Tetrahedron Letters No. 15, pp 1299 - 1302, 1978. Pergamon Press. Printed in Great Britain.

ISOLATION, CHARACTERIZATION AND MOLECULAR STRUCTURE OF o-TROPOQUINONE

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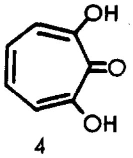
(Received in Japan 2 February 1978; received in UK for publication 27 February 1978)

Cyclohepta-4,6-diene-1,2,3-trione (o-tropoquinone) **1** is a higher analogue with a *vic*-triketone1) of cyclopentadienone **2**2) and o-benzoquinone **3**3) and might constitute a new redox system with 3-hydroxytropolone **4**, similar to p-tropoquinone **5** — 5-hydroxytropolone series4). We have described the formation of **1**5): Although some derivatives (**6a**, **6b**) have been isolated, free quinone **1** was failed to be isolated due to the high electrophilicity of C2-carbonyl group of **1**5). We now wish to report the successful isolation, molecular and crystal structures and physical properties of this intriguing molecule.

1 n=3
2 n=1
3 n=2



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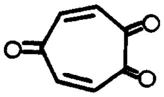

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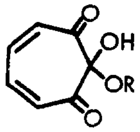

6a R=H
6b R=Me

Isolation **6a** was thermolysed (65°C, 0.005 Torr.) in an apparatus equipped with a condenser having a temperature gradience. **1**, deep red crystal, deposited in 52% yield on the warm (60°C) part and **4** (8% yield) on the cold (room temp.) part of the condenser. Analytically pure **1** thus obtained melts gradually from 125°C and decomposes at 131°C with accompanying gas evolution. **1** is thermally more stable than **2**, **3** or **5** showing no appreciable decomposition at room temp. under dry atmosphere in the dark for 3 weeks. **1** is also stable in aprotic polar solvents (*e.g.* anhydrous acetone or acetonitrile) at room temp., contrary to **3** which dimerizes in such solvents6).

Molecular Structure An X-ray analysis was performed on a crystal coated with petrolatum in order to prevent hydration during data collection. The crystal of **1** belongs to monoclinic system of space group $P2_1/a$, with 4 molecules in a unit cell of dimensions, $\underline{a}$=12.921(2), $\underline{b}$=6.313(1), $\underline{c}$=7.348(1) Å, β=95.84(2)°. A Total of 902 unique reflections was collected by CuKα radiation and used for further analysis. The structure was solved by direct method and refined by full-matrix least-squares calculation. The final R value was 7.7%.

The molecular dimensions are shown in Fig. 1. The molecule in the crystalline state does not have two-fold symmetry. The C1-C2 bond (1.562 Å) is significantly longer than that normally accepted for $C(sp^2)$-$C(sp^2)$ bond (1.48-1.51 Å), while the chemically equivalent C2-C3 bond is almost normal. Concurring with this, C2 and C3 is largely displaced (0.103 Å and -0.136 Å, respectively) from the least-squares plane, the other carbons lying almost planar (0.074∼-0.068 Å from the plane). Oxygens are also asymmetrically placed: O2 and O3 lies off the plane (0.369 Å and -0.434 Å, respectively), whereas O1 is almost on the plane (0.056 Å), thus making the tortional angles of O1-C1-C2-O2 and O2-C2-C3-O3 9.9° and -21.2°, respectively.

These significant deformations from the planar $\underline{C_{2v}}$ structure is attributable to both intra- and intermolecular factors. The first intramolecular factor would be the steric repulsions between two oxygens: Supporting observation is that the distances of O1...O2 and O2...O3 are 2.605 and 2.637 Å, respectively, both of which are shorter than in almost planar o-benzoquinone (2.757 Å)[7] and indantrione (2.941 Å)[8], and also less than the sum of van der Waals radii[9]. The second would be the dipole-dipole interaction between closely-situated carbonyl groups. In fact, C2=O2 (1.200 Å) is somewhat shorter than those of saturated ketones. The intermolecular factor is the electrostatic attractive interaction (vide infra) of the carbonyl groups. Thus all these factors seems to be counterbalancing in crystal with favorable p-orbital overlap of carbonyl groups in a planar system.

The crystal structure viewed along $\underline{a}$-axis is shown in Fig. 2 together with some short intermolecular contacts. Each molecule is surrounded by four neighbours (related by two-fold screw axis), forming a two dimensional mesh of the molecules, and the meshes in turn being stacked parallel to (100) by a/2 apart. There are five intermolecular short-contacts, all involving carbonyl groups. Since the shortest distances 2.77 Å (for O3...C2) and 2.87 Å (for O1...C2) as shown are shorter than the sum of the van der Waals radii, 3.2 Å[9], there must be an attractive interaction involving C2. This interaction may be responsible for O3 to bend toward C2 of the neighbouring molecule. The similar contact and arrangement of the

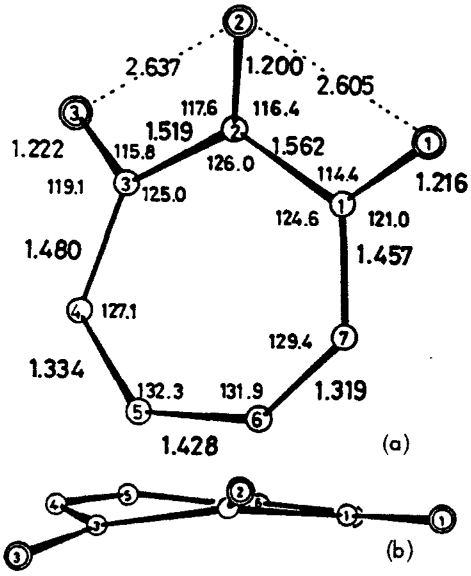

Fig. 1 (a) Molecular dimensions of 1
(b) Molecular structure viewed along a-axis

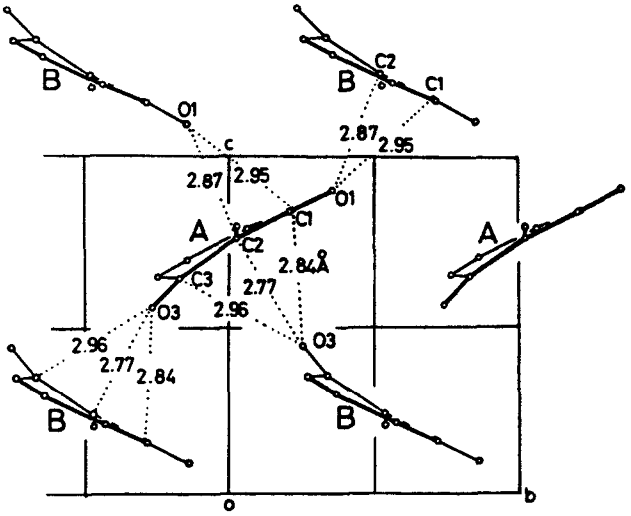

Fig. 2 Crystal packing of 1 viewed along a-axis

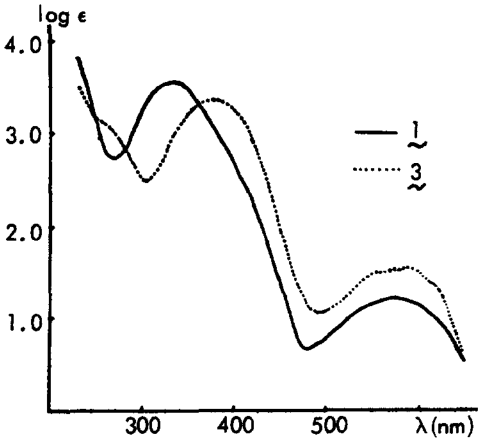

Fig. 3 Electronic spectra of 1 and 3

molecules have been observed for indantrione[8], but the present case presents even shorter contact.

Physical Properties Mass spectrum (25 eV) of 1 exhibits M+2 ion peak [m/e 138 (25%)] stronger than the molecular ion peak [m/e 136 (2%)], the fact common in quinones of higher oxidation potential, and also shows respective M-28 peaks [m/e 110 (21%) and 108 (18%)]. The rest of the fragmentation coinsides with that of 3; [m/e 92 (4%), 80 (48%), 64 (11%), 52 (100%)]. IR (nujol): ν 1713, 1653 (sh), 1647 (sh), 1636 (s), 1620, 1588, 1442, 1295, 1280, 1204, 998, 852, 678 cm^{-1} is also very similar with that of 3. The electronic spectrum of 1 (Fig. 3) exhibits two maxima, at λmax 334.5 nm (log ε 3.54, π-π*) and at 574 nm (log ε 1.2, n-π*). The latter maximum coinsides in wave length with that of 3 except the lack of fine structure. The half-wave potential of 1 (E_1 = -0.14 volt vs. SCE in CH_3CN at 25°, supporting electrolyte: 0.05 M Et_4NClO_4) is more positive than that of 3[10]. PMR and CMR spectra of 1 (Table 1) resembles to those of 3[11]; chemical shift of the central carbonyl carbon appears in higher field than the other two as in the case of diphenyltriketone1). This might reflect the decreased polarization in the former due to dipole-dipole interaction with adjacent conjugated carbonyls and supplement the result of the X-ray analysis. If the intramolecular factors are the major origin of nonplanarity, **1** may well exist in nonplanar conformation even in solution.

Acknowledgement The authors are grateful to Mr. A. Kawamata for experimental assistance.

Table 1 PMR and CMR spectra11)

	δ (ppm)						J_{H-H} (Hz)			
positions	1(3)	2	4(7)		5(6)		4,5(6,7)	5,6	4,6(5,7)	4,7
			C	H	C	H				
1	188.7	185.5	131.4	6.44	137.1	7.01	12.59	8.26	0.58	0.75
312)	180.4		130.8	6.35	139.7	7.19	9.89	5.88	1.52	0.99

References and Footnotes

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10) **1** gave an irreversible redox wave; and only one potential, showing instability of the anion radical under the condition employed. We are grateful to Prof. N. Tanaka, Dr. Y. Kato and Dr. T. Ogata for their measurement of $E_{1/2}$. o-Benzoquinone· M.E. Peover, J. Chem. Soc., 4540 (1962).

11) PMR measured in acetone-d_6, CMR CD_3CN (for **1**) and $CDCl_3$ (for **3**)12). All chemical shifts were expressed by δ from TMS. Analyses of AA'BB' systems in PMR were carried out using Swalen's program. [J.D. Swalen and C.A. Reilly, J. Chem. Phys., 37, 21(1962)]. PMR Spectrum of **1** isolated is slightly different from that reported previously5). This difference might originate from the interactions of **1** and 2,3-dichloro-5,6-dicyanohydroquinone.

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