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Spectroscopy and photochemistry of a series of alkyl-substituted o- and p-benzoquinones and their mono-oxime O-methyl ethers[†]

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Abstract. Following our previous reports on the spectroscopy and photochemistry of methyl ethers of cyclic α -oxo oximes, we have now studied a number of o- and p-benzoquinone mono-oxime O-methyl ethers and, for comparison, some corresponding o- and p-benzoquinones. The ground-state electronic structure of o-benzoquinones is described satisfactorily by the sum of the two propenal fragments. The structure of the corresponding (E)- and (Z)-mono-oxime ethers can be described similarly as the sum of the propenal and (E)- or (Z)-(methoxyimino)propene fragments. This method fails when used for the construction of the ground-state electronic structure of the isomeric p-benzoquinones and their mono-oxime ethers.

The UV spectra of o-benzoquinone mono-oxime ethers are quite different from those of the parent o-benzoquinones in that the free lying $n^+\pi^*$ absorption of the latter is, for the former, shifted to lower wavelength and apparently hidden under the long-wavelength $\pi\pi^*$ absorptions. For the p-benzoquinone mono-oxime O-methyl ether 12, however, the long-wavelength $n\pi^*$ absorption remains visible.

Direct irradiation of the *tert*-butyl-substituted o-benzoquinone mono-oxime O-methyl ethers (E)-5–(E)-7 dissolved in acetonitrile at λ 350 nm leads (in addition to E-Z isomerization) to the formation of the (E)-azobenzenes 16–19 by dimerization of the respective phenylnitrenes. However, in addition, the 2,4-di-*tert*-butyl derivative (E)-7 undergoes mainly γ -hydrogen abstraction, probably from the $S^1(n\pi^*)$ state, leading to subsequent cyclization to the relatively stable dienol (E)-14, which eventually isomerizes thermally to the enone (E)-15. Evidence is presented that (Z)-7 exhibits only Z-E photoisomerization and no photocyclization, as has been observed previously with the saturated six-membered ring analogue. Direct irradiation of the corresponding 3,5-di-*tert*-butyl-o-benzo-quinone (3) at 350 nm leads to decarbonylation with formation of cyclopentadienone 13. Sensitized irradiation of mono-oxime O-methyl ether (E)-7, using 1-acetylnaphthalene and 1-fluorenone as triplet sensitizers and acetonitrile as solvent, leads to E-Z isomerization only with eventual photostationary state [E]/[Z] ratios of 0.78 and 0.88, respectively.

The *p*-benzoquinone mono-oxime O-methyl ethers 11 and 12 are photostable against 254, 300 and 350 nm radiation; however, any occurring E-Z isomerization escapes detection for symmetry arguments.

Introduction

As a sequel to our studies on the photochemistry of α -oxo oxime ethers', we have turned our attention to the mono-O-oxime methyl ethers of o- and p-benzoquinones. In these compounds, the O=C-C=N-O chromophore is extended by a conjugated butadienediyl bridge, as with the ortho isomer, or its two constituents are separated by two bridging ethenylene moieties, as with the *para* isomer. Derivatives of o- and p-benzoquinone are of biological importance^{2,3}; others are employed as initiators for photopolymerization of composite mixtures, *e.g.*, in dental applications⁴.

Results and discussion

The spectroscopy and photochemistry of a series of monooxime O-methyl ethers of o-benzoquinone (4-7) and p-benzoquinone (11 and 12) has been studied, and their behaviour compared with that of the corresponding benzoquinones.

⁺ Photochemistry of α-oxo oxime ethers 14. For part 13, see F. Stunnenberg, H. Cerfontain, J. A. J. Geenevasen and W. Hielkema, Recl. Trav. Chim. Pays-Bas 110, 31 (1991).

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Electronic structure and UV spectroscopy

o-Benzoquinones and their mono-oxime ethers. The ground sate electronic structure of o-benzoquinone (1) can be considered as the sum of two propenal (acroleine) parent fragments. MINDO/3 calculations were found to predict correctly the orbital sequence of propenal⁵, established by photoelectron (PE) spectroscopy⁶⁻⁸, whereas *ab-initio*^{6,9} and other types of semi-empirical calculations^{7,10} failed to do so. The order of the four highest occupied levels is $n^+ > \pi^- >$ $n^- > \pi^+$ (Figure 1). The nature of the π orbitals and their order correspond with the MINDO/3 calculations. The sequence and splitting of the lone-pair levels are in agree-ment with those reported by *Hug* et al.¹¹. Note that the lone pairs of the two carbonyl groups of o-benzoquinone interact via through-bond interaction (TBI)^{12,13} rather than via through-space interaction (TSI), just like those of aliphatic saturated 1,2-diketones¹⁴. Also, the magnitude of the lonepair splitting (ΔE 1.63 eV) is comparable to that of the saturated 1,2-diketones¹⁴. The various MO energies are collected in Table I.

The π system is more extended for the *o*-benzoquinones than for the 1,2-diketones and the first electronic transition of the *o*-benzoquinones lies at significantly longer wavelength, due to the lower energy of the LUMO π^* level. For



the o-benzoquinones 1-3, the $n^+\pi^*$ transition maxima are found at 565, 546 and 552 nm, respectively^{15,16}, whereas the $n\pi^*$ transition maximum of a planar saturated s-cis 1,2-diketone is found at 506 nm¹⁴. Calculations indicate that



Figure 1. Orbital diagram of 1 and (E)- and (Z)-4, constructed from the orbitals of the respective fragment compounds.

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Compound							
Compound	π	π	n	n	π	Method	
propenal	10.9	13.8	10.1			exptl	
1	10.09	12.16	10.00	12.53	13.91	MINDO/3 MNDO	
(E)-3-(methoxy)propene	8.6		10.0	10.82	13.30	exptl	
(Z)-3-(methoxy)propene	9.47	11.24	11.08	10.0	13.35	MNDO MNDO	
	9.37	10.80	10.73	11.68	12.03	MNDO	
(Z)- 4	9.31	10.23	10.53	12.19	12.01	MINDO/3 MNDO	
8	10.97	10.95	9.68	11.56	14.51	MNDO MNDO/3	
11	9.64 8.99	10.69	9.15	9.44	11.92 11.32	MNDO MNDO/3	

Table I Ionization potentials of various quinone derivatives and fragment compounds.

^a Tentative assignment.

the second transition is also of $n\pi^*$ character, resulting from promotion of an electron from the n^- MO to the LUMO¹⁷, and that the ΔE between the two $n\pi^*$ transitions is approximately 1.3 eV^{15,17}, *i.e.*, the same value as reported for planar 1,2-diketones¹¹. Experimentally, the second transition is obscured by the more intense $\pi\pi^*$ absorption, which is for 1 and 2 at 390 nm and for 3 at 402 nm (ε 1500 $1 \cdot mol^{-1} \cdot cm^{-1}$). The occupied π orbital consists mainly of contributions from the diene chromophore. The LUMO on the contrary is a more delocalized orbital. A second $\pi\pi^*$ absorption is found around 250 nm, as a shoulder on the very intense $\pi\pi^*$ transition around 200 nm for 1 and 214 nm for 2, of which the molar extinction coefficients are both approx. $6000 \ l \cdot mol^{-1} \cdot cm^{-1}$. The UV absorption spectrum of 2 is shown in Figure 2.

In the same way as the electronic structure of *o*-benzoquinone was constructed from two propenal fragments, the corresponding mono-oxime *O*-methyl ether isomers (*E*)and (*Z*)-4 may be build up from propenal and the respective (*E*)- and (*Z*)-(methoxyimino)propene as fragments. However, for 3-(methoxyimino)propene, MINDO/3 fails to reproduce the correct orbital sequence for the two highest occupied MOs, as was also observed for simple oximes such as methanal oxime and 2-(methoxyimino)propane¹⁹. PE spectroscopic data²⁰ show that the HOMO is of π character and that it has a lower energy than the lone-pair MO,



Figure 2. UV absorption spectra of 2 (methanol) and (E)-7.



Figure 3. He I PE spectrum of (E)-7.

the data being 8.6 vs. 10.0 eV, respectively. As with the simple oximes, MNDO predicts the observed orbital sequence of 3-(methoxyimino)propene correctly. The actual construction of (E)- and (Z)-4 from the basic fragments is shown in Figure 1. The π orbital levels of (E)- and (Z)-4 are very similar, but the levels of the lone-pair orbitals are different. In both (E)- and (Z)-4, TBI prevails over TSI, as was concluded for (E)- and (Z)-ethanedial mono-oxime²¹. The observed splitting is much larger for (Z)-4 (1.66 eV) than (E)-4 (0.95 eV). The lone-pair MOs of the carbonyl and iminyl moieties of (E)-4 interact only weakly and the highest lone-pair level has mainly $n_{\rm CO}$ character, while the second lone-pair level has its main contribution from the $n_{\rm N} + n_{\rm O}$ MO of 3-(methoxyimino)propene. As for (Z)-4, complete delocalization of the lone-pair orbitals occurs due to the favourable geometric orientation of the lone pair orbitals for TBI.

The UV spectra of the *o*-benzoquinone mono-oxime ethers are very different from those of the corresponding *o*-benzoquinones (Table II). Typically, the spectrum of (E)-2,4--di-*tert*-butyl-6-(methoxyimino)-2,4-cyclohexadien-1-one

[(E)-7], shown in Figure 2, contains two $\pi\pi^*$ absorptions located at 310 and 390 nm. There is no evidence for a $n\pi^*$ transition which is probably hidden under the long wavelength $\pi\pi^*$ absorption, as was observed with the α -bis-(methoxyimino)alkanes²².

On the basis of the orbital energies and the absence of an apparent $n\pi^*$ transition in the UV spectrum, the orbital sequence as calculated by MNDO is preferred for *o*-benzoquinone mono-oxime ethers. The PE spectrum of (*E*)-7 (Figure 3) leads to the same conclusion. It contains three major low energy bands at 8.22, 8.85 and 9.53 eV, of which the latter clearly consists of two overlapping bands, centered at 9.53 and 9.9 eV. The sharp bands at 8.22, 8.85 and 9.9 eV is attributed to a lone-pair MO in view of its broadened nature, whereas the second lone pair is probably hidden under the π band at 8.85 eV²³.

For aliphatic α -oxo oxime ethers, of which the $n\pi^*$ transition is usually apparent in the UV spectrum only as a

Table II UV absorption data of benzoquinones and their mono-oxime ethers

Com- pound	Solvent	λ _{max} (nm)	ϵ (1 · mol ⁻¹ · cm ⁻¹)	Ref.	
1		200		15.16	
•		253		15.16	
		356/366	/2500	15,16/17	
		565/580	/ 25	15,16/17	
2	MeOH	214	6300		
		258	2600		
		386	1200		
		546	20		
3	MeOH	245	2900		
		402	1500		
		552	48		
(E) -7	MeOH	300	3300		
		374	2800		
	cyclohexane	310	3300		
		390	2800		
8		240/242	17000/	32/17,33	
		258/304	372/	32/17,33	
		450/498	17.4/	32/17,33	
9	MeOH	254	16500		
		317	450		
		450	30		
10		483	30	34	
12	EtOH	250	2300		
	1	315	22000		
		417	24		
	cyclohexane	427	24		

shoulder, the nature of the lowest triplet is $\pi\pi^{*24}$. This may also be the case with the *o*-benzoquinone mono-oxime ethers, especially since the singlet-triplet energy gap is larger between states of $\pi\pi^*$ character than of $n\pi^*$ character.

between states of $\pi\pi^*$ character than of $n\pi^*$ character. p-Benzoquinones and their mono-oxime ethers. Various studies on both the ground and excited states of p-benzoquinone (8) have appeared. As to the ground state, there is a long standing dispute regarding the order of the four highest occupied orbitals²⁵⁻³². MINDO/3 appears again to be superior to MNDO in predicting the orbital sequence as found with most of the theoretical studies and by PE spectroscopy²⁹⁻³¹. The agreement with the experimental ionization data for the π levels is very good, but the calculated lone-pair splitting is overestimated (0.67 vs. 0.29-0.46 eV). MINDO/3 does place the out-of-phase n^- lone-pair level at higher energy than the in-phase n^+ level. Attempts to construct p-benzoquinone from the basic fragments (see before) have failed.

The excited singlet state sequence of the *p*-benzoquinones is easily assigned. For **8–10**, there is, at long wavelength, an $n\pi^*$ transition at 450 (17.4), 450 (30 1 · mol⁻¹ · cm⁻¹) and 483 nm, respectively^{17,33-35}. In addition, there are two other absorptions, both of $\pi\pi^*$ character at about 250 and 300 nm. Extensive theoretical studies revealed that the $n\pi^*$ band actually consists of two almost degenerate $n\pi^*$ levels of $n^-\pi^*$ and $n^+\pi^*$ character with a splitting of about 0.1 eV¹⁸.

For both 8 and 9, the lowest triplet state is of $n\pi^*$ character; for 10, the nature of the lowest triplet state is uncertain^{36,37}. The singlet- $n\pi^*$ -singlet- $\pi\pi^*$ energy gap of 10 is $\simeq 1.4$ eV. In the series of saturated α -oxo oxime ethers, the average singlet $n\pi - \pi\pi^*$ gap is 1.3 eV, while the triplet $\pi\pi^*$ level is 0.1 eV lower in energy than the triplet $n\pi^*$ level²¹. This renders the $n\pi^*$ and $\pi\pi^*$ triplet states of the *p*-benzoquinones close to degenerate; the substituents will then be decisive in determining which is the state of lower energy. Calculations were performed on *p*-benzoquinone monooxime *O*-methyl ether (11) using both MINDO/3 and



MNDO. The orbital sequence predicted by MINDO/3 is $\pi^- > n_{\rm CO} > n_{\rm N} - n_{\rm O} > \pi^+$, whereas that by MNDO is $\pi^- > \pi^+ > n_{\rm CO} > n_{\rm N} - n_{\rm O}$. Both types of calculation indicate that there is very little interaction between the lone pairs of the C=O and C=N-O fragments, the former having the highest occupied lone-pair MO. The presence of a long wavelength $n\pi^*$ absorption in the UV absorption spectrum of 11 renders unlikely the orbital sequence predicted by MNDO. This band at 427 nm ($\epsilon 24 \ 1 \cdot mol^{-1} \cdot cm^{-1}$) is followed by two $\pi\pi^*$ absorptions at 315 ($\epsilon 22000$) and 250 nm ($\epsilon 2300 \ 1 \cdot mol^{-1} \cdot cm^{-1}$). The discussion on the nature of the lowest excited triplet state of the *p*-benzoquinones 8-10 (see above) is also applicable to their mono-oxime *O*-methyl ethers.

Photochemistry

Irradiation of a solution of 3,5-di-*tert*-butyl-o-benzoquinone (3) (0.3M) in acetonitrile- d_3 at 350 nm at 30°C leads,

according to ¹H NMR analysis, to decarbonylation, the only initial product being 2,4-di-*tert*-butyl-2,4-cyclopentadien--1-one (13)³⁸. Subsequently, ingrowing high-field NMR signals are observed, which have been assigned tentatively to the Diels-Alder dimer of 13^{40} . No products resulting from γ -hydrogen abstraction were observed⁴¹.

Irradiation (λ 350 nm) of a solution of (E)-2,4-di-tert-butyl--6-(methoxyimino)-2,4-cyclohexadien-1-one[(E)-7] (0.3M) in acetonitrile- d_3 at 30°C leads to the formation of (Z)-7, the bicyclooctadienol 14 and small amounts of methanol and (E)-3,5,3',5'-tetra-tert-butyl-2,2'-dihydroxyazobenzene (16) as primary products. The dienol 14 is eventually fully converted into the bicyclooctenones (E)- and (Z)-15 (Figure 4). The molar ratio of 16/(14 + 15) is equal to 1/18. The conversion of 4 into the dienol 14 is suggested to proceed (Scheme 1) via initial abstraction by the excited carbonyl group of one of the $(\gamma$ -)hydrogens of the adjacent tert-butyl group. Subsequent ring closure of the resulting conjugated 1,4-diradical gives the dienol 14 which, upon ketonization, leads to formation of enone 15 as eventual product⁴³. Ketonization of the enol 14 to yield 15 is a thermal process, as shown by the following experiment. A solution of (E)-7 in acetonitrile- d_3 was irradiated at λ 350 nm for 50 min to obtain the optimal content of 14 (26%), a relatively small amount of (E)-15 (8%) and no (Z)-15 (Figure 5). After being subsequently stored for 18 hin the dark, the mixture contained no trace of 14 which had apparently been completely converted into (E)-15, since no trace of (Z)-15 was formed. Thus, the (Z)-15 formed on prolonged irradiation results by photoisomerization of (E)-15⁴⁷. The thermal precursor of (E)-15 will then be (E)-14, since E-Z isomerization of oxime ethers does not proceed thermally, but only photochemically.

The main primary photoproducts of (E)-7 are (E)-14 and (Z)-7 (see Figure 5). The absence of (Z)-14 infers that (Z)-7 only undergoes Z-E isomerization and no cyclization. This



Scheme 1. Product formation upon direct irradiation of (E)-7 at 350 nm.



Figure 4. Product formation upon irradiation of (E)-7 at 350 nm.

difference in behaviour of (E)- and (Z)-4 is similar as observed with saturated five-, six- and seven-membered cyclic α -oxo oxime O-methyl ethers^{21,48}.

The ketonization (E)-14 \rightarrow (E)-15 is relatively slow. This observation may be explained in terms of stabilizing intramolecular hydrogen bonding of the hydroxy hydrogen with the imine nitrogen of (E)-14, which is thought to be moderately strong⁴⁹⁻⁵¹, and the repulsive dipolar intercarbonyl-iminyl interaction of (E)-15. The observation that (E)-14, in contrast to (E)-15, does not photoisomerize around the C=N bond is thought to substantiate the proposed explanation of hydrogen bonding in (E)-14⁵².

With β,γ - and δ,ϵ -unsaturated ketones, the γ -hydrogen abstraction proceeds by an excited singlet-state mechanism⁴⁴⁻⁴⁶. Such a mechanism may very well apply to (E)-7, since γ -hydrogen abstraction is known to occur very preferably from $n\pi^*$ states. As was established by triplet photosensitization (see later), the lowest triplet state of (E)-7 is of $\pi\pi^*$ character and exhibits only E-Z isomerization⁵², as observed previously with saturated cyclic α -oxo oxime ethers²⁴. Upon excitation of (E)-7 at 350 nm, the $S^2(\pi\pi^*)$ state is populated (see section Electronic structure and UV spectroscopy). This state is proposed (see Scheme 1) to undergo both N-O homolysis (just as the saturated cyclic α -oxo oxime ethers do²⁴) and internal conversion to the $S^{1}(n\pi^{*})$ state which undergoes γ -hydrogen abstraction leading to the 1,4-diradical 20. Subsequent ring closure of 20 then gives the dienol (E)-14. The conversion of (E)-14 into (E)-15 is a thermal reaction; any (Z)-15 is formed by E-Zphotoisomerization of (E)-15.

The primary products methanol and (E)-azobenzene 16^{53} are formed from the methoxy and iminyl radicals produced by the N-O homolysis, as shown in Scheme 1. Hydrogen abstraction by the carbonyl oxygen of the resulting iminyl radical 21 from the concomitantly produced methoxy radical (or from hydrogen-donating molecules or other species



Figure 5. Photochemical (λ 350 nm) formation of (E)-14 from (E)-7 and its thermal ketonization to (E)-15.

present in the system) yields 3,5-di-*tert*-butyl-2-hydroxyphenylnitrene (18), the driving force for the nitrene formation being the aromatization of the cyclohexadiene system. Dimerization of the nitrene 18^{54} then yields the (*E*)--azobenzene 16.

Irradiation of a 81:19 mixture of (E)-4-tert-butyl [(E)-5] and (E)-5-tert-butyl-2-(methoxyimino)-3,5-cyclohexadien-1one [(E)-6] (in total 0.3M) in various solvents (acetonitrile, 2-propanol, ethanol and cyclohexane) at both 300 and 350 nm leads the formation of the azo compounds 17–19 and methanol as the main products⁵⁵ and not to photoreduction. During photoconversion, the [(E)-5]/[(E)-6] ratio remained constant at 4.3 \pm 0.3. Presuming the difference in position of the tert-butyl to have only a negligible effect on the molar extinction coefficient of the substrate and the quantum yield for nitrene formation, the composition of the azobenzene products 17–19 will be determined statistically to be 1.00/0.23/0.06. In fact, the observed ratio is 1.00/0.25/(0.06 \pm 0.03).

p-Benzoquinone mono-oxime *O*-methyl ether (11) and its 2,6-di-*tert*-butyl derivative (12) in acetonitrile, 2-propanol, ethanol or cyclohexane as solvent appear to be photostable for irradiation at 254, 300 and 350 nm, even upon prolonged irradiation (24 h). However, E-Z isomerization escapes detection for reasons of molecular symmetry. In view of the report on various 2- and 2,6-disubstituted *p*-benzoquinone 4-oxime acetates⁵⁶, the E-Z photoisomerization also takes place, in all likelihood, with 11 and 12.

The sensitized irradiation of (E)-2,4-di-tert-butyl-6-(methoxyimino)-2,4-cyclohexadien-1-one [(E)-7], using 1-acetylnaphtalene and 1-fluorenone as triplet sensitizers and acetonitrile- d_3 as solvent, leads only to E-Z isomerization with an eventual photostationary state [E]/[Z] ratio of 0.78 and 0.88, respectively.

The present, limited study deals with the photochemistry of o- and p-benzoquinones and the corresponding mono-oxime O-methyl ethers, *i.e.*, with four types of compounds of which the chromophores are all different and so, in principle, may be their photochemistry⁵⁷. This appears in fact to be the case, as shown below.

3-Methyl-⁵⁸, 4-methyl-⁵⁸, 4-*tert*-butyl-⁵⁸, 3,5-*tert*-butyl⁵⁸, 3,6di-*tert*-butyl-⁵⁹ and corresponding 2,4-cyclopentadien-1ones; 3- and 4-methyl- and 4-*tert*-butyl-o-benzoquinone in addition undergo α -cleavage with formation of the isomeric bis-ketenes³⁹. In 2-propanol as solvent, o-benzoquinones undergo photoreduction to the corresponding 1,2-benzenediols⁴². Irradiation of 2-*tert*-butyl- and 2,6-di-*tert*-butyl-p--benzoquinone in both alcoholic and non-alcoholic solvents leads to product formation resulting from initial intramolecular γ -H abstraction, whereas irradiation of methyland ethyl-substituted *p*-benzoquinones in (m)ethanol as solvent undergo intermolecular photoreduction to yield the corresponding 1,4-benzenediols⁶⁰.

Irradiation of (E)-4- and (E)-5-tert-butyl-o-benzoquinone mono-oxime O-methyl ether [(E)-5 and (E)-6] leads to E-Zisomerization and formation of methanol and the (E)--azobenzenes 16-18 as result of dimerization of the respective photochemically produced phenylnitrenes. The 2,4--di-tert-butyl derivative (E)-7 mainly undergoes γ -hydrogen abstraction with subsequent formation of the enol 14 which slowly isomerizes to the ketone 15. p-Benzoquinone monooxime O-methyl ether (11) and its 2,6-di-tert-butyl derivative (12) are photostable, considering that E-Z isomerization escapes detection.

Experimental

¹H NMR and ¹³C NMR spectra were recorded on Bruker AC-200 or Bruker WM-250 spectrometers. IR spectra were obtained using Perkin-Elmer 254, 298 or 1310 spectrophotometers. UV absorption spectra were recorded on a Cary 14 or Hewlett–Packard 8451-A diode array spectrophotometer. Mass-spectral data were obtained using a Varian MAT 711 spectrometer at 70 eV.

Materials

The benzoquinones 1, 3 and 8-10 were obtained from Janssen Pharmaceutica and used without further purification. 4-tert-Butyl-,2-benzoquinone (2) was prepared by oxidation of 4-tert-butyl-1,2-benzenediol (1.7 g) with ceric ammonium nitrate⁶¹ according to the method of Fischer and Henderson⁶² at a yield of 700 mg (43%).

The mono-oxime ethers were prepared from the corresponding benzoquinones by direct oximation using 1.1 equiv. of O-methylhydroxylamine^{63,64}. Typically, 4-tert-butyl-2-(methoxyimino)-3,5--cyclohexadien-1-one (5) and its 5-tert-butyl isomer 6 were prepared by adding to a solution of 700 mg (4.3 mmol) of the o-benzoquinone 2 in 25 ml of ethanol at 0°C, a solution of 420 mg (5.0 mmol) of O-methylhydroxylamine in 10 ml of water. After complete conversion of the substrate, as established by TLC monitoring, the reaction mixture was worked up by flash chromatography (Merck silica gel 60, 230-400 mesh, dichloromethane). Subsequent ¹H NMR analysis showed the presence of (E)-5 and (E)-6, in a ratio of 1:4.3 (these compounds could not be separated by flash chromatography, using various common solvents) and some dioxime dimethyl ether which was removed by flash chromatography, using diethyl ether as eluent.

Irradiation, analysis and product separation

Solutions of the various substrates in acetonitrile- d_3 were purged with either argon or nitrogen for 10 min prior to the irradiation. For direct irradiation at 300 and 350 nm, pyrex vessels or NMR tubes were used, whereas at 254 nm quartz vessels and quartz NMR tubes were employed. Irradiation was performed in a Rayonet RPR 208 photoreactor equipped with eight RUL-3000Å, eight RUL-3500Å or four RUL-2537Å light sources. Tripletphotosensitized experiments were performed in degassed solutions in benzene at λ 300 or 350 nm. Care was taken to ensure that the photosensitizer absorbed more than 98% of the incident radiation. The triplet sensitizers came from a Baker photosensitizer and quencher kit.

The photoproducts were separated and purified by flash chromatography (Merck silica gel 60, 230-400 mesh), using mixtures of dichloromethane and various alkanes as eluents. Methanol was identified by comparison of its ¹H NMR methyl singlet with that of an authentic sample. The other products were assigned directly on the basis of their spectral data. The composition of the reaction mixtures were determined qualitatively by TLC and quantitatively by multicomponent ¹H NMR analysis on the basis of specific absorptions of the various components⁶⁵.

Spectral data of substrates and products

The detailed structural assignments of the several ¹H NMR absorptions of the various benzoquinones and their mono-oxime O-methyl ethers were made by application of the recently developed "special" NMR techniques, as described in the following section.

- 2 ¹H NMR (CDCl₃, δ)⁶²: 1.235 (s, 9H, *t*-Bu), 6.279 (d, *J* 2.3 Hz, 3-H), 6.389 (d, *J* 10.4 Hz, 6-H), 7.139 (dd, *J* 2.3 and 10.4 Hz, 5-H). ¹³C NMR (APT, CDCl₃, δ): 27.66 (Me₃C), 35.52 (Me₃C), 123.66 (3-C), 129.28 (5-C), 140.02 (6-C), 162.10 (4-C), 180.2 (1-C + 2-C). IR (CHCl₃, cm⁻¹)⁶⁶: 3020, 2960, 2900, 2860, 1690, 1660, 1615, 1560, 1470, 1390, 1365, 1280, 1130, 810; UV [λ_{max} (nm), (ϵ) (1·mol⁻¹·cm⁻¹)]: methanol, 214 (6030), 258 (2590), 386 (1200), 546 (20).
- 3 ¹H NMR (CDCl₃, δ) (cf. Sadtler ≠ 21432): 1.224 (s, 9H, 5-t-Bu), 1.267 (s, 9H, 3-t-Bu), 6.21 (d, J 2.3 Hz, 6-H), 6.93 (d, J 2.3 Hz, 4-H). ¹H NMR (C₆D₆, δ): 0.794 (s, 9H), 1.189 (s, 9H), 6.014 (d, J 2.3 Hz, 6-H), 6.628 (d, J 2.3 Hz, 4-H). ¹³C NMR (APT, CDCl₃, δ): 27.55 (Me₃C-5-C), 28.88 (Me₃C-3-C), 35.10 (Me₃C-3-C), 35.66 (Me₃C-5-C), 121.61 (6-C), 133.20 (4-C), 149.53 (3-C), 162.94 (5-C), 179.75 (2-C), 180.71 (1-C). IR (CHCl₃, cm⁻¹): see Sadtler spectrum ≠ 37950. UV [λ_{max} (nm), (ε) (1·mol⁻¹·cm⁻¹)]: methanol, 245 (2900), 402 (1500), 552 (48).
- (E)-5 ¹H NMR (CDCl₃, δ): 1.13 (s, 9H, t-Bu), 4.12 (s, 3H, OMe), 6.28 (d, J 10.3 Hz, 6-H), 6.83 (d, J 2.5, 3-H), 7.12 (dd, J 2.5 and 10.3 Hz, 5-H).
- (*E*)-6 ¹H NMR (CDCl₃, δ): 1.12 (s, 9H, *t*-Bu), 4.12 (s, 3H, OMe), 6.18 (d, J 1.4 Hz, 6-H), 6.54 (dd, J 1.4 and 10.3 Hz, 4-H), 6.96 (d, J 10.3 Hz, 3-H). ¹H NMR (C₆D₆, δ): 0.81 (s, 9H), 3.87 (s, 3H), 6.07 (dd, J 1.7 and 10.3 Hz, 4-H), 6.22 (d, J 1.7 Hz, 6-H), 6.93 (d, J 10.3 Hz, 3-H). IR (CHCl₃, cm⁻¹)⁶⁷: 3000, 2960, 2920, 2860, 2850, 2820, 1650, 1645, 1610, 1505, 1460, 1400, 1380, 1250, 1060, 1050, 950, 825.
- (E)-7 ¹H NMR (CDCl₃, δ): 1.20 (s, 9H, 4-t-Bu), 1.28 (s, 9H, 2-t-Bu), 4.23 (s, 3H, OMe), 6.81 (d, J 2.3 Hz, 5-H), 6.98 (d, J 2.3 Hz, 3-H). ¹H NMR (C₆D₆, δ): 0.92 (s, 9H), 1.31 (s, 9H), 3.88 (s, 3H), 6.92 (d, J 2.4 Hz, 1H), 7.00 (d, J 2.4 Hz, 1H). ¹³C NMR (APT, CDCl₃, δ): 28.49 (Me₃C-4-C), 29.11 (Me₃C-2-C), 34.96 (2 × Me₃C), 64.05 (OMe), 110.34 (3-C), 133.67 (5-C), 148.12 (6-C), 148.66 (2-C), 149.54 (4-C), 183.04 (1-C). IR (CHCl₃, cm⁻¹): 3000, 2960, 2880, 2820, 1655, 1645, 1620, 1500, 1480, 1380, 1360, 1320, 1060, 1020, 940, 870. UV [λ_{max} (nm) (ϵ) (1·mol⁻¹·cm⁻¹)]: methanol, 300 (3300), 374 (2800); cyclohexane, 310 (3300), 390 (2800). MS (70 eV, m/z): 249 (M⁺), 105 (base); accurate mass: m/z 249.1716, calcd. for C₁₅H₂₃NO₂: 249.1728.
- (Z)-7 ¹H NMR (CDCl₃, δ): 1.21 (s, 9H, 4-t-Bu), 1.28 (s, 9H, 2-t-Bu), 4.24 (s, 3H, OMe), 6.43 (d, J 2.5 Hz, 5-H), 7.02 (d, J 2.5 Hz, 3-H). ¹H NMR (C₆D₆, δ): 0.97 (s, 9H), 1.34 (s, 9H), 3.84 (s, 3H), 6.55 (d, J 2.5 Hz, 1H), 6.92 (d, J 2.5 Hz, 1H). MS (70 eV, m/z): 249 (M⁺), 57 (base).
- 8 ¹H NMR (CDCl₃, δ): (cf. Sadtler \neq 10391): 6.79 (s, 4H). ¹³C NMR (CDCl₃, δ): (cf. Sadtler \neq 2810): 136.6 (C=C), 187.2 (C=O). IR (CHCl₃, cm⁻¹): see Sadtler spectrum \neq 2216.
- 9 ¹H NMR (CDCl₃, δ) (Sadtler ≠ 21402): 1.29 (s, 18H), 6.51 (s, 2H). ¹³C NMR (CDCl₃, δ) (Sadtler ≠ 1349): 29.5 (Me₃C), 35.5 (Me₃C), 130.1 (3- + 5-C), 157.7 (2- + 6-C), 187.7 (1-C), 188.5 (2-C). IR (CHCl₃, cm⁻¹): see Sadtler spectrum ≠ 25564.
- 10 ¹H NMR (CDCl₃, δ) (Sadtler \neq 7544): 2.01 (s, 12H). ¹³C NMR (CDCl₃, δ) (Sadtler \neq 2674): 12.2 (Me), 140.4 (C=C), 187.1 (C=O). IR (CHCl₃, cm⁻¹): see Sadtler spectrum \neq 22413.
- ¹H NMR (CDCl₃, δ): 4.15 (s, 3H), 6.44 (d, J 10.1 Hz, 2H, 2- + 6-H), 7.15 (dd, J 2.1 and 10.1 Hz, 1H), 7.60 (dd, J 2.1 and 10.1 Hz, 1H). IR (CHCl₃, cm⁻¹): 3005, 2980, 2820, 1725, 1640, 1620, 1520, 1220, 1050, 940, 880, 765.
- 12 ¹H NMR (CDCl₃, δ): 1.24 (s, 9H), 1.25 (s, 9H), 4.07 (s, 3H, OMe), 6.85 (d, J 2.5 Hz, 1H), 7.36 (d, J 2.5 Hz, 1H). IR (CHCl₃, cm⁻¹): 2820, 1650, 1615, 1050, 920; UV [λ_{max} (nm), (ϵ) (1 mol⁻¹ · cm⁻¹)]: methanol, 250 (2300), 315 (22000), 417 (24); cyclohexane, 427 (24).
- 13 ¹H NMR (CD₃CN, δ): 1.09 (s, 9H), 1.11 (s, 9H), 4.93 (d, J 1.6 Hz, 1H), 6.70 (d, J 1.6 Hz, 1H).
- (E)-14 ¹H NMR (CD₃CN, δ): 1.06 (s, 9H, *t*-Bu), 1.08 (s, 3H, 8-Me^a), 1.33 (s, 3H, 8-Me^b), 1.67 (m, 7-H^a), 2.24 (m, 7-H^b), 3.69 (m, 6-H), 3.82 (s, 3H, OMe), 5.6 (br.s, OH⁶⁸, 6.55 (4-H).

Table III ¹H NMR data ($CDCl_3$) of the o-benzoquinones and their mono-oxime O-methyl ethers.

Compound	δ (ppm)							
	3-H	4-H	5-H	6-H	t-Bu	OMe		
2	6.28		7.19	6.39	1.24			
3		6.93		6.21	1.27 (3-) 1.22 (5-)			
(E) -5	6.83		7.12	6.28	1.13	4.12		
(E)- 6	6.96	6.54		6.18	1.12	4.12		
(<i>E</i>)-7	6.98		6.81		1.20 (4-) 1.28 (2-)	4.23		
(Z)-7	7.02		6.43		1.21 (4-) 1.28 (2-)	4.24		

- (*E*)-15 The structure was elucidated by application of ${}^{13}C {}^{1}H$ correlation, COSY^{69,70} and DEPT⁷¹ experiments ${}^{1}H$ NMR (CDCl₃, d): 1.03 (s, 3H, 8Me^a), 1.14 (s, 9H, *t*-Bu), 1.34 (s, 3H, 8-Me^b), 1.79 (m, 7-H^a), 2.34 (m, 7-H^b), 2.99 (1-H), 3.47 (6-H), 4.12 (s, 3H, OMe), 6.78 (s, 4-H). ${}^{13}C$ NMR (CDCl₃, δ): 26.59 + 31.11 (Me₂C), 29.22 (Me₃C), 30.10 (6-C), 36.99 (Me₃C), 37.55 (Me₂C), 45.70 (CH₂), 53.19 (1-C), 63.19 (OMe), 111.13 (4-C), 147.38 (5-C), 163.24 (3-C), 196.15 (2-C); IR (CHCl₃, cm⁻¹): 2720 (OMe), 1680 (C=O), 1610 (C=N). UV [λ_{max} (nm), ϵ (1·mol⁻¹·cm⁻¹)]: cyclohexane, 228 (3630), 288 (4770), 357 (139), 373 (119); 392 (87); 413 (54). MS (FD, *m/z*): 249 (M[±]); accurate mass: *m/z* 249.1723, calcd. for C₁₅H₂₃NO₂: 249.1728.
- (Z)-15 ¹H NMR (CDCl₃, δ): 1.05 (s, 3H, 8-Me^a), 1.11 (s, 9H, *t*-Bu), 1.30 (s, 3H, 8-Me^b), 1.85 (m, 7-H^a), 2.32 (m, 7-H^b), 2.92 (1-H), 3.40 (6-H), 4.04 (s, 3H, OMe), 6.21 (s, 4-H).
- **16** ¹H NMR (CDCl₃, δ): 1.379 (s, 18H), 1.493 (s, 18H), 7.430 (d, J 2.3 Hz, 2H, 4- + 4'-H), 7.546 (d, J 2.3 Hz, 2H, 6- + 6'-H), 13.3 (s, 2H, 2 × OH).
- 17 ¹H NMR (CDCl₃, δ)⁷²: 1.33 (s, 18H), 7.024 (d, J 1.9 Hz, 2H, 3- + 3'-H), 7.067 (dd, J 1.9 and 8.4 Hz, 2H, 5- + 5'-H), 7.607 (d, J 8.4 Hz, 2H, 6- + 6'-H), 11.7 (s, 2H, 2 × OH). ¹³C NMR (APT, CDCl₃, δ)^{72.73}: 29.69 (Me₃C), 30.97 (Me₃C), 117.84 (3- + 3'-C), 127.39 (6- + 6'-C), 130.52 (5- + 5'-C), 131.19 (1- + 1'-C), 152.62 (4- + 4'-C), 157.38 (2- + 2'-C). IR (CHCl₃, cm⁻¹)^{72.74}: 3020, 2960, 2930, 2860, 1620, 1560, 1490, 1475, 1460, 1260, 1090, 940. MS (70 eV, m/z): 326 (M[±]), 100 (base), 177 (21.3, M[±] - Ar[•]), 149 (53.0, M[±] - Ar[•]); accurate mass: m/z 326.1990, calcd. for and C₂₀H₂₆N₂O₂: 326.1994.

As observed with 17, azodyes with hydroxy groups *ortho* to the azo group showed, in the IR spectrum, relatively strong azo bands, and only a poorly defined OH stretch vibration or none at all⁷⁴⁻⁷⁶. The mass spectrum of 17 shows the characteristic fragmentation pattern of symmetrical azodyes⁷⁷, the typical ratio of the intensities of the m/z peaks of 177 (Ar-N=N[:]) over 149 (Ar[:]) being 0.40.

19 Specific absorptions of the minor product 19 are apparent in the ¹H NMR spectrum (at 6.9 and 7.7 ppm), but definite assignments have not been made.

¹H NMR assignments of the o-benzoquinones and their mono-oxime methyl ethers

Upon mono-methyl oximation of a given *o*-benzoquinone, in principle, four different isomers may result, but in practice usually one or two isomers are obtained. The structural identification of the isomer formed is not always straightforward. Therefore, extensive ¹H- and ¹³C-NMR studies employing a wide range of advanced techniques were made for the characterization of the parent benzoquinones, for which the assignments are sometimes contradictory^{78,79}, and their mono-oxime *O*-methyl ethers. The ¹H- and ¹³C-NMR data of the *o*-benzoquinones and their mono-oxime ethers are collected in Tables III and IV.

Assignment of 3. The assignment of 4,6-di-tert-butyl-o-benzoquinone (3), established from the spectra obtained by applying the 2D-INADEQUATE⁷⁸, ¹³C-¹³C correlation and ¹³C-¹H correlation (optimized for ³ $J_{C,H}$ coupling⁷⁹) techniques confirmed the assignment given by Elfering and Bos⁸⁰.

Assignment of 2. The two carbonyl groups of 4-tert-butyl-o-benzoquinone (2) have the same ${}^{13}C$ chemical shift, viz. 180.2 ppm. The ${}^{13}C$ chemical shift of 3-C of 2 will be similar to that of the 6-C of 3 which is at 121.68 ppm (for the respective ring numbering, see Substrate sheet 1-12); thus the signal at 123.66 ppm is assigned to 3-C. Also, the chemical shift of the tert-butyl carrying 4-C of 2 is expected to be not very different from 5-C of 3. Hence, the signal at 162.10 ppm is assigned to 4-C. The two remaining signals at higher field at 129.28 and 140.02 ppm were assigned considering the substituent shift effects⁸¹ on to 5- and 6-C, respectively. The given assignment was confirmed by a ${}^{13}C{}^{-1}H$ correlation spectrum.

As for ¹H NMR, 3-H of **2** is expected to have a similar chemical shift as 6-H of **3**. The doublet at 6.28 ppm is, therefore, attributed to 3-H; the small coupling constant of 2.3 Hz is in agreement with this assignment. The assignments of the two remaining signals (a double doublet at 7.19 and a doublet at 6.39 ppm) were made using the NOE difference techniques⁸². Selective irradiation of the *tert*-butyl hydrogens leads to an enhancement of both the signals at 6.28 and 7.19 ppm. The latter signal is, therefore, assigned to 5-H and the remaining signal at 6.39 ppm to 6-H. This assignment accords with that of *Fischer* and *Henderson*⁶².

Assignment of (E)-7. Of the four possible isomers, only one is formed in the applied synthesis. The assignment of the ¹H NMR spectrum is made on the basis of NOE difference experiments. Upon selective irradiation of the high-field *tert*-butyl group at 1.20 ppm, two signals are observed at 6.81 and 6.98 ppm, whereas selective irradiation of the low field *tert*-butyl group leads only to

Table $IV = {}^{13}C NMR$ data (CDCl₃) of the o-benzoquinones and their mono-oxime O-methyl ether.

Compound	δ (ppm)								
	1-C	1-C 2-C	3-C	4-C	5-C	6-C	t-Bu		OMe
							C _{quart}	Me	
2	180.2	180.2	123.66	162.10	129.28	140.02	35.52	27.66	
3	180.71	179.75	149.53	133.20	162.94	121.68	35.10 (3-) 35.66 (5-)	28.88 27.55	
(<i>E</i>)- 5	183.58	147.8	111.85	148.6	129.20	139.83	34.74	28.35	64.41
(E)- 6	183.04	147.01	128.25	118.35	162.10	123.22	35.07	28.03	64.53
(E)- 7	183.04	148.66	110.34	149.54	133.67	148.12	34.96 (2-) 34.96 (4-)	29.11 28.49	64.05

a signal at 6.98 ppm. The signals at 6.81 and 6.98 ppm were, therefore, assigned to 5- and 3-H, respectively. The synthesized compound proved to have the E-configuration, since irradiation of the methoxy signals at 4.23 ppm led to an NOE on 5-H. The ¹H NMR chemical shifts of 3-H of (E)-7 and 4-H of 3 (6.81 versus 6.93 ppm) are about the same as expected on the basis of the C=O and C=NOMe substituent shifts, whereas those of 5-H of (E)-7 and 6-H of 3 (6.98 versus 6.21 ppm) are not.

As for ¹³C NMR, the carbon atoms 3-C, 5-C, OCH₃ and 2-CMe₃ were assigned on the basis of a $2D-J_{C,H}$ correlation spectrum⁷ ". in which only the geminal C-H correlations were visible. The remaining carbons were assigned via a ${}^{3}J_{C,H}$ correlation spectrum. Assignments of (E)-5 and (E)-6. Upon mono-methyloximation of the o-benzoquinone 2, the two isomeric (methoxyimino)cyclohexadienones (E)-5 and (E)-6 were formed in a ratio of 1:4.3. As for (E)-5, only its 3-H is expected to have a similar chemical shift as 5-H of (E)-7. In fact, a signal of the minor isomer was found at 6.83 ppm. Furthermore, knowing that both the 3-H of (E)-5 and the 6-H of (E)-6 will only couple with the 5-H and 4-H, respectively, while the latter two hydrogens couple in addition with the respective adjacent 6-H and 3-H, the 'H NMR assignments listed in Table III emerge.

The ¹³C APT spectrum of the mixture of the two mono-oxime O-methyl ethers confirms the assignments made by ¹H NMR. The 3-C of (E)-5 is expected to have the same chemical shift as 5-C of (E)-7 and the signal at 111.85 ppm is, therefore, attributed to 3-C. On the basis of the same argument, the 6-C signals of both (E)-5 and (E)-6 will have the same chemical shift as 3-C and 6-C of 2. The signals at 123.22 and 139.83 ppm were, therefore, attributed to 6-C of (E)-6 and 6-C of (E)-5, respectively. 4-C of (E)-5 will be found at about the same shift as 4-C of (E)-7, thus at 148.6 ppm. 5-C of (E)-6 corresponds to 4-C of 3 and is put at 162.10 ppm. 5-C of (E)-5 will be (due to the lower degree of substitution) at higher field than 3-C of (E)-7. The remaining signal of (E)-5, at 129.20 ppm is that for 5-C which is, in fact, shifted 4.5 ppm to higher field. This shift is very similar to the shift of 3.9 ppm between the corresponding carbons of the analogous o-benzoquinones, viz., 4-C of 3 and 5-C of 2 (see Table IV). Thus 5-C of (E)-5 is found at 129.90 ppm, i.e., 32.9 ppm upfield compared with the tert-butyl substituted 5-C of (E)-6. Accordingly, a large upfield shift is expected for 4-C of (E)-6 compared with 4-C of (E)-7. The signal of (E)-6 at 118.35 ppm, *i.e.*, 31.2 ppm upfield relative to 4-C of (E)-7, is accordingly attributed to 4-C. The signal at 128.25 ppm is attributed to 3-C of (E)-6 in view of its 18.1 ppm downfield shift relative to 5-C of (E)-7, the shift difference being very similar to that between the 6-C carbons of the corresponding o-benzoquinones 3 and 2.

Calculations

The semi-empirical calculations were performed on a DEC VAX-11/785 computer of the CAOS/CAMM calculating facility at the Catholic University Nijmegen, using MOPAC, a general molecular orbital package^{19,83}.

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