Tetrahedron Letters,Vol.23,No.47,pp 4955-4958,1982 0040-4039/82/474955-04$03.00/0
Printed in Great Britain

[3]PARACYCLO- AND [3]METACYCLO[3](3,7)-p-TROPOQUINONOPHANES

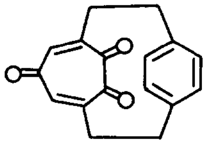
Akira Kawamata, Yoshimasa Fukazawa, Yutaka Fujise and Shô Itô

Department of Chemistry, Tohoku University

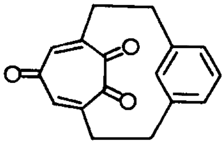
Sendai 980, Japan

Abstract The title phanes were synthesized. Examination of their physical properties including X-ray crystallography disclosed that 1) the p-tropoquinone ring is still bent in both compounds though to a lesser extent than in the corresponding [2.2]phanes, 2) the metacyclo compound prefers syn conformation in solution, and 3) the intramolecular CT interaction is very similar in two compounds.

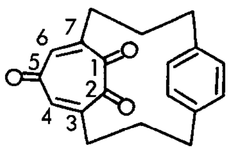
In the previous paper[1] we have shown that the quinone ring of [2]paracyclo[2](3,7)-p-tropoquinonophane (1) is deeply bent and yet sizable intramolecular CT interaction is observed. The CT interaction is also operating to a similar extent in [2]metacyclo[2](3,7)-p-tropoquinonophane (2) despite of the difference in relative position of donating and accepting moieties[2]. In order to evaluate the effect of deformation and geometrical difference on CT interaction, we have synthesized homologous p-tropoquinonophanes, [3]-paracyclo- and [3]metacyclo[3](3,7)-p-tropoquinonophanes (3 and 4).



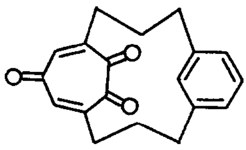
1



2

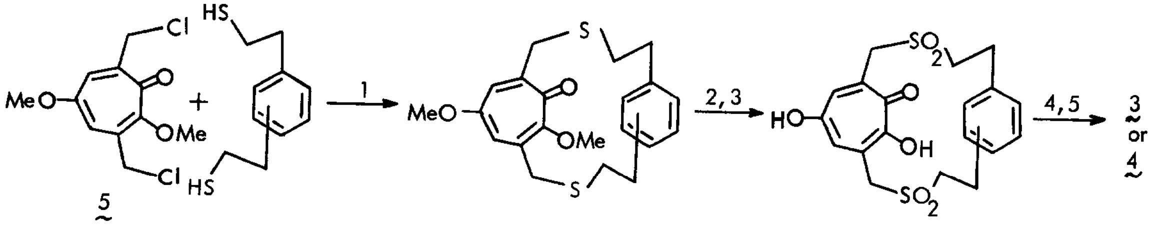


3



4

Synthesis Following the general "sulfur route", the syntheses were effected in 5 steps from the tropolone 5[1], common starting material for tropoquinonophanes. (The property of the products and yield in each step are described below along with the reagents in the order of paracyclo and metacyclo series.)[3]



1. NaOMe/MeOH, yellow plates, m.p. 188-190°, 38%, yellow granules, m.p. 145-148°, 69%.
2. m-CPBA/CH$_2$Cl$_2$, yellow powder, m.p. > 300°, 90%, yellow needles, m.p. 240-242°, 78%.
3. conc. HBr, reflux, yellowish brown powder, m.p > 300°, 93%, greenish yellow powder, m.p. > 300°, 95%
4. Thermolysis at 500°, 0.5 Torr, N$_2$; no purification. 5. DDQ/acetone, 11%, 1.3% yields in two steps.

Physical Properties The tropoquinonophanes **3**, yellow prisms, m.p. 157-158°, and **4**, yellow plates, m.p. 145-147°, show in their mass spectra peaks correspond to the three consecutive elimination of CO (m/e 266, 238, 210), besides those correspond to $M+2^+$ (m/e 296) and M^+ (294), making a sharp contrast to the spectra of **1** and **2** where only two decarbonylations are observed. Carbonyl region of their IR spectra exhibits two groups of strong absorptions at 1660 (s), 1610 cm^{-1} (s) and 1660 (s), 1612 cm^{-1} (s), respectively, in contrast to only one strong absorption (1668 cm^{-1}) in **2** and a strong (1677 cm^{-1}) and a weak (1617 cm^{-1}) absorptions in **1**. These spectral characteristics, being in accord with those of 3,7-dimethyl-p-tropoquinone (**6**), indicate that the tropoquinone ring is less strained in **3** and **4** than **1** and **2**.

Geometry X-ray crystallographic analysis of **3**$^{5)}$ disclosed the geometry as shown in Figs. 1 and 2. While the benzene ring is nearly planar, tropoquinone ring is bent to a tub form to a lesser extent than those in **1**$^{6)}$. The latter ring in **3** is twisted somewhat unlike that in **1** where the ring is almost symmetrical (mirror plane), probably because of the dipole-dipole repulsion between the vicinal carbonyl groups. This twisting may be associated with the asymmetrical conformation of C_3 bridges.

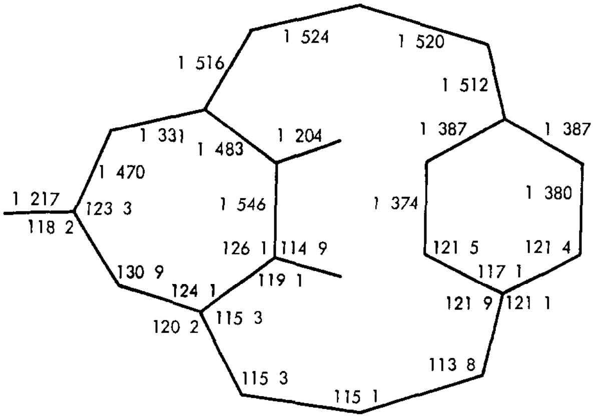


Fig. 1 Averaged bond lengths and angles in **3**

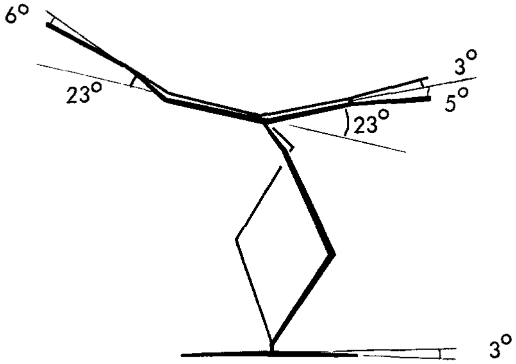


Fig. 2 Side view of **3** with dihedral angles

In PMR spectrum of **3**, the quinone hydrogens (6.37 ppm) and the benzene hydrogens (6.83 and 6.95 ppm) appear at higher field than the corresponding hydrogens in **6** (6.76 ppm) and p-xylene (7.05 ppm), suggesting the near-parallel orientation of two rings and absence of ring flipping. However, the appearance of these hydrogens as singlets and that of the bridge hydrogens, which consists of a well-defined double doublet (2.99 ppm, 2H), a narrow triplet (2.71 ppm, 4H) and a complex multiplet (1.7-2.5 ppm, 6H), suggests at least two dynamic processes occurring at room temperature in solution; conformational change of bridge and the rotational vibration of two rings about their own vertical axis associated with the former change. Compound **4** also exists in a conformational equilibrium as is judged from the shape of bridge proton signals.

However, the appearance at higher field of the quinone (6 08 ppm (2H, s)) and benzene hydrogens (AB_2X at 6.57 (1H), 6.87 (2H) and 7.06 ppm (1H)) compared with the reference compounds and the larger up-field shift (0.68 ppm) of the quinone hydrogens in 4 than those (0.39 ppm) in 3 suggest the preferred syn conformation for 4[7].

CMR chemical shifts of quinone carbons in 3 and 4 shown in Table 1[8], also support the conformations.

Table 1. Chemical shifts (δ) of quinone carbons in 3 and 4 compared with those of 6, 1 and 2.

	δ		$\Delta\delta^{*1}$			
Compds	3	4	3 - 6	4 - 6	1 - 6	2 - 6
$\delta_{1,2}^{*2}$	182.77	190.65	-9.89	-2.01	-10.50	-11.23
δ_5	189.75	189 80	+1.91	+1.96	+4.12	+4.98
$\delta_{3,7}$	148.92	147.61	+5.06	+3 72	+5.09	+5.96
$\delta_{4,6}$	136.45	135.15	-0 80	-2.10	-1 23	-3.18

*1 - up-field shift, + down-field shift. *2 tropoquinone numbering

Up-field shift of $C_{1,2}$ in 3 is comparable despite of the longer bridges with those in 1 and 2, showing the decrease of the carbonyl polarization due to the nearly eclipsed conformation of the two adjacent carbonyl groups Much smaller up-field shift in 4 indicates the polarization and therefore staggered arrangement of the carbonyl groups. This arrangement is possible in syn conformation where no serious steric repulsion is expected between the inward carbonyl and benzene ring. Small down-field shift of C_5 in 3 and 4 compared with those in 1 and 2 are explicable with the more effective conjugation with adjacent double bonds, and the less pronounced bending of tropoquinone rings as is shown by X-ray analysis. The shift (Δδ) for $C_{3,7}$ and $C_{4,6}$ tend to be smaller in [3 3]phanes, 3 and 4, than in [2 2]phanes 1 and 2. However, chemical shifts of $C_{3,7}$ and $C_{4,6}$ would be subjected to change of hybridization by strained σ-frame, extent of conjugation with α-diketone part and/or C_5-carbonyl, and steric compression of p-orbitals with those of the facing benzene carbons, and therefore, the observed change can not be rationalized in a simple way

Charge-Transfer Interaction Electronic spectra in cyclohexane of 3 [λmax 268, 330 (sh), 400 (sh) and 470 nm (sh)] and 4 [λmax 262, 318 and 480 nm (sh)] (Fig. 3) are very similar to those of 1 and 2. From the comparison of the spectra with those in acetonitrile and with that of 6 in the presence of hexamethylbenzene, the broad shoulder at 350-450 nm is attributed to the intramolecular CT absorption. The intensity of the absorption is in the order of 4 > 3 ≃ 1 > 2, and may be reflecting the extent of the overlapping

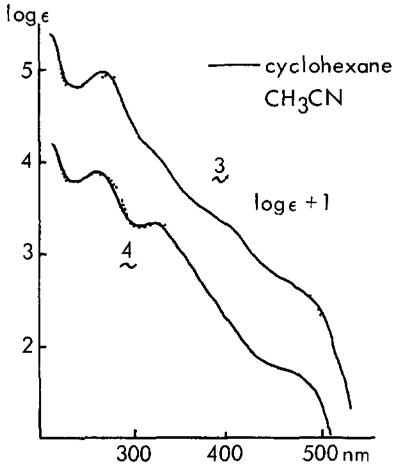


Fig 3 Electronic spectra of 3 and 4 in cyclohexane and in MeCN

of two rings.

In order to estimate transannular interaction, polarographic half-wave reduction potentials[9] of 3 and 4 and their electron affinities calculated therefrom[10] were compared in Table 2 with those of 1, 2 and 6.

Table 2. Reduction potentials and electron affinities of 3 and 4

Compds	1	2	3	4	6
E_1	-0.64	-0.64	-0.53	-0.52	-0.35
E_A	0.77	0.77	0.88	0.89	1.06
ΔE_A*	-0.29	-0.29	-0.18	-0.17	

*change caused by phane formation

As in the cases of 1 and 2, electron affinity is reduced in 3 and 4 compared with that of 6, showing a sizable transannular interaction. However, the change caused by phane formation (ΔE_A) is smaller and therefore LUMO level is lower in 3 and 4 than 1 and 2, reflecting the smaller deformation of tropoquinone ring in the former two. It is interesting to note that 3 and 4 have the same electron affinity, despite of the difference in the overlapping of two rings, as in 1 and 2[2].

References and Notes

1) A. Kawamata, Y. Fukazawa, Y. Fujise and S. Itô, Tetrahedron Letters, 23, 1083 (1982).

2) A. Kawamata, Y Fujise and S. Itô, to be published.

3) By-products of the pyrolysis in each series are 3,7-dimethyl-p-tropoquinone 6[1] (6% yield) and [3]metacyclo[3](2,6)-p-benzoquinone[4] (0.4% yield), respectively.

4) T. Shinmyozu, T. Inazu and T. Yoshino, Chemistry Letters, 1319 (1978).

5) The compound 3 crystallizes in the monoclinic system of space group $P2_1/a$ with 4 molecules in a unit cell of dimensions a= 17.451(5), b= 13.028(4), c=6.901(1)Å, β= 108.49(2)°. The structure was solved by MULTAN78 and refined by block-diagonal least square method. The final R value was 8 3%. Final crystallographic coordinates have been deposited in the Cambridge Crystallographic Data Center.

6) Crystal of 1 contains 12 molecules in a unit cell, with three molecules with different conformations. Preliminary analysis disclosed that the a-diketone part (C_1C_2) deviates by 35° and monoketone part (C_5) by 30° from the plane of $C_3C_4C_6C_7$, although R value still remains 12%.

7) This is in accord with the case of [3.3]metacyclophane and its dithia analog. a. T. Otsubo, M. Kitasawa and S. Misumi, Bull. Chem. Soc. Jpn., 52, 1515 (1979). b. W. Anker, G. W. Bushnell and R.H. Mitchell, Can. J. Chem , 57, 3080 (1979).

8) Chemical shifts of other carbons are 3 138.70, 130.79, 130.33, 35.24, 32.79, 27.67, 4 142.89, 129.69, 128.63, 127.39, 34.91, 32.39, 28 25.

9) Experimental conditions See ref. 1)

10) G. Briegleb, Angew. Chem., 76, 326 (1964).

(Received in Japan 10 August 1982)