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HEPTAFULVALENE-3,4-DIONE, A NOVEL p-TROPOQUINONE METHIDE-TYPE COMPOUND

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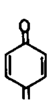
Abstract: The title compound has been synthesized and its physico-chemical properties have been clarified, providing valuable informations to characterize p-tropoquinone methide system.

p-Tropoquinone methide 2 and its derivatives have remained vertually unknown so far whereas p-tropoquinone, a 7-membered analogue of p-benzoquinone, has been synthesyzed by S. Ito et al..[1] We have recently disclosed the fundamental properties of [6.7]quinaren-9-one 3,[2] a compound in which the exo-methylene of p-benzoquinone methide 1 is replaced with a cycloheptatrienylidene group. Therefore our attention has been focused on clarifying the properties of heptafulvalene-3,4-dione, a novel tropoquinone methide derivative, 4. The comparison of 4 with 3 would provide the valuable informations to characterize 2, since the theoretical calculations of these compounds predict that the frontier MO characters of 1 and 2 would be well succeeded to those of 3 and 4, respectively. From these viewpoints, 4 has now been synthesized and its essential features have been evaluated on the basis of its physico-chemical properties and MO calculations.

5-(7-Tropyl)tropolone[3] was first thermally isomerized and then treated with trityl fluoroborate to give 5.[4] A dichloromethane solution of 5 (2.8×10^{-3} mol/l) was treated with 1.0 equivalent of triethylamine at -70 °C under argon atmosphere to afford a deep blue solution of 4, which was structurally elucidated by 200 MHz ^{1}H NMR spectral analysis of the solution [Fig. 1: $\delta(CD_2Cl_2)$ 6.84 (d, J=12.5 Hz, H-2,5), 7.64 (d, J=12.5 Hz, H-1,6), 7.72~8.08 (m, mc=7.90, H-8~11), 8.33 (br.d, J=10.3 Hz, H-7,12)]. Compound 4 is too unstable to be isolated in a solid state, but is rather stable as a solution in polar solvents.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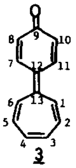

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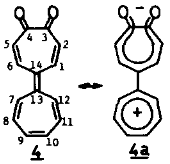

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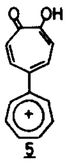
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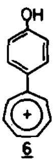
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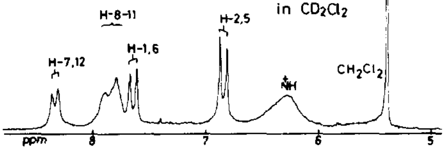
Fig.1. ^{1}HNMR spectrum of 4 at -35°C in CD_2Cl_2



A diatropicity of the cycloheptatrienylidene ring of 4 induced by the contribution of 4a is much suggestive. The ^{1}H NMR chemical shifts of H-8~11 of 4 are by 2.3 and 0.9 ppm downfield from those of H-2~5 of heptafulvene and H-3~6 of tropone, respectively, whereas which are by 1.29 ppm highfield from those of the corresponding protons of 5. In addition the cycloheptatrienylidene ring of 4 is more diatropic than that of 3, since the signals for H-8~11 of 4 appear 0.92 ppm downfield from those for H-2~5 of 3.[2] This means that the electron withdrawing capability of p-tropoquinonoid moiety is more significant than that of p-benzoquinonoid one in acting toward the cycloheptatrienylidene moiety. Actually, the extent of the net charge separation is shown to be greater in 4 than in 3 (the total electron density at phenoxy part is -0.208 e) by CNDO/2 method calculations (Fig. 2).

Noticeably however, the charge on each O atom of 4 is far lesser, even though the sum of the

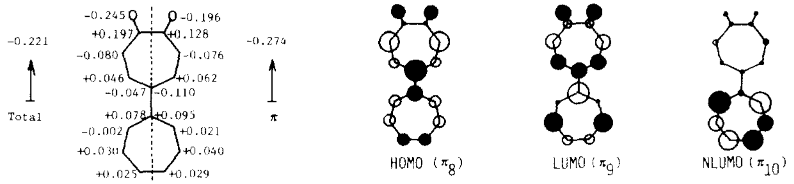


Fig. 2. Total and π charge densities and 2pπAO coefficients of frontier MOs calcd. by CNDO/2 method on 4.

charges on the two O atoms is greater, than that of 3 (total electron density: -0.319 e). According to CNDO/S and PPP-CI calculations,[5] the electronic spectral E1 band ($\pi_8 \rightarrow \pi_{10}$), observed as a shoulder of the E2 band ($\pi_8 \rightarrow \pi_9$), is regarded to be an intramolecular C-T band since the π_8 exhibits relatively large 2pπAOs on the dioxo-ring and the π_{10} is characteristic of one of the degenerate LUMOs of tropylium ion (Fig. 2).

The HOMO level of 1 (-11.32 eV) is about 0.41 eV higher than that of 2 (-11.73 eV) in CNDO/2 calculations. In addition, the π-HOMO coefficient at O atom (0.5410) of 1 is very large while that of 2 (0.2638) is relatively small compared with those of other carbons of respective compounds. Although the exo-methylene carbons of 1 and 2 carry very large π-LUMO coefficients (0.5371 and 0.4922, respectively), the LUMO of 2 (-0.03 eV) lies at 0.48 eV lower level than that of 1 (+0.45 eV). Such frontier MO features of 1 and 2 correspond fairly well to those of 3 and 4, respectively. Not only the electron density at O atom of 4 is relatively small in the HOMO, but also the HOMO of 4 (-8.94 eV) lies at 0.185 eV lower than that of 3, predicting the poor nucleophilicity of 4 compared with that of 3. Actually, the observed pK_a value for 5, 2.31 ± 0.05 in 50% aqueous acetonitrile, is about 2.67 smaller than that of 6 (pK_a = 4.98 ± 0.03). In a solution of higher concentration 3 causes an intermolecular head-to-tail reaction to give its oligomer,[2] while 4 can exist as a monomer because of the poor nucleophilicity of the oxygen atom. The observed low reduction potentials of 4 (E_1 = -0.45 V, E_2 = -0.84 V vs SCE in MeCN) are in good correspondence with the calculated low LUMO energy level of 4 (-0.06 eV, 0.28 eV lower than that of 3).

Polyolefinic heptafulvalene molecule 7 is distorted into the shape of the letter S[6] due to the steric interference between the opposite ortho protons to the pivot bond in two rings. In 4, however, not only the rings themselves seem to be planar as judged from the diatropicity (vide supra), but also co-planarity between the two rings appears to be not so distroyed as revealed by the high electronic spectral absorption intensity of the E2 band.[7] This would mainly result from the resonance stabilization energy which overcomes the steric strain more significantly in 4 than in 7.

References

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2. K. Takahashi, T. Nozoe, K. Takase, and T. Kudo, Tetrahedron Lett., 25, 77 (1984).
3. T. Nozoe, T. Tezuka, and T. Mukai, Bull. Chem. Soc. Jpn., 36, 1470 (1963); The details of our improved procedures for the preparation will be reported eleswhere by T. Morita, K. Moue, K. Takase, and K. Takahashi.
4. 5: Brownish orange crystals, mp. 178-180 °C (decomp.), 55% yield: IR (KBr) 3150, 3030, 1620, 1610, 1570, 1530, 1490 cm^{-1}; UV-VIS (MeCN) λmax 282 nm (log ε 4.02), 350sh (3.92), 366 (3.96), 440 (4.11); ^1H NMR 90 MHz (MeCN) δ 7.52 (d, J=12.0 Hz, H-2,5), 7.89 (d, J=12.0 Hz, H-1,6), 9.19 (br.s, $W_{\frac{1}{2}}$=8.0 Hz, H-7~12).
5. The observed transition energies, E1 at 2.18 eV and E2 at 2.54 eV (in benzene) are well reproduced by PPP-CI calculations to take place at 2.62 eV (oscillator strength f=0.021) and 2.82 eV (f=1.51), respectively.
6. R. Thomas, P. Coppens, Acta Cryst., B28, 1800 (1972).
7. Full data of UV-VIS spectrum of 4 (in MeCN): λmax 236 nm (log ε 4.30), 280 sh (3.64), 294 (3.64), 343 (3.86), 545 (E2) (4.30). E1 band goes behind the tail of E2 in acetonitrile.

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