a rate constant  $\approx 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  support the assignment of these species as the lowest triplet state of **1b–1e**. In the case of **1b**, there are in fact two triplet species responsible for the fast (20 ns) and “slow” (400 ns) components of the decay of the absorption at 590 nm, both quenched by O<sub>2</sub> with a rate constant around  $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which are identified as the triplet state

of the two rotamers of **1b**, respectively, noted  $\alpha$  and  $\beta$  in Scheme 5. Their absorption band is so broad that the slight differences which may exist between the T–T absorption spectra of the two rotamers do not appear but they have different kinetic properties, reflecting quite different reactivities as it will be shown later. In contrast, in the case of **1e** where similar rotamers could be expected, the decay of the transient absorption was well fitted by a single exponential indicating that either one rotamer is largely predominant or that the triplet states of both rotamers have similar kinetic properties or that the equilibration between the two rotamers is faster than their decay. We favor the last hypothesis: the lifetime of <sup>3</sup>**1e** is larger than that of <sup>3</sup>**1b** and the interconversion of rotamers may be much faster for <sup>3</sup>**1e** than for <sup>3</sup>**1b**.<sup>2</sup>

The second transient absorption observed in the 400–500 nm range in the case of **1b** and **1c** and suspected in the case of **1d**, is formed from the triplet and reacts with AcOH with a rate constant around  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . It is assigned to the **X** species which may be drawn as a zwitterion or a biradical (see Scheme 1). Its absorption spectrum, with a maximum at 440 nm is reminiscent of those of the semiquinone radical ( $\sim 420$  nm) or radical anion (425 nm) and suggests a biradical structure but the fact that in the case of **1b**, the **X** species is not affected by O<sub>2</sub> and is protonated by AcOH at a rate close to the diffusion controlled limit support a zwitterionic structure.

### 4.2. Nature of the lowest triplet state

The absorption spectrum of **1a** and **1e** in hexane shows a small  $n\pi^*$  band extending from 430 to 520 nm with a low absorption coefficient ( $\epsilon \approx 30$ ) and some structure at 510 and 482 nm. The faint structure at 510 nm, also observed on the absorption spectrum of **1b**, defines precisely the level of the S<sub>1</sub> ( $n\pi^*$ ) state: 234.5 kJ/mol for **1a**, **1b** and **1e** indicating that the  $n\pi^*$  excitation, localized on a carbonyl group, is unaffected by substitution on the phenyl group.

The level of the S<sub>2</sub> ( $\pi\pi^*$ ) state can be estimated from the wavelengths where the absorption of the intense near-UV  $\pi\pi^*$  band is  $\frac{1}{3}$  of the maximum: 299 kJ/mol (400 nm) for **1a** and 314 kJ/mol (381 nm) for **1e**. The energy difference between the S<sub>2</sub> ( $\pi\pi^*$ ) states of **1a** and **1e** is thus  $\approx 15$  kJ/mol and nearly the same value would be obtained from the wavelengths of the maximum absorption, 362 and 345 nm (16 kJ/mol), or those where the absorption is  $\frac{1}{10}$  of the maximum, 414 and 394 nm (14.7 kJ/mol).

From the onset of the phosphorescence spectra in a methylcyclohexane glass (585 and 566 nm), the T<sub>1</sub> states of **1a** and **1e** are located at 204.5 and 211.5 kJ/mol above the ground state. The lowest triplet state of **1e**, T<sub>1</sub>, is an  $n\pi^*$  state since: (i) it efficiently abstracts H atoms to cyclohexane

<sup>2</sup> The activation energy for equilibration of the rotamers,  $\Delta E$ , is probably lower for <sup>3</sup>**1e** than for <sup>3</sup>**1b** because the enhancement of the double bond character of the bond linking quinone to phenyl should be lower in an  $n\pi^*$  state such as <sup>3</sup>**1e** than in a  $\pi\pi^*$  triplet such as <sup>3</sup>**1b**.

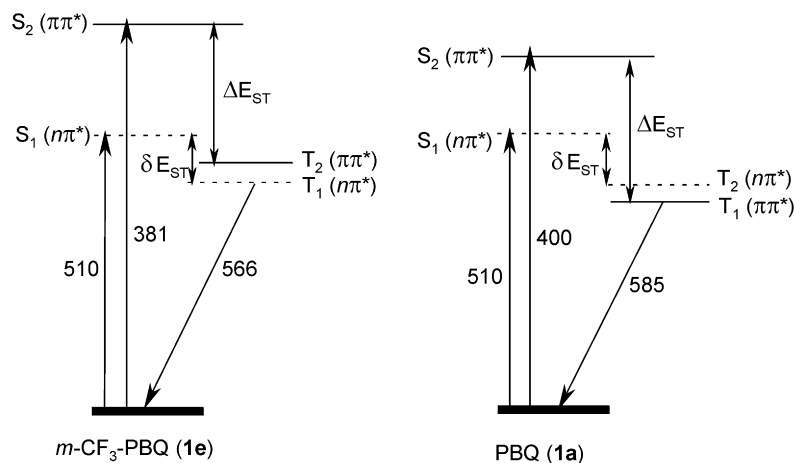


Fig. 7. Energy ordering for the singlet and triplet states of **1a** and **1e** in non-polar solvents (numbers close to the arrows are wavelengths in nm).

and alcohols, (ii) its phosphorescence spectrum is structured with a  $1630\text{ cm}^{-1}$  progression (564, 621 and 690 nm) close to the value of the C=O stretching mode of a quinone<sup>3</sup> at  $1650\text{ cm}^{-1}$ , (iii) the energy gap  $\delta E_{ST}$  between  $S_1$  ( $n\pi^*$ ) and  $T_1$  is  $\approx 22\text{ kJ/mol}$  is similar to those reported for compounds known to have  $n\pi^*$   $S_1$  and  $T_1$  states.<sup>4</sup> In contrast, the lowest triplet state of **1a** is a  $\pi\pi^*$  state because (i) it does not abstract efficiently an H atom to *i*-propanol,<sup>5</sup> (ii) its phosphorescence spectrum does not present any structure, (iii) the  $n\pi^*$  triplet state of **1a** should be, as for **1e**,  $211.5\text{ kJ/mol}$  above the ground state, i.e. about  $7\text{ kJ/mol}$  above the phosphorescent state, since we noticed above that substitution on the phenyl does not affect the  $n\pi^*$  states.

Assuming that the energy splitting between the  $\pi\pi^*$  states  $S_2$  and  $T_1$ ,  $\Delta E_{ST}$ , is  $94.5\text{ kJ/mol}$  for **1e** as it is for **1a**, i.e. assuming that the  $\text{CF}_3$  substituent raises equally both the excited singlet and triplet  $\pi\pi^*$  states, the  $T_2$   $\pi\pi^*$  triplet state of **1e**, would be at  $219.5\text{ kJ/mol}$  above the ground state, i.e. about  $8\text{ kJ/mol}$  above  $T_1$ . The resulting energy ordering of the  $S_1$ ,  $S_2$ ,  $T_1$  and  $T_2$  states of **1a** and **1e** in non-polar solvents is shown in Fig. 7.

In a polar solvent such as acetonitrile, the  $S_0$ – $S_2$   $\pi\pi^*$  transitions of **1a** and **1e** are slightly red shifted, so that the  $S_2$  level is lowered by about  $5\text{ kJ/mol}$  and would be around  $294\text{ kJ/mol}$  for **1a** and  $309\text{ kJ/mol}$  for **1e**. In contrast, the  $S_0$ – $S_1$   $n\pi^*$  transition is blue shifted, loses its structure as it collapses with the tail of the  $\pi\pi^*$  transition and reaches  $\frac{1}{3}$  of its maximum amplitude around  $494\text{ nm}$  so that the  $S_1$   $n\pi^*$  state is around  $242\text{ kJ/mol}$  for both compounds, about

$7.5\text{ kJ/mol}$  higher than in a non-polar medium. Assuming that the energy splittings  $\delta E_{ST}$  and  $\Delta E_{ST}$  are the same as in non-polar solvents, i.e.  $22\text{ kJ/mol}$  for  $n\pi^*$  states and  $94.5\text{ kJ/mol}$  for  $\pi\pi^*$  states, one gets the following triplet state ordering in acetonitrile:  $T_2$  ( $n\pi^*$ ) at  $220\text{ kJ/mol}$  for **1a** and **1e**,  $T_1$  ( $\pi\pi^*$ ) at  $199\text{ kJ/mol}$  for **1a** and at  $214.5\text{ kJ/mol}$  ( $558\text{ nm}$ ) for **1e**. Thus, in acetonitrile, the lowest triplet of **1e** would be  $\pi\pi^*$ , about  $6\text{ kJ/mol}$  below the  $n\pi^*$  triplet, in agreement with the unstructured phosphorescence spectrum obtained in an ethanol glass, starting from  $560\text{ nm}$  (10% intensity point).

This determination of the nature of the lowest triplet state from experimental data seems more reliable than the predictions of theoretical chemistry. The only assumption is that the values of  $\Delta E_{ST}$  for  $\pi\pi^*$  and  $n\pi^*$  states do not depend on the solvent polarity and are the same for both compounds. This seems reasonable and is supported by the agreement between the level of  $T_1$  calculated for **1e** by using this assumption and the phosphorescence spectrum of this compound in an ethanol glass. In contrast, theoretical chemistry methods require an optimization of the molecular structure in the triplet states, with special care on the tilt angle between the phenyl and the quinone moieties which greatly influences the relative energies of the  $\pi\pi^*$  and  $n\pi^*$  states [11]. Even though, the possibility for these methods to give the correct energy ordering of  $n\pi^*$  and  $\pi\pi^*$  triplet states very close in energy ( $5$ – $8\text{ kJ/mol}$ ) for solvated molecules may be questioned.

#### 4.3. Reaction mechanism

The mechanism previously proposed for the photocyclization of **1a** is also valid for **1b**–**1e** and is now confronted by the observation of the **X** intermediate. It involves three steps: the formation of the triplet state, the cyclization of this triplet to give **X** and, finally, the conversion of **X** to the final product **2**.

<sup>3</sup> The IR spectrum of phenylbenzoquinone shows a strong band at  $1650\text{ cm}^{-1}$  (two peaks at  $1642$  and  $1658\text{ cm}^{-1}$ ).

<sup>4</sup>  $\Delta E_{ST} = 25\text{ kJ/mol}$  for benzophenone and acetone,  $21\text{ kJ/mol}$  for acetophenone.

<sup>5</sup> The difference between the lifetimes of this species in isopropanol ( $250\text{ ns}$ ) and acetonitrile ( $650\text{ ns}$ ) is mainly due to a lower activation energy for the cyclization reaction since the major photoproduct in isopropanol is **2a** and not the reduction product (see Ref. [6]).



#### 4.3.1. Formation of triplet

The quantum yield of formation of the triplet state of substituted benzoquinones is usually considered to be close to unity as it is for benzoquinone itself. However, this is not true in the case of **1b** in polar solvents. As shown in Tables 1 and 2, the quantum yield of formation of **2b** is close to unity in non-polar solvents when small amounts of acetic acid (~1 mM) or methanol (~100 mM) are added in the solution but it is low in EtOH (0.21) and even lower in MeOH (0.16). This is due to the low quantum yield of formation of the **1b** triplet state in these solvents, revealed by the decrease of the amplitude of the transient absorption at 590 nm as the polarity of the solvent increases (see Table 4). This is explained by a competition between intersystem crossing and the formation of a “solvent stabilized charge transfer excited state” which rapidly reverts to the ground state by back electron transfer, as in the case of *p*-MeO-phenylbenzoquinone [8].

#### 4.3.2. Decay of the triplet and formation of the X species

In the case of **1b**, the non-linearity of the Arrhenius plots,  $\ln(1/(\text{triplet lifetime}))$  vs.  $1/T$ , indicates that several processes contribute to the decay of both the short- and long-lived **1b** triplet rotamers, **T $\alpha$**  and **T $\beta$** . The deactivation to the ground state, quenching by the small amount of O<sub>2</sub> remaining after flushing the solution with N<sub>2</sub> and dimerization by reaction with **1b** molecules in the ground state are responsible for the temperature independent (or nearly independent) part of the decays, predominant in the low temperature range with a rate constant  $\approx 2.5 \times 10^5 \text{ s}^{-1}$  for both triplet rotamers. The reaction **T**  $\rightarrow$  **X** is responsible for the temperature dependent part of the decay of **T $\alpha$**  with  $\Delta E = 22.6 \text{ kJ/mol}$  and a pre-exponential factor,  $A = 5 \times 10^{11} \text{ s}^{-1}$ , indicative of a spin allowed process slightly slowed by entropy factor. At room temperature, the rate constant for this cyclization reaction **T $\alpha$**   $\rightarrow$  **X $\alpha$**  is around  $5 \times 10^7 \text{ s}^{-1}$  since **T $\alpha$**  has a 20 ns lifetime and gives **X $\alpha$**  with a yield close to unity.

The non-linearity of the Stern–Volmer plot,  $\phi_0/\phi$  vs. [O<sub>2</sub>] (see Fig. 1) is well explained by the existence of two triplet rotamers, with different lifetimes but both involved in the global reaction and the overall quantum yield may be, in a convenient solvent, close to unity. These two facts indicate that the decay of **T $\beta$**  is due to its cyclization for about 90% at room temperature since its decay rate, around  $2.5 \times 10^6 \text{ s}^{-1}$ , is about 10 times larger than the temperature independent rate of deactivation to the ground state. The kinetic parameters of the temperature dependant part of the decay of **T $\beta$** ,  $\Delta E = 33.4 \text{ kJ/mol}$  and  $A = 2 \times 10^{12} \text{ s}^{-1}$ , may be assigned either to cyclization to give **X $\beta$**  or to isomerization to give **T $\alpha$**  which rapidly cyclizes to **X $\alpha$** . The NMR analysis of **2b** indicated a 98:2 ratio for the  $\alpha$  and  $\beta$  isomers, whereas in LFP experiments, the amplitudes of the transient absorptions assigned to **T $\alpha$**  and **T $\beta$**  are similar. Therefore, the temperature dependant part of the decay of **T $\beta$**  mainly corresponds to the conversion **T $\beta$**   $\rightarrow$  **T $\alpha$** . The 33.4 kJ/mol

activation energy measured for this process indicates that, in the excited triplet state, the bond between the quinone and the anisyl moieties has a relatively strong double bond character and suggests a rather planar structure of the triplet. This is reminiscent of the case of biphenyl, the triplet state of which is known to be planar with a strong double bond character for the bond linking the two phenyl rings [12,13].

In the case of **1e**, two other processes contribute to the decay of the triplet state: abstraction of a H atom or of an electron to the solvent. This triplet species being (mainly)  $n\pi^*$ , it easily abstracts H atom to the solvent: its lifetime is around 1.3  $\mu\text{s}$  in CCl<sub>4</sub> and 1  $\mu\text{s}$  in acetonitrile but is only 30 ns in cyclohexane.

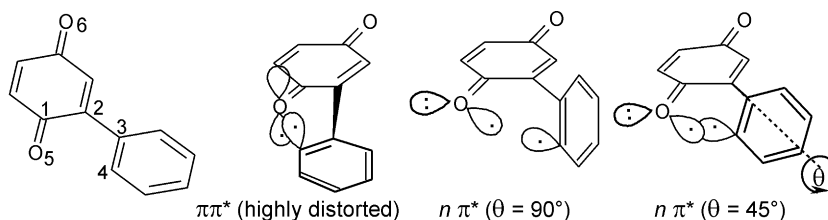
In addition, the CF<sub>3</sub> substituent largely increases the oxidative properties of the quinone making possible the transfer of an electron from the solvent to the triplet state. This explains the decrease of the triplet lifetime when the solvent is changed from chlorobenzene (520 ns), to benzene (220 ns), toluene (50 ns) and anisole ( $\approx 10$  ns). However, no transient absorption characteristic of the semiquinone radical anion could be detected indicating that probably, a fast back electron transfer occurs within the solvent cage and regenerates the ground state of **1e**. This explains why the quantum yield of the reaction is much lower in benzene than in CCl<sub>4</sub> when both solvents are acidified with AcOH (1 M).

#### 4.3.3. The cyclization step and the structure of X

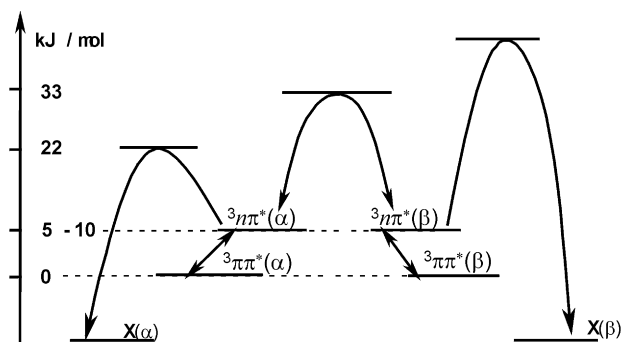
Considering the molecular geometry and orbital interactions, the formation of the O<sub>5</sub>–C<sub>4</sub> bond seems much easier from an  $n\pi^*$  triplet than from a  $\pi\pi^*$  triplet. Rotation of the phenyl ring around the C<sub>2</sub>–C<sub>3</sub> bond by a 30–45° angle gives a structure where the filled “p” orbital on C<sub>4</sub> has a sufficient overlap with the electron deficient “n” orbital (first structure in Scheme 3), whereas it has no or little interaction with the  $\pi^*$  orbital on the oxygen. The ideal tilt angle between the phenyl and quinone planes is probably much smaller than the value “close to 90°” postulated by Hageman and Verhoeven: inspection of molecular models and of geometries calculated in MOPAC using MP3 parameters (CACHe, from Oxford Molecular) indicate that in a “near-perpendicular” conformation, the distance between C<sub>4</sub> and O<sub>5</sub> is much too long for the reaction to occur, whereas a tilt angle around 30° gives the best compromise between the alignment and overlap of the n and  $\pi$  orbitals and the distance between C<sub>4</sub> and O<sub>5</sub>.<sup>6</sup>

Cyclization from a  $\pi\pi^*$  state would require a strongly distorted structure: in order to bring C<sub>4</sub> close enough and below (or above) the O<sub>5</sub> atom, the C<sub>2</sub>–C<sub>3</sub> bond must be largely out of the quinone plane and the bond angles at C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> must be noticeably decreased. In both cases, some twisting of the C=O double bond concerted with the rotation

<sup>6</sup> All the bond lengths and angles being kept the same as in the ground state, increasing the tilt angle  $\theta$  between the phenyl and the quinone from 30° to 90° increases the distance between O and C atoms from 2.8 to 3.6 Å.



Scheme 3.



Scheme 4.

of the phenyl would help to improve the proper alignment of orbitals.

The effect of  $-\text{OMe}$  and  $-\text{CF}_3$  substituents on the rate constant of the cyclization step is also in agreement with the electrophilic character of the attack initiated by the half-filled “n” orbital of a carbonyl on the  $\pi$  electrons of a C=C double bond in a “perpendicular approach”, whereas the attack initiated by the half-filled “ $\pi^*$ ” orbital of the carbonyl on the empty “ $\pi^*$ ” orbital of a C=C double bond in a “parallel approach” should be nucleophilic [14].

As determined above, the lowest triplet state, is a  $\pi\pi^*$  state (except in the case of **1e** in non-polar solvents), but the activation energy of the cyclization step, around 20–30 kJ/mol depending on the compound and the solvent, is much larger than the energy splitting between the  $\pi\pi^*$  and  $n\pi^*$  triplet states. It thus seems that the cyclization occurs from the  $n\pi^*$  triplet state populated, in the case of **1a–1c** by thermal activation of the  $\pi\pi^*$  triplet which is about 10 kJ/mol below in energy. Such “state switching during the reaction” are well known [15].<sup>7</sup>

Scheme 4 gives a picture of our view of the cyclization step in the case of **1b**. Since the cyclization occurs from a triplet state with a pre-exponential factor around  $10^{12} \text{ s}^{-1}$ , **X** is most certainly formed initially as a triplet biradical which, then, rapidly equilibrates with a singlet biradical or is converted into a zwitterionic structure. A biradical structure is supported by the fact that the absorption spectrum of **X**, with a maximum at 440 nm, is reminiscent of those of the semiquinone radical ( $\sim 420 \text{ nm}$ ) [17] and hydroquinone rad-

ical anion (425 nm) [18], but a zwitterionic structure would better consistent with the fact that the lifetime of **X** is not affected by  $\text{O}_2$ .

#### 4.3.4. Decay of **X** and formation of the final product

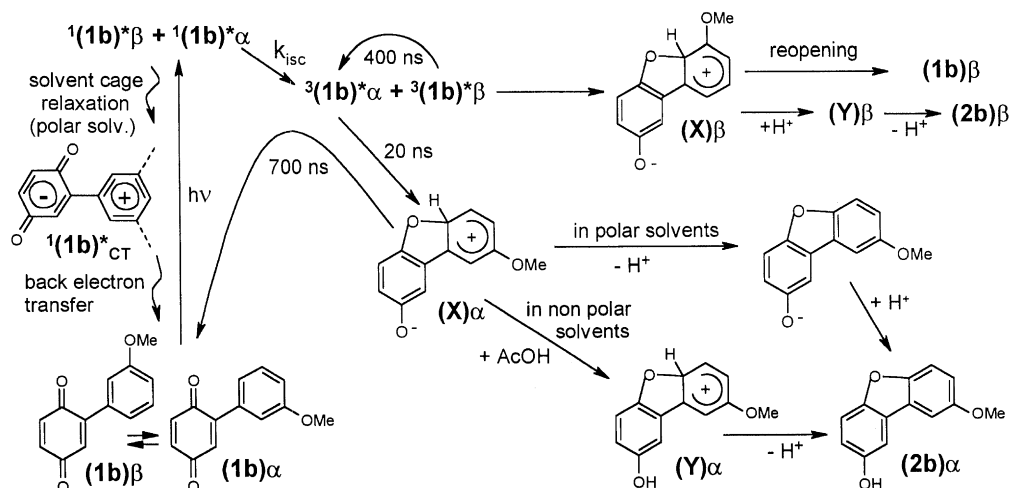
In polar solvents, the fate of **X** depends on the substitution. **Xb** and **Xc** rearrange to the final product **2** by a solvent assisted transfer of a proton from  $\text{C}_4$ , the cyclization center, to  $\text{O}_6$ . No acid is required to trigger this process. This solvent assisted transfer of the proton does not work in the case of **Xd** and **Xe** which probably reopen to the starting compound **1**. The Me- and MeO-substituents favor a structure of **X**, where the quinone moiety is negatively charged and the xyl or anisyl moiety is positively charged: this increases the acidity of the H on  $\text{C}_4$  and this H can easily be expelled as a proton if the solvent helps. In contrast, the  $\text{CF}_3$  (or Cl) substituent decreases the acidity of the H on  $\text{C}_4$  and there is no spontaneous release of a proton by **Xd** and **Xe**, even in polar solvents.

In benzene or other non-polar solvents, whatever is the substituent, **X** does not give the final product **2** because there is no way to transfer a proton from  $\text{C}_4$  to  $\text{O}_6$ . Instead, **X** reopens to **1** so that the cyclization is ineffective. In the case of **1b**, this reopening occurs with a rate constant  $k_{\text{reop}} = 1.4 \times 10^6 \text{ s}^{-1}$  at room temperature in benzene and the linear Arrhenius plot of the lifetime of the “440 nm transient of **1b**”, i.e. **Xb**, yields an activation energy for reopening  $\Delta E = 38.5 \text{ kJ/mol}$  and the associated frequency factor,  $A = (3.5 \pm 1.5) \times 10^{13} \text{ s}^{-1}$  is in agreement with an intramolecular process slightly favored by entropy.

In the presence of catalytic amounts of acetic acid, **Xb** is protonated at  $\text{O}_6$  by AcOH, with a rate constant close to the diffusion controlled limit, to give  $\text{AcO}^-$  and **Yb** which is not observable because it rapidly expels as a proton, the H atom located on  $\text{C}_4$  to give finally, the stable product **2** and regenerate AcOH (Scheme 5).

The yield of the reaction  $\text{X} \rightarrow \text{Y}$ ,  $\phi_{\text{X} \rightarrow \text{Y}} = k_{\text{prot}}[\text{AcOH}] / (k_{\text{reop}} + k_{\text{prot}}[\text{AcOH}]) = 1 - (\tau_{\text{X}} / \tau_{\text{X}}^0)$  since  $1/\tau_{\text{X}}^0 = k_{\text{reop}}$  and  $1/\tau_{\text{X}} = (k_{\text{reop}} + k_{\text{prot}}[\text{AcOH}])$ ,  $\tau_{\text{X}}^0$  and  $\tau_{\text{X}}$  being the lifetime of **X** in the absence and presence of AcOH. The values of  $\phi_{\text{X} \rightarrow \text{Y}}$ , calculated from the values of  $\tau_{(440 \text{ nm})}$  given in Table 4 and plotted as a function of  $[\text{AcOH}]$  in Fig. 8, mimic accurately those of the overall quantum yield,  $\Phi$ , equal to  $\phi_{\text{isc}} \times \phi_{\text{T-X}} \times \phi_{\text{X-Y}} \times \phi_{\text{Y-2}}$ . The ratio slope/intercept of the linear plots of  $1/\Phi$  vs.  $1/[\text{AcOH}]$  gives

<sup>7</sup> See also [16].



Scheme 5.

$k_{\text{reop}}/k_{\text{prot}} = 3 \times 10^{-4}$  for **1b** and  $8.7 \times 10^{-4}$  for **1c**, whereas the reciprocal of the intercept gives  $\phi_{\text{isc}} \times \phi_{\text{T-X}} \times \phi_{\text{Y-2}} \approx 0.9$  in both cases. With the value  $k_{\text{prot}} = 4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  determined for **Xb** from the data of Table 4, one gets  $k_{\text{reop}} = 1.38 \times 10^6 \text{ s}^{-1}$ , i.e.  $\tau_0 = 724 \text{ ns}$  in excellent agreement with the 700 ns lifetime measured for **Xb** in neat benzene.

The same procedure can be used to estimate the lifetimes of the species **Xc–Xe**, which cannot to be measured directly by LFP because they are too short with respect to the lifetime of the parent triplet states. With  $k_{\text{prot}} \approx 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , this gives  $k_{\text{reop}} \approx 4.4 \times 10^6 \text{ s}^{-1}$ , i.e.  $\tau_0 \approx 230 \text{ ns}$  for **Xc**, whereas the value  $\tau_0 \approx 130 \text{ ns}$  roughly estimated from LFP (Fig. 4) yields  $k_{\text{reop}} \approx 4.4 \times 10^6 \text{ s}^{-1}$  and then  $k_{\text{prot}} \approx 8.8 \times$

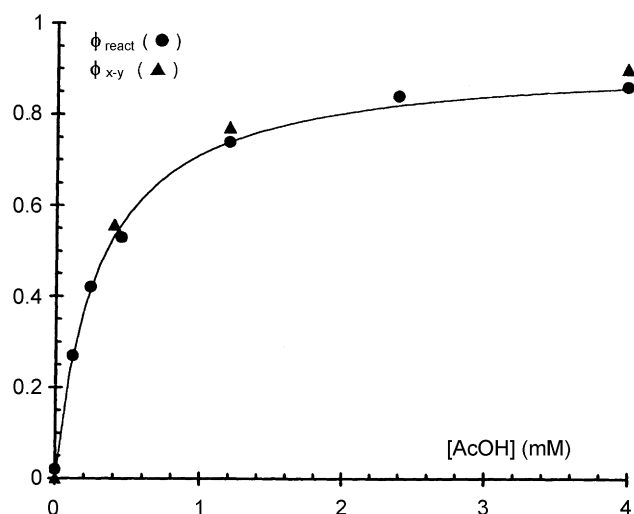


Fig. 8. Effect of acetic acid on: (●) the measured overall quantum yield of cyclization  $\phi_{\text{react}}$  (values from Table 1 excepted for  $[\text{AcOH}] = 4 \text{ mM}$ , obtained by non-linear interpolation) and (▲) on the yield of protonation of the **X** species,  $\phi_{\text{x-y}}$ , calculated from the data of Table 4 according to the equation given in text.

$10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Thus LFP measurements and changes of the reaction quantum yield as a function of  $[\text{AcOH}]$  agree to give a value of  $k_{\text{prot}}$  close to the diffusion controlled rate and a value of  $k_{\text{prot}}$  ( $4 \pm 1$ ) times larger for **1c** than for **1b**.

In the case of **1d** and **1e**, the Cl and  $\text{CF}_3$  substituents decrease the electronic charge on the  $\text{O}_6$  center so that the protonation of **X** requires a strong acid. From the values of Table 3, it is clear that trifluoroacetic acid (TFA) is much more efficient than acetic acid to trigger the reaction. The intercept of the plot  $1/\Phi$  vs.  $1/[\text{TFA}]$  gives  $1/\Phi_{\text{max}} = 4.5$  and its slope  $(k_{\text{reop}}/k_{\text{prot}})/\Phi_{\text{max}} = 0.0325$ . Assuming that  $k_{\text{prot}}$  is around  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , this yields a 30 ns lifetime for **Xe** compatible with the faint absorption of this species appearing as a shoulder around 400 nm on the time resolved absorption spectra of **1e** in Fig. 5. The value of  $\Phi_{\text{max}}$  is limited to 0.22 by the yield of cyclization step **T**  $\rightarrow$  **X**,  $\Phi_{\text{T-X}} = k_{\text{T-X}}/(k_{\text{T-X}} + k_{\text{d}} + k_{\text{CT}})$ , which is low in benzene due to the high value of  $k_{\text{CT}}$  associated to the charge transfer process between the solvent and the triplet mentioned above. Since the triplet lifetime of **1e** is around 220 ns, the relation  $\Phi_{\text{T-X}} = k_{\text{T-X}}\tau_{\text{T}}$  gives  $k_{\text{T-X}} \approx 10^6 \text{ s}^{-1}$ , a value compatible with the triplet lifetime of **1e** in  $\text{CCl}_4$  and acetonitrile, around 1  $\mu\text{s}$ , if one assumes that in these solvents and at the low concentration, the main deactivation pathway of the triplet is the cyclization to **X**.

This value of  $k_{\text{T-X}}$  for **1e** is about 50 times smaller than the rate constant of cyclization of the  $\alpha$  rotamer of the **1b** triplet state, in spite of the fact that the lowest triplet state of **1e** is  $n\pi^*$ , whereas it is  $\pi\pi^*$  in the case of **1b**. Clearly, the rate of cyclization is not determined by the nature of the lowest triplet, but instead by the value of the activation energy needed to reach the transition state, a value which probably depends on the nature of substituents. If the frequency factor for the cyclization of **1e** is around  $5 \times 10^{11} \text{ s}^{-1}$  as it is for **1b**( $\alpha$ ), this activation energy would be around 32.5 kJ/mol in the case of **1e**, 10 kJ/mol larger than for **1b**( $\alpha$ ).

## 5. Discussion

The mechanism of the cyclization reaction, as it results from this study, is significantly different from the mechanism proposed by Hageman and Verhoeven [7] (“H&V” in the following). We will review the points of agreement and those of disagreement between the two proposed mechanisms. Then it will be shown that our mechanism may account not only for our results (see above) but also for those obtained by H&V, in quite different conditions of concentration.

In the series of substituted phenylbenzoquinones investigated here, the real cyclization step, i.e. the formation of the **X** intermediate from the triplet, occurs in all cases, independent of the  $n\pi^*$  or  $\pi\pi^*$  nature of the lowest triplet state and of the polarity of the solvent. This conclusion is contrary to some major statements of H&V.

We agree with their identification of an  $n\pi^*$  triplet as responsible for cyclization and a  $\pi\pi^*$  triplet as responsible for dimerization. We willingly acknowledge this identification as a major contribution of H&V to the elucidation of the reaction mechanism. In our 1991 paper on the photocyclization of **1a**, we had stated that “*the reaction proceeds via a triplet state which... is mainly  $\pi\pi^*$* ” and, even after the publication of the H&V’s paper, we have been for a while reluctant to accept the idea of a cyclization via an  $n\pi^*$  triplet because **1e**, with an  $n\pi^*$  lowest triplet state, cyclizes with low quantum yields in solvents acidified with acetic acid. We finally realized that the nature of the lowest triplet state is unimportant for the cyclization reaction because the energy splitting between the  $n\pi^*$  and  $\pi\pi^*$  triplets is much smaller than the activation energy required for the cyclization (except in a few cases, see later). Even more, in diluted solutions, the quantum yield and the chemical yield of cyclization are better for compounds such as **1b** with a  $\pi\pi^*$  lowest triplet state than for **1e** which has an  $n\pi^*$  lowest triplet state: the rate constant for cyclization is larger, the conversion of **X**  $\rightarrow$  **2** is easier and do not require a strong acid as in the case of **1e** and a  $\pi\pi^*$  lowest triplet state minimizes the formation of reduction products and other by-products arising from the semiquinone radicals generated by reaction of the  $n\pi^*$  triplet with the solvent.

The dichotomic statement of H&V “*dimerization and no cyclization in non-polar solvents, cyclization and no dimerization in polar solvents*” is unjustified even if it seems supported by products analysis. The formation of the cyclized **X** intermediate occurs as well in polar as in non-polar solvents and this is, most probably, also true for dimerization. The  $n\pi^*$  and  $\pi\pi^*$  triplet states yielding, respectively, these two competing processes can easily interconvert and even if the solvent polarity may slightly modify their relative energy, “*the expected effect is in the wrong direction to explain the observations*”, as noticed by H&V [7]. In fact, for a given compound, the relative efficiency of the cyclization to **X** and dimerization reaction depends mainly on the concentration of the solution but the yield of the stable cyclization product **2** depends on the polarity and the acidity of the solvent.

In a non-polar solvent, with no acid added in the solvent, **X** reopens to the starting compound and the only stable product is the dimer which rapidly precipitates. The neat result is an apparently specific dimerization with a quantum yield  $\phi_{\text{dim}} = k_{\text{dim}}[\mathbf{1}]\tau_{\text{T}}$ , where  $\tau_{\text{T}}$  is the triplet lifetime. This yield depends on the concentration and is about zero in the diluted solutions investigated during this study, where the system seems photostable.

In a polar solvent, **X** rearranges to the stable product **2** or it reopens, depending on the ease for the proton transfer from C<sub>4</sub> to O<sub>6</sub>,<sup>8</sup> whereas the dimer, still formed with a yield  $\phi_{\text{dim}} = k_{\text{dim}}[\mathbf{1}]\tau_{\text{T}}$ ,<sup>9</sup> remains in solution. According to H&V, a secondary photolysis may quantitatively convert the dimer to the 2-hydroxydibenzofuran product so that the next result is an apparently specific cyclization with a quantum yield depending on both the solvent and the concentration. The relative importance of the pathway involving the dimer increases with the concentration but the quantum efficiency of this pathway is small because of: (i) the low absorption of the dimer, (ii) the screening effect of **1** and **2** and (iii) the low yield of formation of <sup>3</sup>**1**\* by reopening of the dimer, probably <5%. This explains the small value (0.12) of the quantum yield of disappearance of **1a** in methanol measured by H&V when **[1a]**  $\approx$  30 mM, whereas we found much higher values in diluted solutions, around 0.8 when **[1a]**  $\approx$  3.5 mM and 0.5 when **[1a]**  $\approx$  0.35 mM.<sup>10</sup>

H&V pay much importance to the tilt angle between the phenyl ring and the quinone moiety and claim that a “near-perpendicular” conformation is the geometry required for the cyclization of the  $n\pi^*$  triplet, whereas the “near-planar”  $\pi\pi^*$  triplet would give only dimerization. On this basis, they define two classes of phenylbenzoquinones: those where substitution (in *ortho* position on the phenyl or the quinone moieties) imposes a “near-perpendicular” geometry would give only cyclization and the others, such

<sup>8</sup> This depends on the acidity of the **X** species which may spontaneously eject a proton from C<sub>4</sub> and on the acidity of the solvent which may protonate **X** on the O<sub>6</sub> position.

<sup>9</sup> With respect to a non-polar solvent, the energy level of the  $n\pi^*$  triplet is raised up in a polar solvent: this favors the  $\pi\pi^*$  triplet and, consequently, an increase of  $f_{\text{dim}}$ . However, for several of the investigated compounds, the triplet lifetime is shorter in polar solvents and this will decrease the yield of dimerization. Viscosity of the solvent will also affect the value of  $k_{\text{dim}}$ .

<sup>10</sup> These values of the quantum yield of disappearance of **1a** in MeOH,  $\phi_{\text{dis}} \approx \phi_{1-2}$  since **2a** is (nearly) the only photoproduct in this solvent, may be accounted as follows. From the 400 ns lifetime of <sup>3</sup>**1a**,  $k_{\text{T-X}} + k_{\text{dim}}[\mathbf{1a}] \approx 2.5 \times 10^6 \text{ s}^{-1}$  when **[1a]** = 0.35 mM and assuming that  $k_{\text{dim}} = 7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , one gets  $k_{\text{T-X}} = 2.25 \times 10^6 \text{ s}^{-1}$ . Then, the yields of formation of **X**,  $\phi_{\text{T-X}} = k_{\text{T-X}}/(k_{\text{T-X}} + k_{\text{dim}}[\mathbf{1a}])$ , and of the dimer,  $\phi_{\text{dim}} = k_{\text{dim}}[\mathbf{1a}]/(k_{\text{T-X}} + k_{\text{dim}}[\mathbf{1a}])$ , can be calculated for any value of **[1a]**. If  $\phi_{\text{X-2}} = 0.9$  (i.e. 10% reopening) and if the photolysis of the dimer gives **2a** with a 5% yield only, the values of  $\phi_{1-2} = 0.9\phi_{\text{T-X}} + 0.05\phi_{\text{dim}}$  calculated with **[1a]** = 0.35, 3.5 and 30 mM would be 0.815, 0.46 and 0.135, close to the experimental values of  $f_{\text{dis}}$ . Alternatively, if  $k_{\text{dim}} = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and if the decomposition of the dimer does not give **2a** but only **1a**, the same calculations yield  $\phi_{1-2} = 0.837, 0.513$  and 0.119, also in agreement with experiments.

as **1a–1e** with a “near-planar” geometry, would give only dimerization. Since the cyclization of compounds of the second class does occur in polar and acidic solvent, H&V postulated that the cyclized product results from the photolysis of the dimer. Our LFP measurements, as well as those previously published [6] as those reported here, clearly demonstrate that direct cyclization from the triplet occurs for compounds **1a–1e**. The “near-planar”  $\pi\pi^*$  triplet is easily converted into the close lying  $n\pi^*$  triplet in which the tilt angle can easily reach the value (probably 30–45°) required for the cyclization to occur.

H&V demonstrated that *ortho* substitution favors the cyclization with respect to dimerization but this may (and we think it does) result from a decrease of the rate of dimerization rather than from an increase of the rate of cyclization due to a “near-perpendicular” geometry. The minimization of the dimerization does not result directly from the highly twisted geometry,<sup>11</sup> but from the fact that the non-planarity induced by *ortho* substituents on the phenyl largely increases the energy level of the singlet and triplet  $\pi\pi^*$  states: the blue shift of the  $S_0$ – $S_2$   $\pi\pi^*$  transition of the *o*-Me with respect to those of the *m*-Me and *p*-Me substituted compounds indicates that *ortho* substitution raises up the lowest  $\pi\pi^*$  singlet state of the *o*-Me by 32–43 kJ/mol and the lowest  $\pi\pi^*$  triplet state should be raised up by a similar amount since  $\Delta E_{ST}$  is probably about the same for these three compounds. Thus, the lowest triplet state of the *o*-substituted compounds is clearly  $n\pi^*$  and the  $\pi\pi^*$  triplet responsible for dimerization can hardly be populated by thermal activation.

The fact that 3-chloro-2,6-diphenyl-*p*-benzoquinone, also studied by H&V, gives only the 1-chloro-2-hydroxy-4-phenyl dibenzofuran seems more significant since, in this case, the competition is not between cyclization and dimerization but between cyclization on the phenyl in 2-position, pushed out of plane by the Cl atom, and cyclization on the phenyl in 6-position which may be nearly in the plane of the quinone. However, the observed selectivity may also be explained by a substituent effect comparable to the effect which makes one rotamer of the *meta* substituted phenylbenzoquinones much more reactive than the other. The selectivity observed in the present study for the *m*-OMe (**1b**) and those reported by H&V for the *m*-Me and the *m*-Cl substituted molecules are the same and our measurements indicate that the triplet state of both rotamers of **1b** are formed in similar amounts. Therefore, the selectivity on the cyclization product cannot be explained by electronic effects or by a large predominance of one rotamer and it remains enigmatic. This selectivity may be increased at high concentration by the competition between cyclization and dimerization because the less reactive triplet rotamer has a longer lifetime

and thus a larger probability to encounter a ground state molecule to give the dimer.

## 6. Conclusion

The elucidation of the mechanism of photocyclization of phenylbenzoquinones requires studies combining time resolved spectroscopy with quantum yield measurements and products analysis after continuous irradiation. Measurements under continuous irradiation alone cannot reveal the fact that cyclization of the triplet into the **X** intermediate does occur in a non-polar solvent since **X** reopens to the starting product. They cannot explain “amazing” results such as the drastic decrease of the quantum yield of cyclization of **1b** when going from slightly acidified non-polar solvents to polar solvents, whereas the reverse is observed for many other compounds. Only flash-photolysis gives the explanation: a 10-fold decrease of the quantum yield of formation of the triplet state. Similarly, the changes in the lifetime of the **1e** triplet state in various solvents by up to two orders of magnitude will result in large variations of the photocyclization quantum yield. Some of these variations could be correctly explained on the basis of products analysis (e.g. H-abstraction to the solvent to explain the decrease of the quantum yield in the series of alcohols after detection of phenylhydroquinone) but the six times decrease of  $\phi_{cycl}$  expected on the basis of the triplet lifetimes when going from  $CCl_4$  to benzene (both solvents being acidified with trifluoroacetic acid) would be very difficult to explain correctly without the help of time resolved spectroscopy.

Finally, it must be noticed that depending on substituents and experimental conditions (concentration, temperature, solvent), the photochemistry of phenylbenzoquinones can be tuned over a large number of reactions: reduction, cyclization, dimerization or deactivation by a reversible electron transfer either intramolecular or between the solute and the solvent.

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<sup>11</sup> The phenyl and cyclohexenedione moieties being nearly orthogonal in the dimer, a twisted geometry of the triplet and ground states reactants would prefigure the final geometry and should be even favorable for dimerization.

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