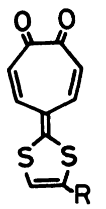
CHEMISTRY LETTERS, pp. 805-808, 1981.

SYNTHESIS AND PROPERTIES OF 7-(1,3-DITHIOL-2-YLIDENE)-3,5-CYCLOHEPTADIENE-1,2-DIONE (OR 7,10-DITHIASESQUIFULVALENE-1,2-QUINONE) DERIVATIVES[1)]

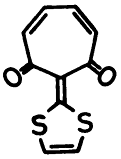
Kazuko TAKAHASHI,* Kahei TAKASE, and Yoshihiko NODA
Department of Chemistry, Faculty of Science, Tohoku University
Sendai 980

Three stable 4-tert-butyl, 5-bromo, and 3,5-dibromo derivatives of 7,10-dithiasesquifulvalene-1,2-quinone (or o-tropoquinone dithiolide) were synthesized and their physical and chemical properties were discussed on the basis of their spectroscopic data and the frontier electron density distribution, a stabilizing (reactivity-lowering) effect of the sulfur atoms on these compounds being well displayed in the density distribution.

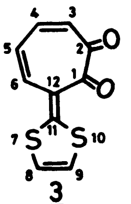
In the course of our study on the fulvalenequinone systems, we recently reported the syntheses and some of the ground state properties of heptatriafulvalene-3,4-quinones[2)] and heptatriafulvalene-1,2-quinones[3)] as the novel quinonoid derivatives of heptatriafulvalene. The heptatriafulvalenequinones, unlike to unstable heptatriafulvalene,[4)] are stable enough to be isolated as orange or red needles, presumably because the electron-attracting carbonyl groups reduce the effective number of electrons to the more favorable Hückel-type arrangement in each ring. Contrary to expectation from this fact, heptafulvalenequinones are too unstable to be isolated and any physical data except electronic spectra useful for the investigation of the ground state properties has never been obtained so far,[5)] whereas heptafulvalene itself has been isolated and confirmed to have a polyolefinic character.[6)] Dithiasesquifulvalenequinones are interesting in one regard because they are iso-π-electronic with unexpectedly unstable heptafulvalenequinones and in another regard because they are dithio-derivatives of novel tropoquinone methide. We have now synthesized the three derivatives of 7,10-dithiasesquifulvalene-1,2-quinone 3 and compared their properties with our previously reported 3,4-quinone isomer 1[7)] and with other's 1,6-quinone isomer 2,[8)] which are reported herein.



1 : R = Ph
1' : R = H

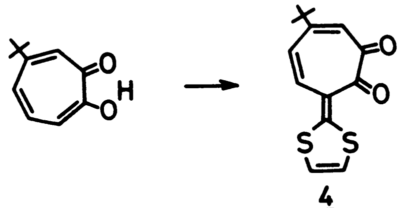


2

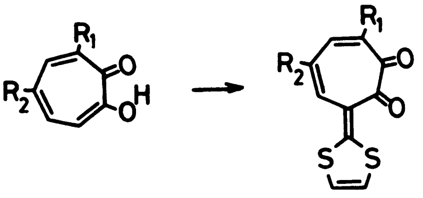


3

4-tert-Butyltropolone[9,10)] reacted with 2-methylthio-1,3-dithiolium iodide[11)] in refluxing acetonitrile (4 h) in the presence of 2 molar equivalents of pyridine to give 4-tert-butyl-7,10-dithiasesquifulvalene-1,2-quinone 4 [deep red needles, mp. 238-240 °C, 9%, m/e (%) 278 (37), 250 (100), 22 (38); λmax (MeCN) 223 nm (log ε 3.04), 250 (3.83), 304



4

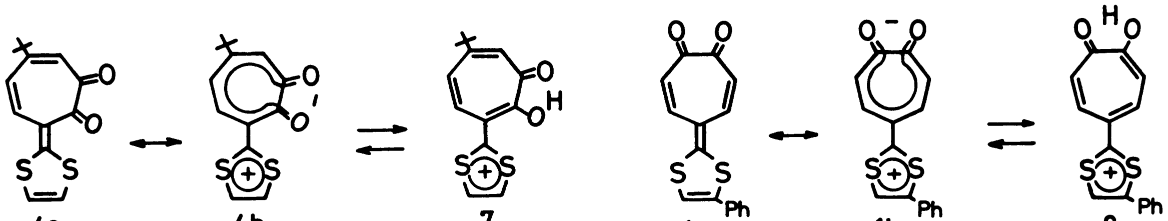


5 : R_1 = H, R_2 = Br

6 : R_1 = R_2 = Br

(3.79), 510 (4.22)]. In similar reaction conditions but more easily, 5-bromotropolone[12] and 3,5-dibromotropolone[13] reacted with the dithiolium iodide to give 5 and 6, respectively [5: deep violet needles, mp. 261-262 °C, 16%, m/e (%) 300 (22), 272 (100), 244 (100); λmax (MeCN) 255 nm (log ε 4.03), 317 (4.03), 362, sh (3.43), 535 (4.27)] [6: deep violet needles, mp.> 300 °C, 22%, m/e (%) 380 (50), 352 (100), 324 (40); λmax (MeCN) 255 nm (log ε 4.02), 320 (3.96), 370, sh (3.38), 555 (4.20)].[14]

These quinones (4, 5, and 6) as well as 1 and 2 are stable on exposure to air and/or sunlight in solid state and are quite stable in hydrous or anhydrous solvents, while heptatriafulvalene-1,2-quinone derivatives are unstable in solution.[3] The electronic spectral solvent effect on the longest wavelength absorption maxima of 4, 5, and 6 showed a red shift on going from less polar to polar solvents (Table 1, Fig. 1) indicating a larger contribution of the quinonoid structure (4a-type) rather than the dipolar structure (4b-type) to the ground state. The ^{1}H NMR spectral H-8,9 chemical shifts of 4 appeared at lower field by 1.5 ppm than those of H-4,5 of 2-(6-tert-butyltropolon-3-yl)-1,3-dithiol[15] but appeared at higher field by 0.81 ppm than that of 1[16] (Table 2). These facts, together with the IR spectral carbonyl band of 4 which appeared at higher frequency by 30 cm^{-1} than that of 1 and with the larger vicinal proton coupling constant J5,6 of 4 compared with J1,2 of 1 in ^{1}H NMR, suggest that the compound 4 is more olefinic than 1, even though the dipolar structure contributes to the ground state to a considerable extent. In these three derivatives of 3, the carbonyl bands in IR are found at lower frequency and the H-8,9 chemical shifts in



4a 4b 7 1a 1b 8

Table 1 : Effect of the Solvent Polarity on the Longest Wavelength Transitions of 4, 5, 6, and 1 (λ, nm)

Compd.	DMSO	MeCN	Me_2CO	CH_2Cl_2	Benzene	Dioxane
4	525	510	506	505	503	503
5	545	535	530	534	528	524
6	562	554	538 565	555	549	543
1	553	544	540	548	530	526

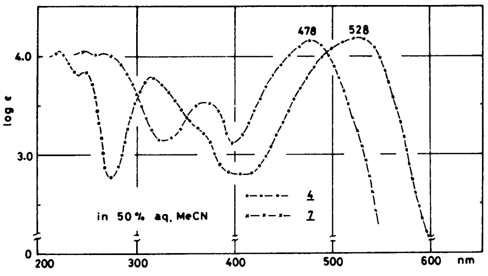
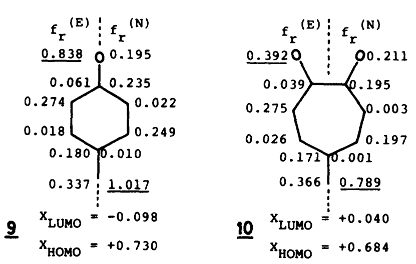


Fig.1 Electronic Spectra of 4 & 7

Table 2 : IR (KBr, cm^{-1}) and ^1H NMR (δ : ppm, J : Hz) Data of 4, 5, 6, 1, and 2

Compound	4	5	6	1	2
IR	1630 s 1498 s 1487 vs	1610 s 1588 s 1549 vs	1604 s 1576 s 1542 vs	1600 w 1550 s	1505
^1H NMR 7-membd. ring	6.75 H-3 d 6.46 H-5 dd 7.18 H-6 d J3,5=1.8 J5,6=12.5	6.43 H-3 d 7.32 H-4 dd 7.77 H-6 d J4,6=1.7 J3,4=12.6	—— 8.12 H-4 d 7.84 H-6 d J4,6=1.7	6.54 H-2,5 d 7.09 } H-1,6 d 7.17 } J1,2=11.7	6.7~7.0 m
H-8,9	7.61	8.26	8.35	8.42	8.12
Solvent	$CDCl_3$	DMSO-d_6	DMSO-d_6	DMSO-d_6	DMSO-d_6

^1H NMR are found at lower field in the order of $4<5<6$, indicating that the bromo substituent at the seven-membered ring affects to increase the contribution of the corresponding dipolar structure. In acidic conditions, both 4 and 1 were protonated quantitatively and reversibly to give conjugate acids 7 and 8, respectively. The observed pKa value of 7 (1.26±0.03) is larger than that of 8 (0.55±0.05) in 50% aqueous acetonitrile[17] proving that the tropolone moiety conjugates more effectively with the dithiolium ion moiety in p-tropoquinone methide type 1 rather than in o-tropoquinone methide type 4. The H-8,9 chemical shifts of 4 appeared at higher field by 0.51 ppm than that of 2, and a mutual comparison of the H-8,9 chemical shifts in ^1H NMR spectrum suggests that the contribution of the dipolar structure to the ground state would increase in the order of $4<2\leqq 1$.[18] In order to evaluate the chemical properties of 1, 2, and 4, the frontier electron density distribution of three o- and p-tropoquinone dithiolides, including p-benzoquinone methide 9 and p-tropoquinone methide 10, has been calculated by LCAO·MO method (Fig. 2).[19] The deviation of the $f_r^{(E)}$ at the oxygen atom from the values of other carbons in 10 is relatively small as compared with that in 9, but the LUMO of 10 lies at a very low level and the $f_r^{(N)}$ at the exo-carbon atom of 10 is still very large, indicating that 10 should show very high electrophilicity at the exo-carbon atom. The $f_r^{(N)}$'s in the dithiolides 1', 2, and 3, on the other hand, are relatively small at the exo-carbon atom and relatively large at the sulfur atoms instead, indicating stabilizing effect of the sulfur atoms on these compounds, and agreeing well with the actual low reactivity of 1, 2, and 4 towards nucleophiles (stable in hydrous solvents and in weak



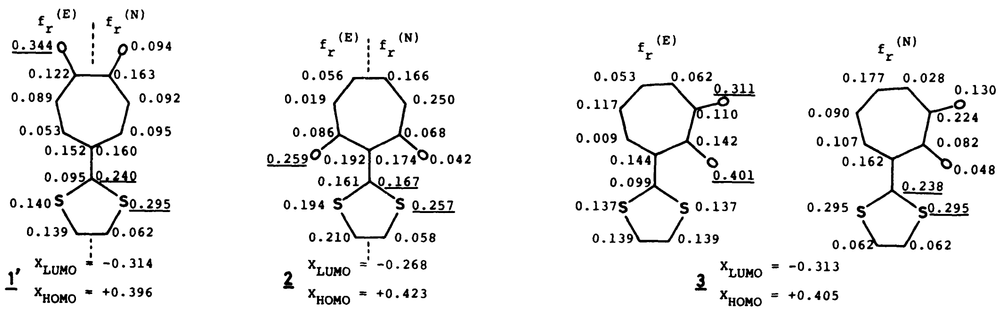
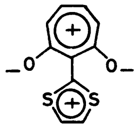


Fig. 2. Frontier electron densities ($f_r^{(E)}$: for electrophilic attack, $f_r^{(N)}$: for nucleophilic attack) and eigen values ($E_i = \alpha + X_i\beta$) of the HOMO (X_{HOMO}) and the LUMO (X_{LUMO}) in tropoquinone methides

bases). The values of $f_r^{(E)}$, as well as the π-electron densities, at the oxygen atoms of 1' and 3 also gave reasonable correlations with the pKa values of 8 and 7 respectively.

References and Notes

1) The Chemistry of Fulvalenequinone System V.
Part IV: K. Takahashi, K. Morita, and K. Takase, Chem. Lett., 1977, 1505.
2) K. Takahashi and K. Takase, Tetrahedron Lett., 1972, 2227;
K. Takahashi, T. Fujita, and K. Takase, Tetrahedron Lett., 1971, 4507.
3) K. Takahashi, K. Morita, and K. Takase, Tetrahedron Lett., 1977, 1511.
4) 7,8-Diaminoheptatriafulvalene has been reported to be unstable: Z. Yoshida, H. Konishi, H. Kobayashi, and H. Ogoshi, The 8th Sympo. on Nonbenzenoid Aromatic Compounds. October 1975 at Kyoto, Abstracts p. 104.
5) K. Takahashi, T. Goto, K. Moue, S. Kagabu, and K. Takase, 1st International Sympo. on the Chemistry of Nonbenzenoid Aromatic Compounds. August 1970 at Sendai, Abstr. p. 13. Details will be reported in this series in near future.
6) W. von E. Doering, Kekūle Sympo., Butterworths Sci. Publ., London (1959) p. 44; R. Thomas, P. Coppens, Acta Cryst., B28, 1800 (1972).
7) K. Takahashi, K. Morita, and K. Takase, Chem. Lett., 1977, 1505.
8) J. Nakayama, M. Ishihara, and M. Hoshino, Chem. Lett., 1977, 287.
9) T. Nozoe, K. Takahashi, and H. Yamamoto, Bull. Chem. Soc. Jpn., 42, 3277 (1969).
10) Attempted preparation of 3 by the reaction of tropolone with 2-methylthio-1,3-dithiolium iodide was unsuccessful.
11) E. Campaigne and R. D. Hamilton, J. Org. Chem., 29, 1711 (1964); R. Gompper and E. Kutter, Angew. Chem. Int. Ed. Engl., 2, 687 (1963).
12) J. W. Cook, A. R. Gibb, and R. A. Raphael, J. Chem. Soc., 1951, 2244.
13) T. Nozoe, Y. Kitahara, K. Yamane, and A. Yoshikoshi, Proc. Japan Acad., 27, 18 (1951).
14) All new compounds gave satisfactory elemental analyses.
15) 2-(6-tert-Butyltropolon-3-yl)-1,3-dithiol was obtained by the reaction of 4-tert-butyltropolone with 1,3-dithiolium tetrafluoroborate in the presence of triethylamine. The chemical shifts of H-4,5 of this compound appeared at 6.10 ppm in $CDCl_3$.
16) The H-8,9 of 1' would resonate at about 0.2 ppm higher field than H-9 of 1, judging from the chemical shift difference between the corresponding protons in 2,5-dibromo derivatives of 1 and 1' (our unpublished data).
17) pKa values are determined by UV method with Hitachi No 323 spectrophotometer.
18) The contribution of the resonance structure such as 2c, proposed by other's,[8)] would not be important for the ground state of 2, since the seven-membered ring protons of 2 show much the same chemical shifts as those of 4 or 1 in ^{1}H NMR spectrum (Table 2).



2C

19) The coulombic integrals for the heteroatoms and the carbon atoms bonded to the heteroatoms are expressed by $\alpha_x = \alpha + a\beta$ and $\alpha_{adj} = \alpha + b\beta$, respectively, using a = 1.0, b = 0.2 for oxygen atom and a = 0.5, b = 0.2 for sulfur atom. The resonance integrals for the carbon-heteroatom bonds are expressed by $\beta_{C-x} = d\beta$, using d = 1.0 for C-O bond and d = 0.6 for C-S bond.

(Received March 14, 1981)