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THE CHEMISTRY OF FULVALENEQUINONE SYSTEM. III.[1)]

SYNTHESIS AND PROPERTIES OF A HEPTATRIAFULVALENE-1,2-QUINONE DERIVATIVE.

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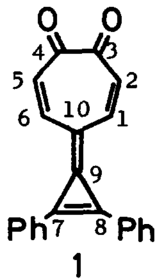
The chemistry of non-benzenoid quinones has recently been developed.[2)] In the field of seven-membered ring systems, diazoketone type quinones[3)] and very recently p- and o-tropoquinone[4,5)] have been synthesized. However little is known concerning with other tropoquinonoid compounds, especially tropoquinone methide type compounds. In the course of our studies on the fulvalenequinone systems, we are much interested in a new quinone 2 which is anticipated to have a more strained conformation compared with our previously reported p-isomer 1.[1)] We now wish to describe the synthesis and some of the ground state properties of 3,5-dibromo-7,8-diphenylheptatriafulvalene-1,2-quinone 3, as the first example of the o-tropoquinone cyclopropenide.



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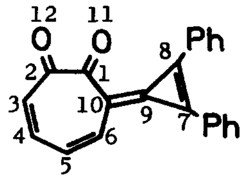

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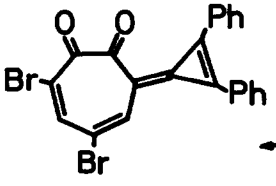
3,5-Dibromotropolone was smoothly cyclopropenylated by treatment with an equimolar mixture of 1,2-diphenyl-3-ethoxycyclopropenium ion[6)] and triethylamine in acetonitrile at room temperature for 20 min. to give 3 as reddish violet needles (mp. 152-3°C ; 30% yield ; m/e(%) 468(4) M , 440(5)M-CO, 388(8)M-Br, 360(3)M-COBr, 280(97)$M-COBr_2$, 252(100)$M-C_2O_2Br_2$). Contrary to stable quinone 1 and its dibromo derivative 4,[7)] compound 3 proved to be rather unstable ; 3 degenerated gradually in solid state upon standing above room temperature, and collapsed completely within 10-60 min. in chloroform, dichloromethane, or acetonitrile solution depending upon the concentration (3 was stable in a dilute solution). In the infra-red spectrum of 3 (ν max (KBr) 1822m, 1620s, 1608s, 1594s, 1578s, 1495m, 1483m, 1410vs, 1376vs, 1295vs, 1172m cm^{-1}) the



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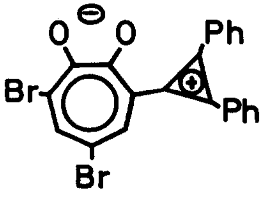

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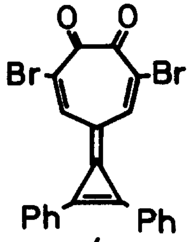

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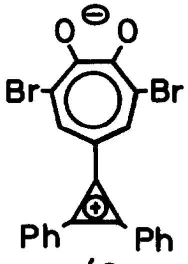


4a

C=O and C=C stretching bands appeared at regions similar to those of 4 (ν max (KBr) 1829m, 1625s, 1612s, 1595s, 1585s, 1572s, 1431vs, 1352vs, 1172m cm^{-1}), which is considered to be contributed by dipolar structure 4a in the ground state. However in the nmr spectrum of 3 (Table 1), the chemical shifts of the phenyl protons ortho to the three-membered ring appeared at relatively higher field than those of the corresponding protons of 4 suggesting that the contribution of the dipolar structure 3a would not be so significant in 3 as in 4 (and 3 would be almost comparable to diphenylcyclopropenone 5[6]) (Table 1). The electronic spectrum of 3 (λ max (MeCN) 260 nm (log ε 4.41), 293(4.33), 335sh(3.86), 365(3.74), 395sh(3.64), 502sh(4.04), 532(4.14)) is shown in Fig. 1, where the longest wavelength absorption maximum is shifted bathochromically by 80 nm with less intensity, compared with that of 4. The observed absorption maxima for 3 in acetonitrile are in adequate agreement with the calculated transition energies obtained by the appli-

Fig. 1 : Electronic Spectra of the Fulvalenequinones 3 and 4.

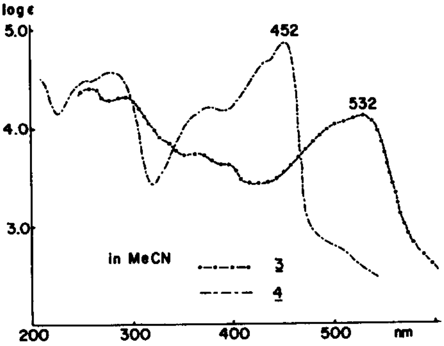


Table 1 : NMR Spectral Data of Heptatriafulvalenequinones and their Conjugated Acids. δ ppm*

Compd.	Solvent	7-mem. ring		Ph at 3-mem. ring	
		H-4	H-6	o-H	m,p-H
3	$CDCl_3$	8.36 J=2.0 Hz	7.92	8.03	7.68
4	$CDCl_3$	8.52		8.16	7.82
6	CF_3CO_2H	8.95	8.80	8.53	7.97
8	CF_3CO_2H	9.32		8.52	8.05
7	$c.H_2SO_4$	9.64	9.48	8.57	8.08
9	$c.H_2SO_4$	9.67		8.48	8.00
5	$CDCl_3$	——		7.98	7.59

* CH_2Cl_2 was used as the internal standard, 5.30 ppm.

Table 2
Calculated Electronic Structure and Spectrum of Heptatriafulvalenequinone 2.[10]

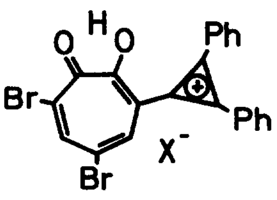
Bond	Bond length(Å)*	Atom	Charge density*	Transition energy ΔE(ev)	f(cgs)	(Observed)** ΔE(ev)
1-2	1.468	1	0.692			
2-3	1.446	2	0.736	2.58	0.763	2.33 2.47
3-4	1.365	3	1.021			
4-5	1.440	4	0.932	3.40	0.186	3.14
5-6	1.366	5	1.046	3.69	0.162	3.39
6-10	1.441	6	0.962			
10-1	1.470	10	1.125	4.46	0.248	4.23
10-9	1.366	9	0.892	4.64	0.232	4.77
9-8	1.405	8	0.901			
8-7	1.337	7	0.924			
7-9	1.437	11	1.405			
		12	1.411			

* The data of phenyl groups at C-7, C-8 are not listed due to limited space.

** The spectrum of 3 in MeCN.

cation of the semiempirical variable bondlength SCF·LCAO-π-MO·CI method[8] to planar model of 2[9] as listed in Table 2. This fact suggests that 3 would have a nearly coplanar structure whose sterically strained high-energy state is stabilized by strong conjugation effect between the three- and seven-membered rings. The solvent polarity influences to a lesser extent on the shift of the longest wavelength transition of 3 : 532 nm (in MeCN), 535(in acetone), 540(in CH_2Cl_2), 533(in benzene), 530(in dioxane).

Quinone 3 was not protonated in acetic acid but reversibly protonated in trifluoroacetic acid or in a 1:3 mixture of acetic acid and 70% perchloric acid with formation of the conjugated acid 6 (X=ClO_4 : yellow needles ; mp. 162-3°C ; λ max ($MeCN-HClO_4$) 294 nm (log ε 4.63), 310(4.60), 442(3.91), 480sh(3.70) ; ν max (KBr) 1620s, 1595s, 1500m, 1412br.vs, 1350m, 1163s, 1090br.s cm^{-1}). One more protonation of 6 proceeded smoothly in conc. sulfuric acid to give a dication 7[11] (λ



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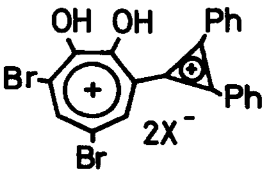

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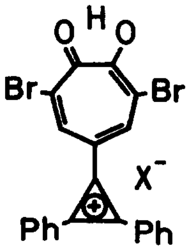

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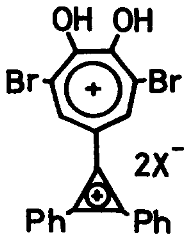

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max (conc. H_2SO_4) 305 nm (log ε 4.56), 424(3.93)). The nmr signals of 6 and 7 are shown in Table 1 together with those of the cations 8 and 9 obtained by the protonation of p-isomer 4 in a similar manner. Although the chemical shifts of phenyl protons of 6 are in nearly the same low field as those of 8, the chemical shifts of the seven-membered ring protons of 6 appear at higher field by 0.52 ppm than that of 8. This is mainly because the positive charge of the three-membered ring is difficultly distributed into the seven-membered ring in potentially non-planar 6 compared with coplanar 8. On the other hand, comparing 7 with 9, the chemical shift differences of their seven-membered ring protons as well as those of their phenyl protons are almost negligible. In this case, it is suggested that neither 7 nor 9 is possible to exist in planar form not only due to the steric crowdness but also due to the electronic repulsion[12] between the positively charged three- and seven-membered rings.

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9) The calculated electronic spectral data of heptatriafulvalene-3,4-quinone are reported in ref. 1).

10) The SCF orbitals were calculated using an entirely automatic program ; One center repulsion integral : I-A approximation where Ic=11.16 ev, Ac=0.03 ev, Io=17.70 ev, and Ao=2.47 ev. Two-center repulsion integral : Mataga-Nishimoto method. Resonance integral : Wolfsberg-Helmholtz's overlap approximation, where eff. nucl. charge Zc=3.25, Zo=4.55, const. Kc-c=0.87 and Kc-o=0.77.

11) The quinone 1 also gave the dication in conc. sulfuric acid, see ref. 1).

12) In ditropylium dication, the dihedral angle between the two rings has been estimated from M.O. calculation in consideration of spectral data to be around 70-78° : I. S. Akhrem, E. I. Fedin, B. A. Kvasov, and M. E. Vol'pin, Tetrahedron Lett., 5265 (1967) ; H. Volz and M. V. Lecea, Liebigs Ann. Chem., 750, 136 (1971).