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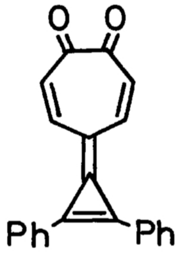
SYNTHESIS OF 5-(1,3-DITHIOL-2-YLIDENE)-3,6-CYCLOHEPTADIENE-1,2-DIONE (OR 7,10-DITHIASESQUIFULVALENE-3,4-QUINONE) DERIVATIVES1)

Kazuko TAKAHASHI, Kazuyoshi MORITA, and Kahei TAKASE
Department of Chemistry, Faculty of Science, Tohoku University
Sendai 980

8-Phenyl-7,10-dithiasesquifulvalene-3,4-quinone (7a) and its halogen derivatives (7b and 7c) are synthesized. Although their IR and NMR data suggest a contribution of dipolar structure (7") to the ground state, the solvent effect on the 1st bands in their ES showed a larger contribution of 7" to the excited state rather than the ground state.

Fulvalenes having so-called "excess electrons", such as heptatriafulvalene and heptafulvalene, are known2) or predicted3) to be non-aromatic since they can not make each ring fit to Hückel rule in their polarized structures. This kind of fulvalenes, however, would be expected to be stabilized by the introduction of electron-attracting groups since the effective number of electrons would be reduced to the more favorable π-electron arrangement in each ring. In order to clarify this argument, we have planned the study on this kind of fulvalene derivatives and have recently reported the preparation of heptatriafulvalene quinone (1)4) as the first example of a stable heptatriafulvalene derivative. In the present paper, we now wish to report the synthesis and some properties of 7,10-dithiasesquifulvalene-3,4-quinone system (2), which is iso-π-electronic with heptafulvalene-3,4-quinone.5)



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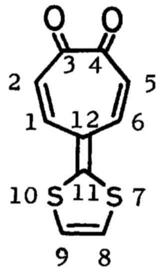
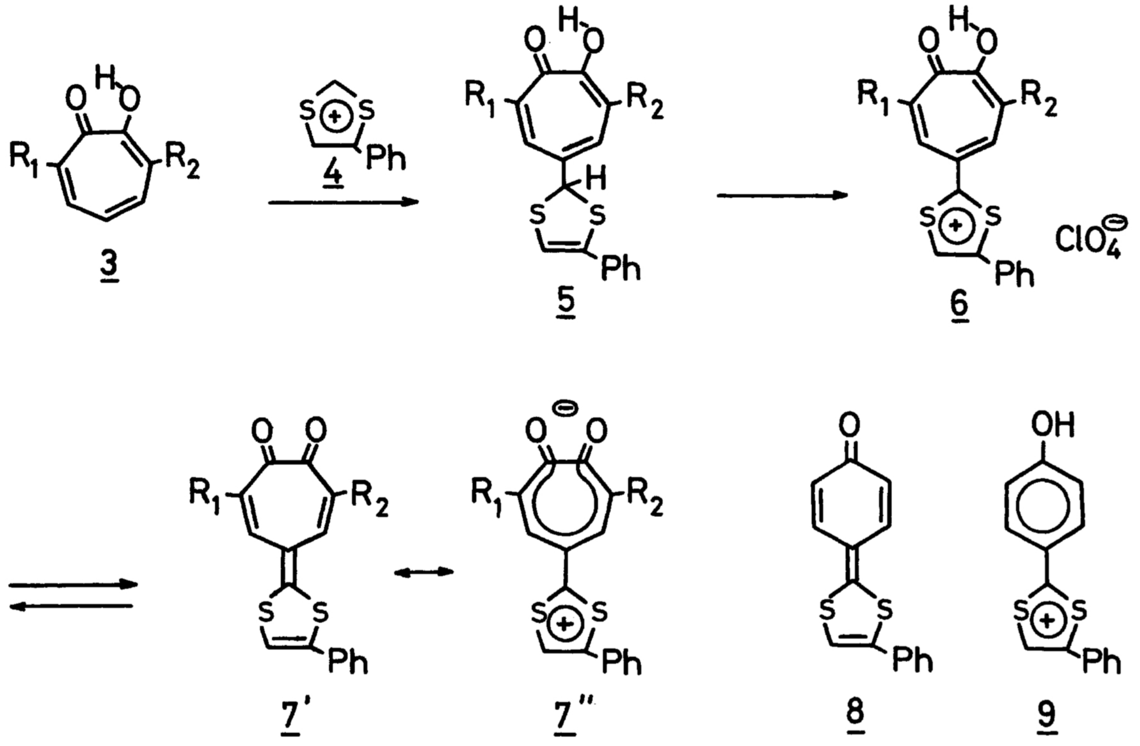


2

On reaction with 1 molar amount of phenyldithiolium perchlorate (4)6) in the presence of 2 molar amounts of triethylamine in acetonitrile, tropolone (3a) gave a dithiolyltropolone derivative (5a, 11%), and halotropolone (3b) or (3c) gave a mixture of 5b (34%) and a dithiasesquifulvalenequinone derivative (7b, 5%) or a mixture of 5c (28%) and 7c (8%), which were separated by silica-gel chromatography. In this reaction, the quinone (7b or 7c) would be formed via an intermediate formation of 6 by hydride abstraction from 5 with excess dithiolium ion and subsequent proton removal from 6 with triethylamine. The quinones (7a, 7b, and 7c) were also stepwise prepared from 5a, 5b, and 5c7) by hydride abstraction with trityl salt leading to the dithiolyliotropolone salts (6a : yellow brown needles, mp 234-236°C (decomp.), 68% ; 6b : brown needles, mp 165-168°C (decomp.), 61% ; and 6c : brown needles, mp 264-265°C (decomp.), 74%) and subsequent proton abstraction from 6 to 7



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a : $R_1 = R_2 = H$.   b : $R_1 = H, R_2 = I$ or $R_1 = I, R_2 = H$.   c : $R_1 = R_2 = Br$.

by using triethylamine in acetonitrile (7a : blue black needles, mp 158-161°C, 97% ; 7b[8]: blue black needles, mp 198-200°C, 75% ; 7c : blue black needles, mp 250-253 °C (decomp.), 90%).

The compounds (7a, 7b, and 7c) are quite stable on exposure to light and air at room temperature in solid state and in commonly used hydrous[9] or anhydrous organic solvents.

As can be seen from Table 1, the IR absorption band of the carbonyl group of 7a appeared at much lower-frequency region, while those of 7b and 7c absorbed at higher-frequency regions due to the halogen substituents. In the NMR spectra (Table 1) the chemical shifts of the 5-membered ring proton (H-9) of 7a, 7b, and 7c appeared at 8.40-8.42 ppm, which are upfield only by 0.4 ppm as compared with those of their conjugated acids (6a, 6b, and 6c). When a similar comparison was made for the compounds (8) and (9),[10] the corresponding 5-membered ring proton (H-5) was found at a higher field by about 1.5 ppm in 8 than in 9. These facts suggest the contribution of a dipolar structure (7") to the ground state of 7. However, the longest wavelength absorption maxima in electronic spectra of 7a, 7b, and 7c showed a blue shift on going from polar to less polar solvents as is shown in Table 2,

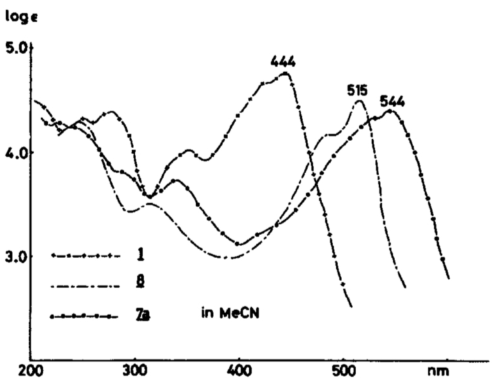
Table 1
Spectral Data of the Dithiasesquifulvalenequinones and their Conjugated Acids

Compd.	ES nm (log ε) in CH_2Cl_2	IR KBr cm^{-1}	^{1}H-NMR 100 MHz δ, ppm*		
			H-2,5	H-1,6	H-9
7a	548(4.40), 534sh(4.45), 338(3.74), 290sh(3.85), 230(4.30)	1550 s 1530 vs 1295 vs	6.54 J=11.7	7.09 7.17	8.42
7b	559(4.74), 522sh(4.42), 390(3.66), 355(3.79), 232(4.35)	1585 vs 1300 vs	6.38 J=12.0 Hz	7.46 8.21	8.42
7c	568(4.85), 532(4.44), 408(3.77), 345(3.75) 242(4.34)	1610 s 1565 vs	——	8.20	8.40
6a	498(4.29), 285sh(4.18), 250(4.30)	1605 1480 1420	8.13 J=10.0 Hz	9.02	8.84
6b	460(4.27), 249(4.39)	1600 1477	7.76 J=10.0 Hz	8.30 9.23	8.84
6c	445(4.10), 264(4.20), 242(4.21)	1602 1475		8.91	8.83

* 7a, 7b, and 7c were measured in DMSO-d_6 and 6a, 6b, and 6c were measured in CF_3CO_2H

indicating that 7 is more polar in the excited state than in the ground state. The NMR chemical shifts of the 7-membered ring protons of 7 do not differ significantly from those of ordinary tropones or tropolones,[11] but higher electron densities at C-2 and C-5 are suggested by the relatively high field chemical shifts of H-2 and H-5. The $J_{1,2}$ value of 7a would be reasonable for the compound of the resonance structure 7'↔7", since the corresponding vicinal coupling constants of the tropolones carring an unsaturated substituent at the 5-position are in the range of 11-12 Hz. The electronic spectrum of 7a is shown in Fig. 1 together with those of 1 and 8. The longest wavelength absorption maximum of 7a is shifted bathochromically by 100 nm from that of 1, and by 29 nm from that of 8, but these three spectra are quite similar in band shape.

Figure 1. Electronic spectra of Quinones (1), (8), and (7a).



Reversible protonations of 7a, 7b, and 7c with trifluoroacetic acid gave 6a, 6b, and 6c. The observed pKa value for 6a, 0.55±0.05 in 50 % aqueous acetonitrile, is about 5.0 smaller than that of 9 (pKa=5.4±0.05).[12] This value for 6a, is too small, even if the pKa difference between tropolone (6.92) and phenol (10.0) is taken into account.[13] This would be due to the fact that the dithiolium group conjugates more effectively with tropolone ring than with phenol group.

Table 2 : Effect of the Solvent Polarity on the Longest Wavelength Transition of Dithiasesquifulvalenequinones (7a, 7b, and 7c) nm

Compd.	DMSO	MeCN	Acetone	CH_2Cl_2	Benzene	Dioxane
7a	553	544	540	548	530	526
7b	566	557	554	559	548	543
7c	571	563	562	568	559	554

References and Notes

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6) A. Takamizawa and K. Hirai, Chem. Pharm. Bull., Tokyo, 17, 1924 (1969).
7) 5a, 5b, and 5c were sensitive to air and so they were provided for the next reactions without further purification.
8) The compound (7b) is R_1=H and R_2=I, R_1=I and R_2=H, or a mixture of the two. It was impossible to know which is correct.
9) Heptatriafulvalenequinone (1) and its halogen derivatives are extremely sensitive to hydrous solvents, see ref. 4).
10) K. Hirai, Tetrahedron, 27, 4003 (1971).
11) D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, J. Amer. Chem. Soc., 91, 5286 (1969).
12) pKa value of 9 was determined by us in the same manner as with 6a in 50% aqueous acetonitrile with Hitachi No. 323 spectrophotometer.
13) A similar example is given by comparison of pKa difference (4.28) between tropolone and 5-nitrotropolone with that (2.86) between phenol and p-nitrophenol.

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