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5,8-DITHIAFULVALENE-1,4-QUINONE [2-(1,3-DITHIOL-2-YLIDENE)-4-CYCLOPENTENE-1,3-DIONE]

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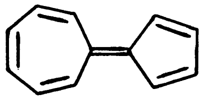
5,8-Dithiafulvalene-1,4-quinone [2-(1,3-dithiol-2-ylidene)-4-cyclopentene-1,3-dione] and its benzo-derivatives were synthesized and their spectroscopic properties were described.

Both sesquifulvalene (1)[1] and 1,4-dithiafulvalene (2)[2], which are iso-π-electronic each other, have the properties of polyolefins rather than aromatic compounds. Kitahara et al. have reported the synthesis and properties of a stable quinone derivative of 1, sesquifulvalene-1,4-quinone (3).[3] This paper describes the synthesis of 5,8-dithiafulvalene-1,4-quinone [2-(1,3-dithiol-2-ylidene)-4-cyclopentene-1,3-dione] (4a) and its benzo-derivatives which are iso-π-electronic with 3.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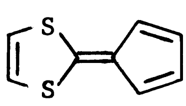
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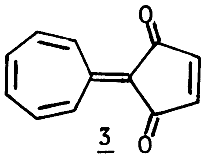
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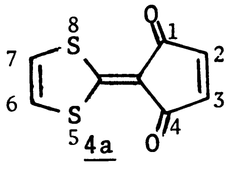
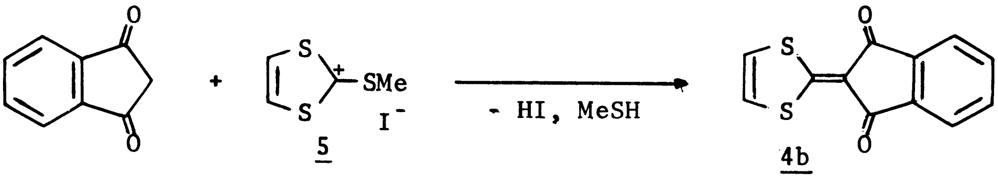
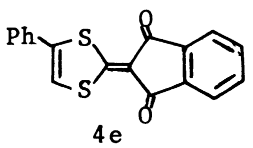
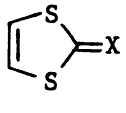


4a

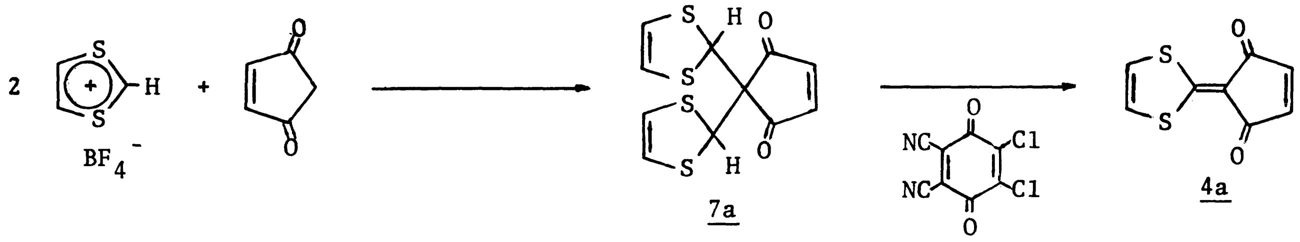
The synthesis of 4e, a derivative of 4a, has been recently reported by two groups,[4,5] which includes the condensation of 1,3-indandione with 2-methylthio- and 2-piperidino-4-phenyl-1,3-dithiolylium salts. We prepared 2,3-benzo-5,8-dithiafulvalene-1,4-quinone (4b), mp > 290°C, yellow needles (from benzene), in 84% yield by the reaction of 1,3-indandione with the iodide salt 5[6] in the presence of pyridine in boiling acetonitrile. Found: C, 58.20; H, 2.46; S, 26.01%. Calcd for $C_{12}H_6O_2S_2$: C, 58.55; H, 2.46; S, 26.00%. However, all attempts to prepare the parent quinone 4a from 5 and 4-cyclopentene-1,3-dione were unsuccessful, products isolated being only 1,3-dithiol-2-thione (6a) and intractable tars.




4e

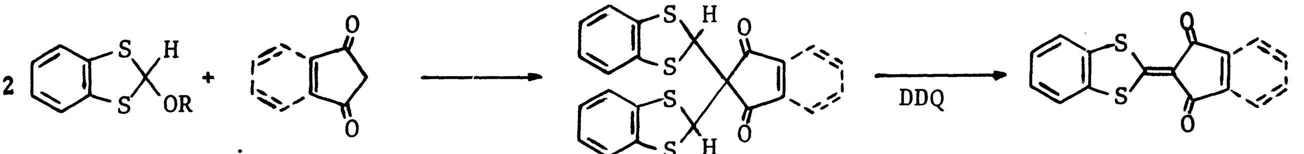

6a; X=S, 6b; X=O

The reaction of 4-cyclopentene-1,3-dione with 2 molar amounts of 1,3-dithiolylium tetrafluoroborate[7)] in an aqueous ethanol at room temperature gave compound 7a in 76% yield; mp 166-167°C (decompn.), $\nu_{C=O}$ 1680 cm^{-1}, δ ($CDCl_3$) 5.72 (2H, s), 5.90 (4H, s), and 7.46 (2H, s). The oxidation of 7a with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in dioxane at room temperature gave rise to the parent quinone 4a, mp ca. 237°C (decompn.), red prisms (from benzene), in 76% yield in addition to 1,3-dithiol-2-one (6b) (23%).[8)] 4a, Found: C, 49.29; H, 2.12; S, 32.63%. Calcd for $C_8H_4O_2S_2$: C, 48.99; H, 2.06; S, 32.63%. 4-Cyclopentene-1,3-dione also reacted with 2 molar amounts of the benzodithiole 8[9)] in acetic acid at room temperature to give 2,2-bis(1,3-benzodithiol-2-yl)-4-cyclopentene-1,3-dione (7c) in 66% yield; mp 178°C (decompn.), $\nu_{C=O}$ 1680 cm^{-1}, δ ($CDCl_3$) 5.75 (2H, s), 7.0-7.4 (4H, AA'BB' m), and 7.45 (2H, s). Compound 7c, on oxidation with DDQ, was converted into 6,7-benzo-5,8-dithiafulvalene-1,4-quinone (4c) (90%), mp 243-245°C (decompn.), yellow needles (from dioxane) and 1,3-benzodithiol-2-one (9) (40%). 4c, Found: C, 58.31; H, 2.54; S, 26.00%. Calcd for $C_{12}H_6O_2S_2$: C, 58.55; H, 2.46; S, 26.00%. The reaction of 1,3-indandione with 8 gave 2,2-bis(1,3-benzodithiol-2-yl)-1,3-indandione (7d), mp > 290°C, quantitatively,[10)] and then the oxidation of 7d with DDQ resulted in the quantitative formation of 2,3-benzo-6,7-benzo-5,8-dithiafulvalene-1,4-quinone (4d), mp > 290°C, greenish yellow needles (from benzene). Found: C, 64.81; H, 2.78; S, 21.56%. Calcd for $C_{16}H_8O_2S_2$: C, 64.87; H, 2.73; S, 21.61%. Quinones 4 thus obtained have high melting points, are thermally stable, and are scarcely soluble in organic solvents.



7a

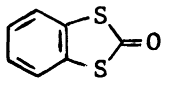
4a



8 R = $CH_2CH_2Pr^i$

7c, 7d

4c, 4d



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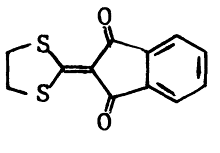

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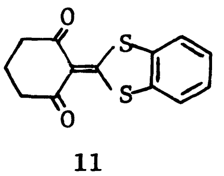

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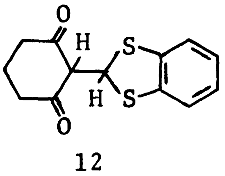


12

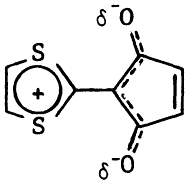
2-(1,3-Dithiolan-2-ylidene)-1,3-indandione (10) and 2-(1,3-benzodithiol-2-ylidene)cyclohexane-1,3-dione (11) were also prepared for comparison with 4; 10, mp 251-254°C, was obtained by the reaction of 2-methylthio-1,3-dithiolanylium methylsulfate[11)] with 1,3-indandione in 66% yield and 11, mp 208-209°C, by the oxidation of compound 12[12)] with DDQ in 97% yield. The spectroscopic data of compounds 4, 10, and 11 are summarized in the Table.

Spectroscopic Data of Quinones

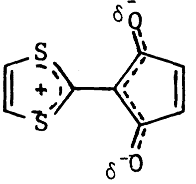
Compounds	IR (Nujol) $\nu_{C=O}$ (cm^{-1})	UV ($CHCl_3$) λ_{max} (nm) (log ε)	H NMR (δ, TMS)[a)]
4a	1647	380 (4.39), 288 (3.00)	6.98 (2H, s), 7.52 (2H, s)
4b	1653	411 (4.69), 309 (3.59), 297 (3.46)	7.69 (4H)[b)], 7.74 (2H, s)
4c	1656	378 (4.53), 290 (3.42)	7.10 (2H, s), 7.4-7.5, 7.9-8.0 (4H, AA'XX' m)
4d	1665	411 (4.79), 309 (3.75), 297 (3.65)	c)
10	1666	368 (4.43), 355 (4.49), 307 (4.11) 295 (3.90)	3.51 (4H, s), 7.6-7.9 (4H, AA'BB' m)[d)]
11	1640 w 1595	387 (4.64), 305 (3.41)	2.07 (2H, quintet), 2.72 (4H, t), 7.4-7.6 7.8-8.0 (4H, AA'XX' m)[d)]

a) Determined at 100 MHz with DMSO-d_6 as solvent at 100°C unless otherwise stated. b) Singlet with fine line structure. c) A well-defined spectrum could not be obtained owing to the insolubility of the sample.

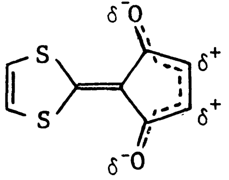
The carbonyl frequency of 4 falls in the same range of 1647-1665 cm^{-1} as those of 3 and its derivatives.[3)] A high-frequency shift of the carbonyl absorption is observed when the C_6-C_7 double bond of 4 is saturated; 4b absorbs at 1653 cm^{-1} whereas 10 absorbs at 1666 cm^{-1}. The saturation of the C_6-C_7 double bond also results in the fairly large hypsochromic shift of the UV absorption maximum; the longest absorption of 4b appears at 411 nm and that of 10 at 368 nm. These data suggest that the C_6-C_7 double bond enters into the cyclic conjugated system, that is, the entirely delocalized polar structure 13a makes a predominant contribution to the ground state of 4 over the partially delocalized structure 13b. The dithiole ring protons of 4b resonate at δ 7.74 and the cyclopentenedione ring protons of 4c at δ 7.10. On the basis of these data, in the NMR spectrum of 4a the singlet at δ 7.52 can be assigned to the dithiole ring protons and the singlet at δ 6.98 to the cyclopentenedione ring protons. The olefinic protons of 14a ($CDCl_3$)[13)] and 14b (CCl_4)[14)],



13a

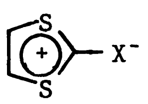


13b

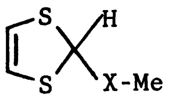


13c

in which cyclic conjugation is impossible due to an insulating sp^3 C-2 carbon atom, resonate at δ 6.07 and 6.20, respectively. Compounds 6a (CDCl$_3$)[13] and 6b (CDCl$_3$), in which the dipolar form 6' allows positive-charge delocalization over the entire ring, exhibit the olefinic proton resonance at δ 7.17 and 6.78, respectively. The appearance of the dithiole ring proton signal of 4a at a lower field than that of of 6 as well as 14, even if the solvent used for measurement is not the same, is suggestive of the pronounced contribution of 13a to the ground state of 4. The bathochromic shift observed in going from 4c (λ_{max} 378 nm) to 11 (λ_{max} 387 nm), on the other hand, indicates that the structure 13c also contributes to the ground state of 4 to some extent. Such a bathochromic shift was also observed with 3 when its C_2-C_3 double bond was saturated.[3]



6'



14a; X = S, 14b; X = O

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- References and Notes -

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14) This compound was prepared in 72% yield by treating 1,3-dithiolylium tetrafluoroborate with methanol in the presence of sodium bicarbonate; bp 70-72°C/13 mmHg, colorless liquid.

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