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SYNTHESIS AND PROPERTIES OF 7-(1,3-DITHIOL-2-YLIDENE)-3,5-CYCLOHEPTADI-ENE-1,2-DIONE (OR 7,10-DITHIASESQUIFULVALENE-1,2-QUINONE) DERIVATIVES¹⁾

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Three stable 4-tert-buty1, 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-quinones²⁾ and heptatriafulvalene-1,2-quinones³⁾ 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 $\underline{3}$ 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.







(3.79), 510 (4.22)]. In similar reaction conditions but more easily, 5-bromotropolone¹²⁾ and 3,5-dibromotropolone¹³⁾ reacted with the dithiolium iodide to give <u>5</u> and <u>6</u>, respectively [<u>5</u>: deep violet needles, mp. 261-262 °C, 16%, m/e (%) 300 (22), 272 (100), 244 (100); $\lambda \max$ (MeCN) 255 nm (log $_{\mathcal{E}}$ 4.03), 317 (4.03), 362, sh (3.43), 535 (4.27)] [<u>6</u>: deep violet needles, mp. > 300 °C, 22%, m/e (%) 380 (50), 352 (100), 324 (40); $\lambda \max$ (MeCN) 255 nm (log $_{\mathcal{E}}$ 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 The ¹H NMR spectral H-8,9 chemical shifts of 4 appeared at lower field by state. 1.5 ppm than those of H-4,5 of 2-(6-tert-butyltropolon-3-yl)-1,3-dithiol¹⁵⁾ but appeared at higher field by 0.81 ppm than that of 1¹⁶⁾ (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 $\underline{1}$ 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 \underline{l} , 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









Table 1	: Effec Wavel	t of the	e Solven ransitio	t Polarit	y on the	Longest
Compd.	DMSO	MeCN	Me ₂ CO	CH ₂ Cl ₂	Benzene	Dioxane
4	525	510	506	505	503	503
5	545	535	530	534	528	524
<u>6</u>	562	554	538 565	555	549	543
<u>1</u>	553	544	540	548	530	526



Table 2 : IR	(KBr, cm ⁻¹) and	d ^l h nmr (ð:	ppm, J : Hz)	Data of <u>4</u> , <u>5</u> , <u>6</u> ,	$\underline{1}$, and $\underline{2}$
Compound	<u>4</u>	<u>5</u>	<u>6</u>	<u>1</u>	<u>2</u>
IR	1630 s 1498 s 1487 vs	1610 s 1588 s 1549 vs	1604 s 1576 s 1542 vs	1600 w 1550 s	1505
¹ H NMR 7-membd. ring	6.75 H-3 d 6.46 H-5 dd 7.18 H-6 d	6.43 H-3 d 7.32 H-4 dd 7.77 H-6 d 14.6=1.7	8.12 H-4 d 7.84 H-6 d	6.54 H-2,5 d 7.09 7.17 [}] H-1,6 d	6.7~7.0 m
	<u>J</u> 5,6=12.5	$\overline{J}_{3,4=12.6}$	04,0-1.7	<u>J</u> 1,2=11.7	
H-8,9	7.61	8.26	8.35	8.42	8.12
Solvent	CDC13	DMSO-d6	DMSO-d6	DMSO-d6	DMSO-d6

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 \pm 0.03) is larger than that of 8 (0.55 \pm 0.05) in 50% aqueous acetonitrile¹⁷⁾ 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 $4 < 2 \leq 1.^{18}$ 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 $\underline{9}$ and p-tropoquinone methide $\underline{10}$, 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 <u>10</u> is relatively small as compared with that in <u>9</u>, but the LUMO of <u>10</u> lies at a very low level and the $f_r^{(N)}$ at the exo-carbon atom of <u>10</u> is still very large, indicating that $\underline{10}$ should show very high electrophilicity at the exo-carbon



atom. The $f_r^{(N)}$'s in the dithiolides <u>1</u>', <u>2</u>, and <u>3</u>, 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 <u>1</u>, <u>2</u>, and <u>4</u> towards nucleophiles (stable in hydrous solvents and in weak



Fig. 2. Frontier electron densities $(f_r^{(E)}; for electrophilic attack, f_r^{(N)}; for nucleophilic attack) and eigen values (E_i = <math>\alpha + X_i \beta$) 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 <u>1</u>' and <u>3</u> also gave reasonable correlations with the pKa values of <u>8</u> and <u>7</u> respectively.

References and Notes

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- 14) All new compounds gave satisfactory elemental analyses.
- 15) 2-(6-tert-Butyltropolon-3-yl)-1,3-dithiol was obtained by the reaction of 4tert-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 CDCl₃.
- 16) The H-8,9 of <u>1</u>' would resonate at about 0.2 ppm higher field than H-9 of <u>1</u>, judging from the chemical shift difference between the corresponding protons in 2,5-dibromo derivatives of <u>1</u> and <u>1</u>' (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 $\underline{2c}$, proposed by other's,⁸⁾ would not be important for the ground state of $\underline{2}$, since the seven-membered ring protons of $\underline{2}$ show much the same chemical shifts as those of $\underline{4}$ or $\underline{1}$ in ¹H NMR spectrum (Table 2).
- 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.

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