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[2]PARACYCLO[2](3,7)-p-TROPOQUINONOPHANE

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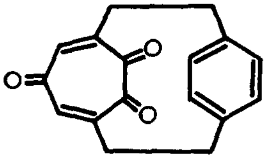
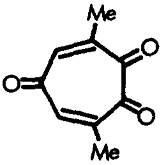
Abstract The title compound 1, a novel cyclophane containing p-tropoquinone, was synthesized starting from 5-methoxytropolone and its physical properties were discussed comparing with those of 3,7-dimethyl-p-tropoquinone and p-benzoquinonophane. The reduced quinone character exhibited by 1 was ascribed to the intramolecular CT interaction and the deformation of the quinone ring.

From our previous study, p-tropoquinone qualified as a more electrically positive quinone than p-benzoquinone[1]. With continuous interest in the intramolecular charge transfer (CT) interaction of phanes[2,3], we have synthesized [2]paracyclo[2](3,7)-p-tropoquinonophane 1. The properties of this first nonbenzenoid quinonophane are described in comparison with its reference compounds, 3,7-dimethyl-p-tropoquinone 2 and [2]paracyclo[2](2,6)-p-benzoquinonophane 3[4].



1



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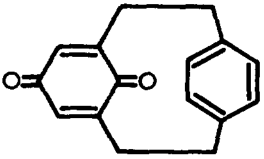

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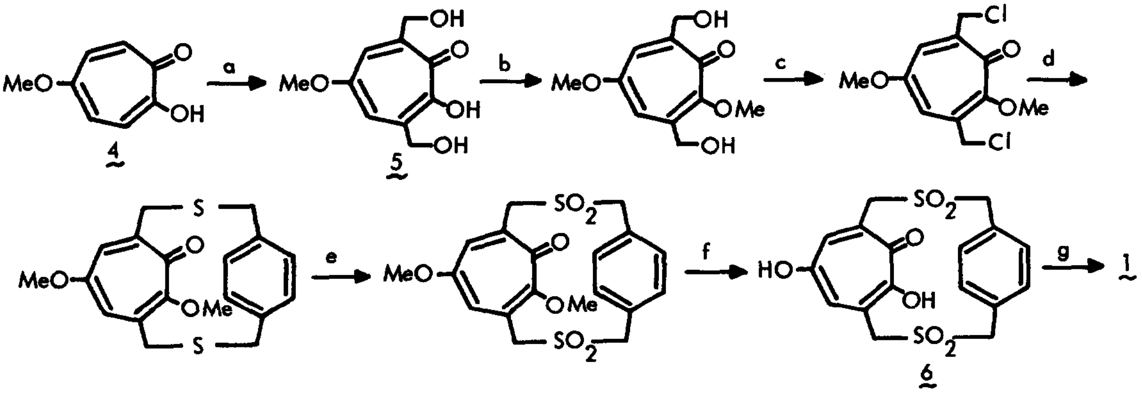
Synthesis Compound 1 was synthesized from 5-methoxytropolone 4[5] as shown in the following scheme.



a: CH_2O, KOH, 71% b: CH_2N_2, 96% c: $SOCl_2$, CH_2Cl_2, 79%
d: 1,4-bis(mercaptomethyl)benzene, MeONa, MeOH, 64% e: m-CPBA, 97%
f: conc. HBr, reflux, 95% g: 1) Δ, 2) DDQ, acetone, 20%

As the product of pyrolysis of **6** (580°, 1.5 Torr. Argon atmosphere) was hardly soluble and difficult to purify, it was oxidized with DDQ without purification to yield the desired **1**, yellow needles, d.p. 208°, in 20% overall yield.

Physical Properties   Mass spectrum of **1** (80°, 25 eV) exhibits the following peaks: $(M+2)^+$ (m/e 268, 6.8%), M^+ (m/e 266, 14.3%), M^+-CO (m/e 238, 6.0%), M^+-2CO (m/e 210, 4.0%) and p-xylylene (m/e 104, b.p.). The fragmentation pattern is very similar to that of **2**6). IR frequencies of **1** in the double bond region (1677, 1645, 1617 cm^{-1}) are slightly higher than the corresponding frequencies of **2** (1667, 1605 cm^{-1}), in contrast with those for **3** (1647, 1640, 1592 cm^{-1}) vs 2,6-dimethyl-p-benzoquinone **7** (1647, 1612 cm^{-1}).

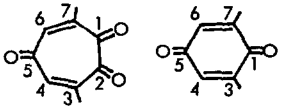
In the PMR spectrum, quinone hydrogens of **1**, appearing at 6.17 ppm, suffer from the ring current effect of the facing benzene moiety (0.59 ppm up-field shift compared with those of **2**; δ=6.76 ppm). The shift value is larger than for **3** (0.36 ppm), being due probably to the geometrical difference of the hydrogens to the benzene ring. Benzene protons of **1** appear as two narrow multiplets at 6.73 and 6.95 ppm, both in somewhat higher field than that of p-xylene (7.05 ppm). The situation is very similar to those of **3**4) and [2]paracyclo[2](2,5)-p-benzoquinonophane2).

NMR chemical shift of quinone carbons in **1** is compared in Table 1 with those of **2**, **3** and **7**8,9). In the benzoquinonophane **3**, the effect of phane formation, Δδ, is generally small suggesting no appreciable change in hybridization, electron density and geometry of p-benzoquinone ring. The exceptionally large down-field shift at the bridging carbons is attributed partly to the "p-orbital compression effect"9) and partly to the possible deformation of the quinone ring at this carbon10). On the other hand, Δδ values in the tropoquinonophane **1** are explicable by a large distortion of 7-membered ring and change in electronic effect originated therefrom. The smaller $\Delta\delta_{3,7}$ is probably due to the reduced "compression effect" (down-field shift) caused by a deeper bending of the quinone ring and/or by increase of electron density (up-field shift) due to the reduced conjugation with C_5=O. Large down-field shift of C_5 is also in accord with the reduced conjugation. The large up-field shift of the diketone carbon is attributed to

Table 1. Chemical shift of quinone carbons in **1**, **3** and reference compounds (ppm in $CDCl_3$)

	1	**2**	$\Delta\delta_{1-2}$	**3**	**7**	$\Delta\delta_{3-7}$
$\delta_{1,2}$*	182.16	192.66	-10.50	187.93	188.15	-0.22
$\delta_{3,7}$	148.98	143.89	+5.09	154.78	145.77	+9.01
$\delta_{4,6}$	135.52	137.25	-1.23	132.24	133.29	-1.05
δ_5	191.96	187.84	+4.12	186.29	187.57	-1.28

*tropoquinone numbering, i.e.:



the decrease of the carbonyl polarization. Two adjacent carbonyl groups in the eclipsed conformation would have large dipole-dipole interaction and reduce the mutual polarization[11]. All of these features culminate in a deeply bent tub conformation of the tropoquinone ring. This is supported by our preliminary X-ray crystallographic analysis, which disclosed that, while four carbons and two oxygens in α-diketone moiety forms a plane parallel to the mean plane of benzene ring, the three carbons and an oxygen in the dienone part are away from the mean plane.

Charge-transfer Interaction (Electronic spectrum and electron affinity) Electronic spectrum in cyclohexane of compound **1** shows absorptions at 257.5 (sh), 306 (sh), 360-390 (sh) and 468 (sh) nm (Fig.). From the comparison of the spectrum with 1) that of **1** in polar solvents 2) that of **2** and 3) that of **2** in the presence of hexamethylbenzene, the broad shoulder around 350-420 nm is attributed to the intramolecular CT absorption. The region is in agreement with that of compound **3**[4].

With the expectation that the CT interaction in **1** is reflected quantitatively in electron affinity, polarographic measurement (vs SCE in CH_3CN at 25°, supporting electrolyte: 0.05M Et_4NClO_4) was carried out on **1** and **2**. Half-wave potentials obtained and electron affinities (E_A) deduced therefrom[12] are shown in Table 2. Smaller E_A of **1** compared with that of **2** clearly indicates the intramolecular CT interaction in **1**. However, the difference (ΔE_A) is much larger here than benzoquinonophane series (ΔE_A=-0.19)[4]. The difference is attributable to the deformation of tropoquinone ring in **1**.

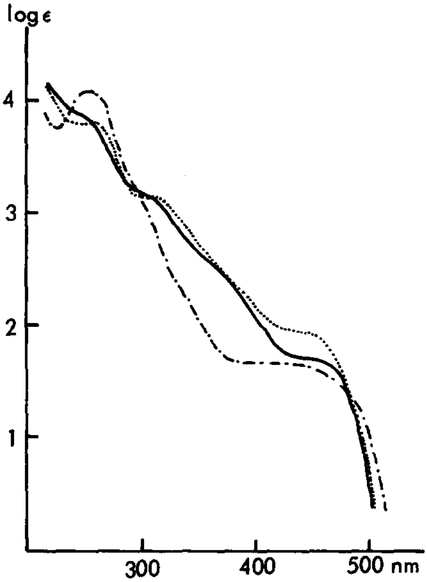


Fig. Electronic spectra of **1** in cyclohexane (———) and in CH_3CN (··········), and **2** in cyclohexane (—·—)

Table 2. Reduction potential and electron affinity of **1** and **2**

Compds	E_1	E_2	E_A	ΔE_A
1	-0.64	-0.98	0.77	-0.29
2	-0.35		1.06	

Thus, the presence of sizable intramolecular CT interaction and the deformation of tropoquinone ring in **1** is clearly demonstrated.

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References and Notes

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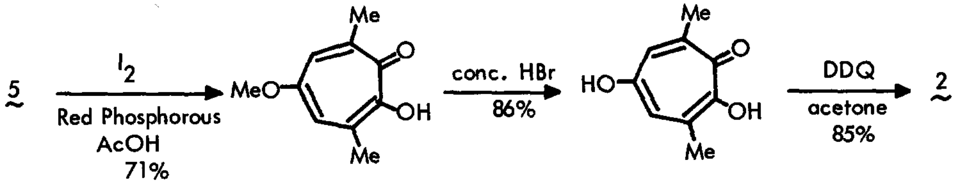
6) 3,7-Dimethyl-p-tropoquinone **2**, yellow plates, m.p. 75-79°, was synthesized from **5** by the following reaction sequences.



7) Signals of other carbons are: **1**, 138.15, 132.09, 131.97 (benzene), 32.54, 31.76 (bridge); **2**, 19.26 (methyl); **3**, 137.30, 131.42, 130.42 (benzene), 36.28, 29.24 (bridge).

8) St. Berger and A. Rieker, *Tetrahedron*, **28**, 3123 (1972). Their assignment of carbonyl carbons was found to be erroneous on the basis of non-decoupled spectral measurements. While the signal at 187.57 ppm appears as a singlet, that at 188.15 does as a complex multiplet. Therefore, their assignment has to be reversed.

9) T. Takemura and T. Sato, *Can. J. Chem.*, **54**, 3412 (1976).

10) In [2.2]metaparacyclophane, the meta-bridged benzene is bent (13°) at the bridging carbons. D.T. Hefelfinger and D.J. Cram, *J. Amer. Chem. Soc.*, **93**, 4754 (1971).

11) The reason for the small Δδ of C_4 and C_6 is not clear. However, it is not directly connected with the polarization of carbonyl groups (cf. ref. 4).

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