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THE NOVEL PHOTOCHEMICAL BEHAVIOR OF TRIPTYCENE-1,4-QUINONE

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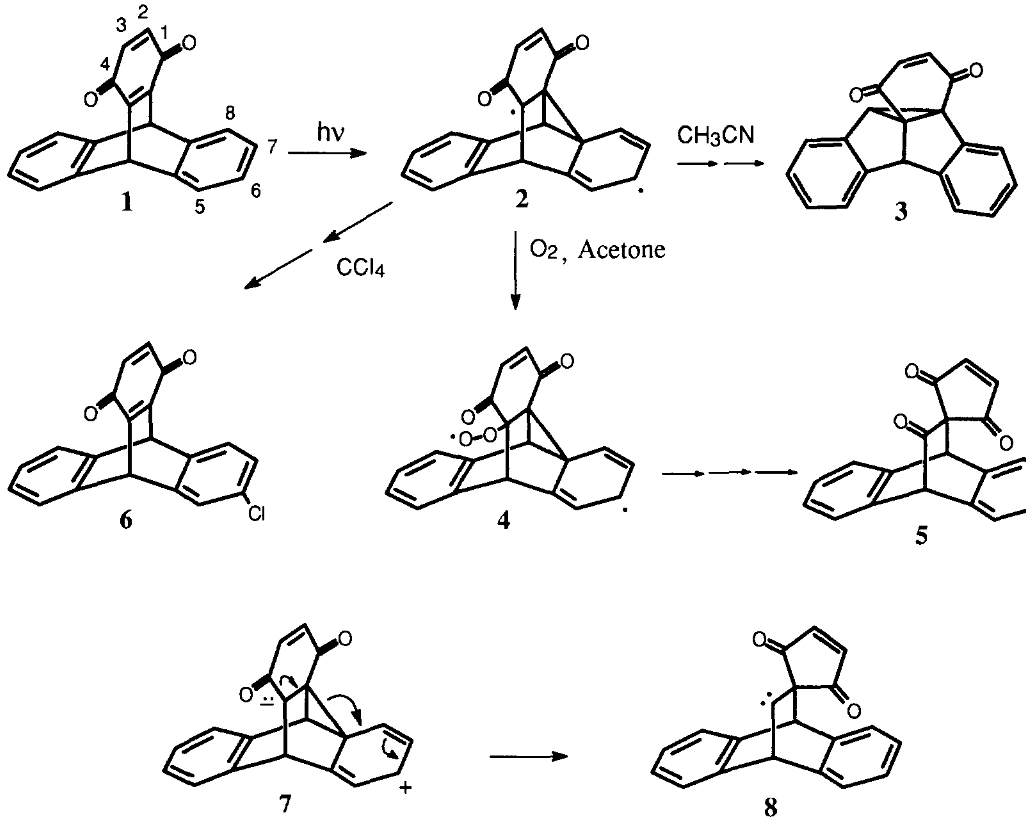
Abstract. Triptycene-1,4-quinone (**1**) reacts photochemically in solution to give different products depending on the solvent employed and on the presence or absence of oxygen. The structures of the photoproducts have been elucidated by spectroscopic methods, independent synthesis and single crystal X-ray diffractometry, and possible mechanistic pathways leading to their formation are presented and discussed. Unexpectedly, quinone **1** was found to be photochemically inert in the crystalline state. The X-ray crystal structure of **1** reveals the probable reason for this behavior.

The intriguing quinone, triptycene-1,4-quinone (**1**), has received a great deal of attention from the point of view of its photophysical properties. Iwamura and Makino[1] as well as Murata et al.[2] and Kitaguchi[3] have shown that this compound, along with several of its derivatives, possesses a charge-transfer excited state as the result of intramolecular electron transfer from one of the aromatic rings to the quinone ring. Triptycene quinone is a potential di-π-methane reactant,[4] and we wondered what effect, if any, the intervention of a dipolar CT excited state would have on its photochemistry. Previous work by Kitaguchi had shown that triptycene quinone undergoes photoreduction ($\Phi = 0.35$) in the presence of xanthene as a hydrogen atom donor,[5] but this report made no mention of any unimolecular photoreactivity of **1**. In the present communication, we report that triptycene quinone does indeed photorearrange in novel and unexpected ways in non hydrogen atom-donating solvents.

Results. Triptycene quinone was prepared according to the procedure of Bartlett[6] and photolyzed under a variety of conditions. Although inert in the crystalline state, irradiation of quinone **1** through Pyrex in carefully deoxygenated acetone, ethanol or acetonitrile led to a single photoproduct isolated as yellow needles, mp 167-169 °C, and assigned the di-π-methane structure **3** (Scheme) on the basis of its spectroscopic properties.[7] Preparative runs in acetonitrile gave isolated yields of photoproduct **3** of approximately 80%. When air was admitted to the acetone photolysis solution, either intentionally or inadvertently, a different photoproduct could be detected by GC. After much experimentation, it was found that the yield of this compound could be maximized at approximately 20% in air-saturated acetone. It was assigned the novel structure **5** on the basis of its spectra and, ultimately, on a single crystal X-ray diffraction study.[8]

Photolysis (350 nm, Rayonet photoreactor) of quinone **1** in deoxygenated carbon tetrachloride led to yet another photoproduct, 6-chlorotriptycene-1,4-quinone (**6**). After 8 hours, GC indicated about 50% conversion; HCl could be detected as a byproduct of the reaction, and no di-π-methane photoproduct **3** was present in the reaction mixture. A control experiment showed that benzene was not chlorinated under the same conditions, indicating that chlorine atoms generated by photolysis of carbon tetrachloride were not responsible for the chlorination of **1**. Photoproduct **6** could be isolated by silica gel column chromatography, and its structure was proved by synthesizing it independently from benzoquinone and 2-chloroanthracene in the same way that triptycene quinone itself was prepared. We also synthesized 5-chlorotriptycene quinone from benzoquinone and 1-chloroanthracene, and this compound was shown to be absent from the photoproduct mixture by GC.



Discussion. An appealing common precursor to all three photoproducts observed in the present study is the cyclopropyldicarbinyl diradical **2**. Similar species have recently been shown by Zimmerman et al. to be true intermediates in the di-π-methane rearrangement of 9,10-ethenoanthracene derivatives.[9] The formation of diradical **2** in this instance is in accord with preferential benzo-quinone bridging (as opposed to benzo-benzo bridging) to give the more stable diradical in which aromaticity has been lost in only one of the two benzenoid rings and the second odd electron is stabilized by being next to a carbonyl group. Continuation of intermediate **2** along the normal di-π-methane mechanistic pathway[4] then leads to photoproduct **3**. As shown in the scheme, formation of the unusual products **5** and **6** can reasonably be attributed to trapping of biradical **2** by oxygen and carbon tetrachloride, respectively; steric factors may cause the reaction of intermediate **2** with carbon tetrachloride to take place at the β rather than the α-position of the benzenoid ring. An attractive alternative mechanism for the formation of triketone **5**, suggested by a referee, involves ring contraction of zwitterion **7** (or its biradical counterpart **2**) to form carbene **8**, which then reacts with oxygen. We tend to favor the mechanism involving oxygen adduct **4**, however, since attempts to trap carbene **8** in alcoholic solvents were unsuccessful. In overall mechanistic terms, there appears to be no need to invoke a CT excited state in these reactions, although its participation cannot be ruled out.

A final point of discussion concerns the lack of photoreactivity of quinone **1** in the crystalline state. Previous studies from our laboratory have documented the interesting photochemical reactivity of a wide range of 9,10-ethenoanthracene derivatives in the solid state,[10] and quinone **1** was expected to behave similarly. Indeed, our primary goal in preparing this material was to be able to investigate its solid state photochemistry. In order to provide insight into the unexpected lack of reactivity of quinone **1** in the solid state, its X-ray crystal and molecular structure was determined.[11] This showed that the quinone and aromatic rings of adjacent molecules in the crystal are interlocked in such a way that benzo-vinyl bridging is sterically impeded. A packing diagram that illustrates this point is given in Figure 1. To a first approximation, the process of benzo-quinone bridging narrows the cleft between the two rings involved from 120° in the starting material to ca. 60° in the initial biradical intermediate (assuming full cyclopropyldicarbinyl biradical formation). These motions are clearly resisted by the presence in the clefts of aromatic rings from adjacent molecules; in effect, the clefts are "filled" and cannot close.[12]

A future publication will deal with the even more unusual photochemical behavior of some 9,10-disubstituted triptycene quinone derivatives.

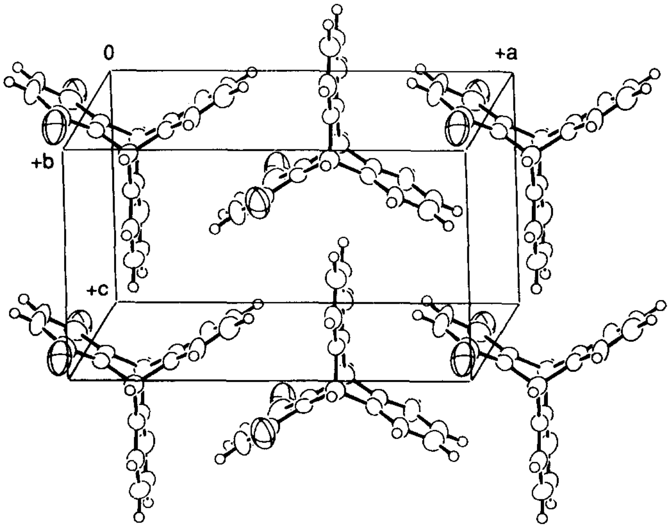


Figure 1. Packing diagram for quinone **1** showing interlocking quinone and aromatic rings.

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References and Footnotes

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7. Photoproduct **3**: mp 167-169 °C. IR (KBr): 1677 (C=O) and 1596 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$): 8.05-7.97 (m, 1H), 7.35-7.03 (m, 7H), 6.63 (s, 2H, vinyls), 5.13 (s, 1H, bis-benzylic methine), 4.37 (s, 1H, cyclopropyl methine). ^{13}C NMR ($CDCl_3$): 192.0, 191.1, 150.3, 149.0, 138.5, 138.1, 133.4, 131.4, 128.7, 128.2, 127.1, 127.1, 126.1, 125.5, 121.8, 121.6, 77.3, 58.9, 58.5 and 51.4. EI MS: 284 (100, M^+), 202 (12). HRMS calcd for $C_{20}H_{12}O_2$ 284.0837, found 284.0838. UV (CH_3CN): 378 ($\varepsilon = 791$) and 277 ($\varepsilon = 3366$) nm. Anal. Calcd for $C_{20}H_{12}O_2$: C, 84.48; H, 4.26. Found: C, 84.26; H, 4.30.
8. Photoproduct **5**: mp 171-174°; space group $Pna2_1$; a = 12.274(3) Å, b = 7.957(3) Å, c = 15.444 Å; Z = 4; R = 3.7%. Full crystallographic details will be published separately.
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11. Quinone **1**: space group Pnma; a = 13.979(2) Å, b = 12.608(7) Å, c = 8.024(2) Å; Z = 4; R = 5.9%. Full crystallographic details will be published separately.
12. A similar argument has been used by us to explain the failure of a ketone to undergo an expected hydrogen atom abstraction reaction in the solid state. See Ariel, S.; Askari, S.; Scheffer, J.R.; Trotter, J. *Tetrahedron Lett.* **1986**, *27*, 783.

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