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Synthesis and Physical Properties of 6,8-Bis(phenylthio)-7H-benzocycloheptene-1,4,7-trione. A Novel D-s-A-s-D Molecular Unit Directed toward Organic Conductors

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The title compound was prepared via a route involving dehydrogenative phenylsulfidation. The NMR and electronic spectra and reduction potential were discussed in comparisons with those of the unsubstituted and mono-substituted analogs. The structure was examined by X-ray crystallography.

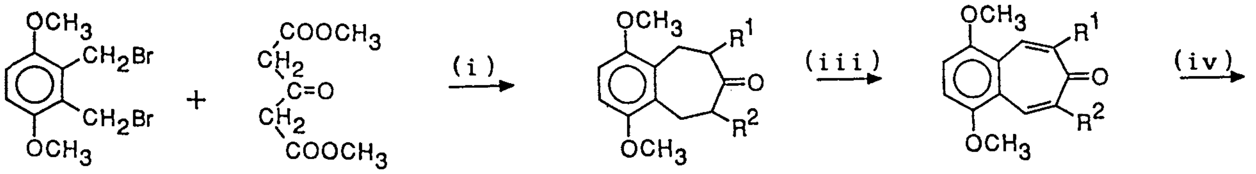
In a previous paper, we reported the synthesis of 7H-benzocycloheptene-1,4,7-trione (1) as a new type of electron acceptor, which showed the first reduction potentials as -0.23 V (SCE) in acetonitrile and -0.31 V (Ag/AgCl) in dichloromethane.[1)]

In order to control the electron affinity of 1, we examined the synthesis of the compounds substituted with phenylthio groups on C_6 and C_8 of 1, because this group may easily be transformed to phenylsulfinyl and phenylsulfonyl groups and the group itself is considered to be an electron donor.

Bernstein et al. proposed D-A-D and A-D-A molecular units, in which the donors (D) and acceptors (A) are chemically attached via bridging atoms and which may form segregated column stackings, for obtaining organic metals composed of single molecules. They observed segregated column stackings in the crystals of compounds such as 2.[2-4)]

Our object, 6,8-bis(phenylthio)-7H-benzocycloheptene-1,4,7-trione 3, will meet the above category of D-A-D molecule. It has a plane of symmetry through the tropone carbonyl, perpendicular to the plane of the fused ring and bisecting the ring. Presently, we synthesized 3, along with monosubstituted phenylsulfide 4 and studied their physical properties.

Condensation of 2,3-bis(bromomethyl)hydroquinone dimethyl ether (5)[5)] with dimethyl 3-oxoglutarate[6)] gave seven-membered keto-diester (6), which was demethoxycarbonylated[7)] to seven-membered ring ketone (7)[8)] in 90% yield. It has been known that cyclohexanone gave 2-phenylthio- and 2,6-bis(phenylthio)-phenols when it was treated with 5 molar excess of diphenyl disulfide in the presence of 5 molar excess of sodium ethoxide.[9)] We studied this reaction on ketone 7 with intention of obtaining substituted tropone directly. In fact, it gave two kinds of substituted benzotropones, 8 and 9,[8)] under the above conditions. The best yield (8 : 9 = 13% and 40%) was obtained when 5 equimolar amounts each of the base and diphenyl disulfide to ketone 7 were used under the usual reaction condition and refluxing was continued 4 h after the addition of



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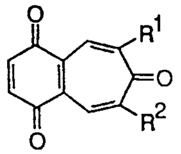
(ii) 6 $R^1 = R^2 = COOMe$ → 7 $R^1 = R^2 = H$

8 $R^1 = R^2 = SPh$
9 $R^1 = H$, $R^2 = SPh$
10 $R^1 = R^2 = H$



3 $R^1 = R^2 = SPh$
4 $R^1 = H$, $R^2 = SPh$
1 $R^1 = R^2 = H$

(i) 20% aq. $KHCO_3/CH_2Cl_2$ ($C_6H_5CH_2NEt_3Cl$), 38 °C, over night (o.n.) (ii) KOH/aq. MeOH, 80 °C, o.n. (Yield: 90% from 5) (iii) NaOEt (5 equiv.)/PhSSPh (5 equiv.)/EtOH, 80 °C, 8 h, then added NaOMe (2 equiv.), 80 °C, 4 h (Yields: 8 14%; 9 41%) (iv) aq. CAN (2.6 equiv.)/CH_3CN-$CHCl_3$, room temp, 1 h (Yield: 8 → 3 87%; 9 → 4 89%).

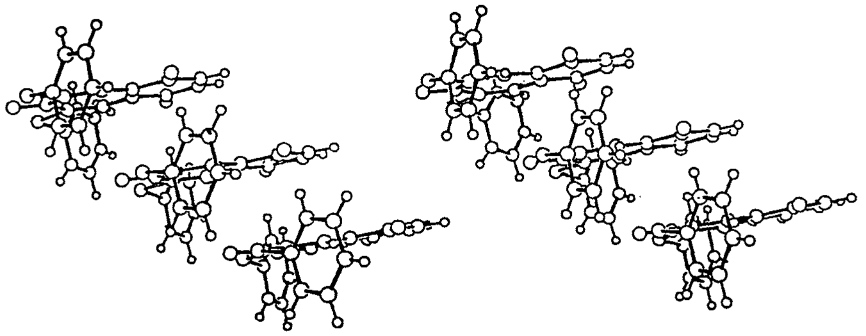


Fig. 1. Stereo Drawing of the three Molecules of 3.

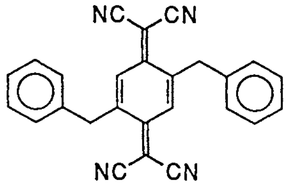


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Table 1. ^1H and ^{13}C NMR Spectra (δ in ppm, J in Hz)

	Compound	10	9	8	1	4	3
^{13}C	Quinone C=O				184.8	184.8 185.0	184.9
	Tropone C=O	189.0	183.9	179.1	186.1	181.3	173.1
^1H	H_2, H_3	7.06^{s}	6.921^{s}	6.783^{s}	7.04^{s}	6.868^{d} 6.952^{d} J=10.1	6.779
	Tropone vinyl-H	8.21^{d} 6.89^{d} J=12.8	7.866^{s} 8.279^{d} 6.935^{d} J=13.4	7.957	7.99^{d} 7.25^{d} J=12.5	7.649^{s} 8.127^{d} 7.276^{d} J=12.8	7.765^{s}
	CH_3O	3.92	3.900 3.556	3.545			

further 2 equimolar amounts of sodium methoxide. The corresponding quinotropones, 3 and 4,[8)] were obtained in good yields by cerium (IV) oxidation of 8 and 9, respectively.

The ^{1}H- and ^{13}C-NMR spectral data of the hydroquinone dimethyl ethers and p-quinones are shown in Table 1. In the ^{1}H-NMR spectra, one of the methoxy signals of 9 and both signals of 8 showed higher field shifts of ca. 0.35 ppm compared with that of 10. This can be rationalized by the effect of the ring current caused by the phenyl group which seems to be forced to face to the methoxy group(s). The X-ray crystal structure analysis of 8 revealed that this conformation is surely present in a crystal.[10)] The proton signals on the six-membered ring appeared almost the same field in every hydroquinone dimethyl ether as that in the corresponding quinone, respectively. The signals moved gradually to the higher field with the increase in the number of phenylthio group. In the ^{13}C-NMR spectra of 1, 4, and 3, the signals due to the quinone-carbonyl appeared in the same region (ca. 185 ppm), while the peaks due to the tropone carbonyl moved steadily to the upper field as the number of the substituent increases. This tendency is also seen in the corresponding hydroquinone dimethyl ethers, 10, 9, and 8. This extraordinary shift (5-8 ppm per substituent) is not in line with the lower field shifts of the signals due to the meta carbons of benzene by substitution with a phenylthio group,[11)] and with the Hammett's substituent constants, $\sigma_m{}^o = +0.14$, $\sigma_p{}^o = +0.06$,[12)] predicting a slight electron-withdrawing ability of the group.

The common characteristics of the electronic spectra of 3 and 4 are the negative solvatochromic shifts.[8)] It seems that the stabilization of the ground state structure may exceed that of the excited states in polar solvents than in less polar ones.

In a region of +0.5- -1.2 V, both compounds, 3 and 4, gave good reversible CV curves. The reduction potentials in acetonirile drop steadily by the substitution with phenylthio group as follows: 4, $E_1 = -0.25$, $E_2 = -0.73$ V;[8)] 3, $E_1 = -0.30$, $E_2 = -0.80$ V (Ag/AgCl). This fact shows that the phenylthio substituent on C_6 and C_8 may exert lowering of the electron accepting ability of the framework, which is in opposite direction expected from the electron withdrawing ability of the group.[12)]

According to the single crystal X-ray analysis of 3, the phenyl groups are holded by sulfur atoms anti to the tropone carbonyl and facing intramolecularly to the quinone carbonyl groups. A row of head-to-tail arrangement of the molecules and a segregated column stacking of rings of 3 are seen in a crystal (Fig. 1). This is one of the fundamental requirements for obtaining organic conductors. The precise feature of the structure of 3 will be discussed together with those of 4 and 8 in a separate paper.

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8) Physical data of compounds, **3**, **4**, **7**, **8**, and **9**. **3** Dark wine red plates, mp 258-260 ^{o}C (dec.); C, H; Mass e/z (%) 402 (M^+ 100), 374 (28); λ_{max} (log ε) (solvent): 219 (4.57), 353 (4.32), 510 nm (4.05) (CH_3CN); 243 (4.33), 358 (4.35), 526 nm (4.07) (CH_2Cl_2). **4** Red prisms, mp 179-180 ^{o}C (dec,); C, H; Mass m/z (%) 294 (M^+ 100), 266 (33), 237 (20); λ_{max} (log ε): 238.5 (4.32), 322 (4.14), 478 nm (3.91) (CH_3CN); 245.5 (4.33), 323.5 (4.15), 492 nm (3.95) (CH_2Cl_2); E_1 = -0.36, E_2 = -0.88 V (CH_2Cl_2; Ag/AgCl). **7** mp 125-125.5 ^{o}C. **8** Yellow needles, mp 236-237 ^{o}C; C, H; Mass m/z (%) 432 (M^+ 74), 404 (48), 389 (44). **9** Yellow needles, mp 161-162 ^{o}C; C, H; Mass m/z (%) 324 (M^+ 98), 296 (75), 281 (100). IR spectra of **1**, **3**, and **4** (cm^{-1} in nujol mull) ν: **1** 1662(s), 1640(m), 1610(s), 1585(s); **4** 1658(s), 1603(s), 1580(m), 1568(s); **3** 1665(m), 1620 (m-w), 1565(vs) (s = strong, m = medium, w = weak, vs = very strong).

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10) **3** Space group Cm; **8** monoclinic, Space group $P2_1/c$.

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