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Electronic Structural Characterization of Cycloheptadienequinone and Cyclopentenequinone Systems on the Models of 2,3,4,5-Dibenzo-7,8-diphenylheptatriafulvalene-1,6-quinone and 5,6-Diphenylcalicene-1,4-quinone

Norio NAMEKATA, Kahei TAKASE, and Kazuko TAKAHASHI*
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

The title heptatriafulvalene- and calicene-quinones have been synthesized. The difference in the degree of the charge separation between these quinones has been ascribed to the increasing contribution of pseudo 6π and 4π electron peripheries in the 7- and 5-membered rings to the respective polarized canonical structures.

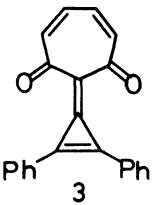
Importance of the quinonoid compounds have been documented extensively in recent years in relation to synthetic dyes applicable to opto-electronics and new-type of redox systems for organic conductors or photoconductors. Non-benzenoid quinonoid compounds will surely bring a significant contribution to these fields, because they have a functionally new type of structure capable of developing novel properties which have never been created by benzenoid systems. From this point of view, it has become important to clarify fundamental properties of these quinones.

In typical odd-membered non-benzenoid quinones 1 and 2 having an electron donating π-electron system X,[1)] stabilization and destabilization effects brought about by π charge transfer from πMO of X to the odd-membered ring unit can in principle be reversed between 1 and 2 because the 7-membered ring of possible dipolar structure 1b incorporates pseudo aromatic 6π electrons while the 5-membered ring of 2b does pseudo antiaromatic 4π electrons.

1a 1b 2a 2b

Therefore, an essential electronic structural difference mainly attributable to such aromatic and antiaromatic contributions should be revealed between these quinones 1 and 2.

It has been suggested that 2-diazo-4,6-cycloheptadiene-1,3-dione (1, $X=N_2$) has a significant contribution of enolate canonical form 1b, while the 2-diazo-4-cyclopentene-1,3-dione (2, $X=N_2$) has a lesser contribution of 2b to their ground states based on the spectroscopic data of their dioxo rings;[2)] however, unfortunately, the diazo groups did not afford useful spectral data to differentiate the electronic structures of 1 and 2. To get a further information on this regard, heptatriafulvalenequinone 3 and calicenequinone 5 would serve as more ideal models for the differentiation between quinones 1 and 2, respectively, because these compounds have an electron donating hydrocarbon chromophore retaining a good coplanar conformation as the whole molecules and therefore would be promising to deposit definite informations for judging their conjugative interaction.3) Although attempts to synthesize 3 were failed, we have now synthesized the title quinones 4, 5, and the reference compound 6, and obtained secure evidence which supports the argument mentioned above.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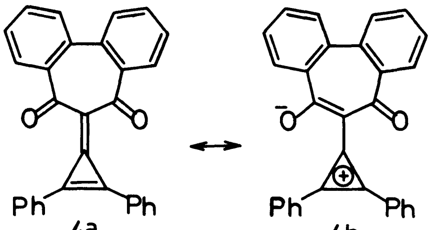
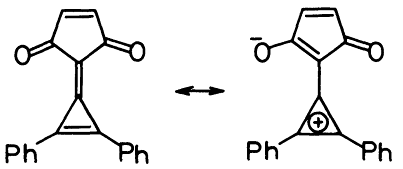
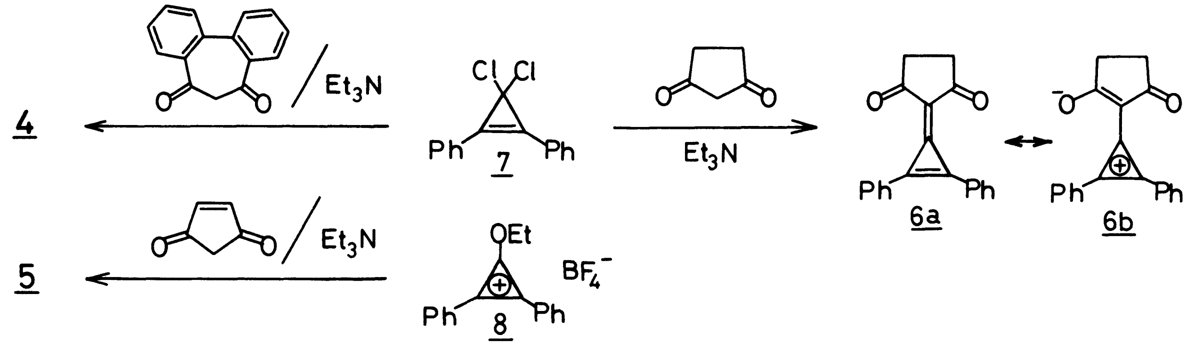

4a 4b


5a 5b

Quinone 4 was successfully prepared in 23% yield as thermally stable crystals by adding a dichloromethane solution of dibenzo-β-tropolone and triethylamine (1 equiv.) into a refluxing dichloromethane solution of 7, followed by a further addition of triethylamine (1 equiv.) into the refluxing reaction mixture. The desired quinone 5 was best prepared in 26% yield by adding triethylamine (1 equiv.) into a solution of cyclopentene-1,3-dione and 8 in dichloromethane at room temperature, followed by stirring the reaction mixture for 1 h. When 7 was treated with cyclopentane-1,3-dione and triethylamine in dichloromethane at room temperature, followed by heating at reflux for 16 h, reference compound 6 was obtained in 22% yield.4) All attempts to prepare 3 by the reaction of β-tropolone with 7, 8, or diphenylcyclopropenium ion were unsuccessful.



^{13}C NMR spectral data of 4, 5, and 6 are shown in Fig. 1.5) The signal of the 3-membered ring carbons carrying phenyl groups of 4 is found downfield by more than 10 ppm from that of 5 and is found downfield by 4.0 ppm from that of reference compound 6. The same carbon signal of 5 appears upfield by 6.5 ppm than that of 6. Concerning to the chemical shift of another carbon of the 3-membered ring constituting the intercyclic bond, the chemical shift of the carbon of 5 is higher by 4.7 ppm than that of 6. The signals of the quinonoid ring carbons situated between two carbonyl groups of 4 and 5 are found downfield by 9 ppm and upfield by 9.5 ppm, respectively, than that of 6. Such an observed difference in chemical shift would be another indication for the charge separation extent,

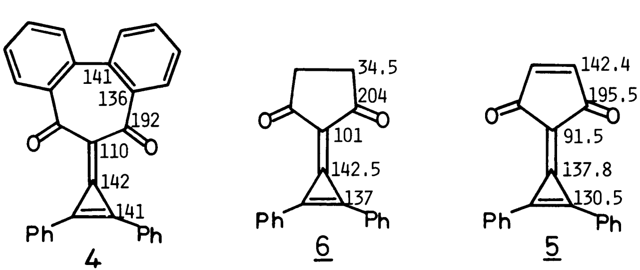


Fig. 1. ^{13}C NMR Chemical Shifts at 50.3 MHz in $CDCl_3$ δ, ppm.

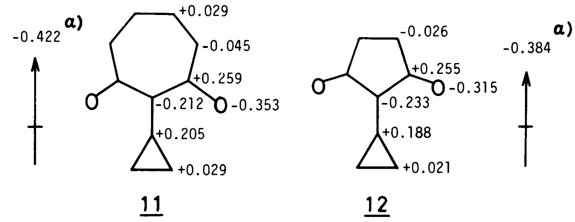
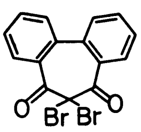


Fig. 2. Total Charge Densities of 11 and 12 Calcd by CNDO/2.

a) Charge densities on the hydrogen atoms are included.

because the signals of these carbons adjacent to the carbonyl groups would shift downfield with an increase in the contributions of 4b, 5b, and 6b in which electron deficient cyclopropenium cation residues are connected directly with these carbons. Thus, from these observations on ^{13}C NMR data, it is clarified unequivocally that the extent of charge separation in 4 is highly enhanced, while that in 5 is considerably weakened as compared with the reference compound 6.

Additional support for this consideration comes from the comparison of the IR spectral carbonyl frequencies of 4 and 5 with those of non-enolizable 9[6] and 10,[7] respectively. The carbonyl frequency of 4 (1605 cm^{-1}) is lower by 85 cm^{-1} than that of 9 (1690 cm^{-1}) and is nearly the same as that of dibenzo-β-tropolone (1600 cm^{-1}). In contrast, the frequency of 5 (1677 cm^{-1}) is lower by only 18 cm^{-1} than that of 10 (1695 cm^{-1}). Therefore, the contribution of 4b to 4 is much more significant than that of 5b to 5 in their ground states.



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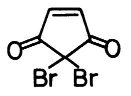

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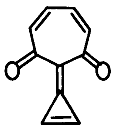

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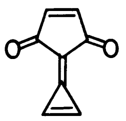

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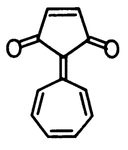

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According to the CNDO/2 calculations, the total electron densities (-0.422 e) on the 7-membered ring moiety and two oxygen atoms of 11 are much greater than those (-0.384 e) on the 5-membered ring moiety and two oxygen atoms of 12 (Fig. 2), that is, a net charge separation is surely increased in 11 as compared with 12. Therefore, the observed difference between 4 and 5 originates unequivocally from the essential electronic structural difference between their parent quinones 11 and 12, which is best ascribed to the increasing contribution of pseudo 6π and pseudo 4π peripheries in the 7- and 5-membered rings to the respective polarized canonical structures.

A different explanation has been reported so far concerning the electronic structural comparison of sesquifulvalene-7,10-quinone 13 with its 8,9-dihydro derivative, describing that, in 13, the electron transfer from the 7-membered ring to the oxygen atoms is restrained by the competition with the one from the C-8,9 double bond (5-membered ring) to the same oxygen atoms; for this reason, the electron transfer from the 7-membered ring is less in 13 than in the dihydro derivative.[8] However, when this idea is extended to the heptatriafulvalenequinone system such as 11 and 4, we should encounter with a definite contradiction, namely, the electron transfer from the 3-membered ring to the oxygen atoms should be restrained more significantly in 11 and 4 than in 12 and 5, respectively, since the carbonyl groups can conjugate more effectively with the butadiene moiety of 11 and the condensed benzene rings of 4 than with the ethylene moieties of 12 and 5. Therefore, 11 and 12 should not be interpreted as simple derivatives of 4,4-diacyltriafulvene.

Quite interestingly, the longest wavelength absorption maximum of 5 (362 nm) in electronic spectrum showed a bathochromic shift of 3 nm from that of 4 (359 nm) in benzene, notwithstanding the former has a shorter conjugation system than the latter. The appearance of the first excitation band in relatively longer wavelength region seems to be a good indication of antiaromaticity of 5, since a pronounced decrease of LUMO-HOMO energy gap has recently been rationalized for various antiaromatic systems.[9)]

References

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2) M. Oda, M. Kasai, and Y. Kitahara, Chem. Lett., 1977, 307.
3) The conjugative interaction has been studied by K. Takahashi, K. Ohnishi, and K. Takase, Tetrahedron Lett., 25, 73 (1984); 27, 5515 (1986).
4) All new compounds gave satisfactory elemental analyses, and the following physical and spectroscopic data;
   4: Pale yellow needles, mp 249-300 °C (dec), MS m/z 412 (M^++2, 14%), 411 (M^++1, 50%), 410 (M^+, base), 382 (M^+-CO, 25%); IR (KBr) 3060, 1820, 1605, 1595, 1570, 1458, 1422 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33-7.73 (12H, m, condensed benzene rings, and meta- and para-positions of Ph), 7.80-8.01 (2H, m, peri positions to CO), 8.30-8.53 (4H, m, ortho-positions of Ph); ^{13}C NMR (Fig. 1); UV-VIS (in MeCN) λ max nm (log ϵ) 240 (4.63), 250 sh (4.60), 282 sh (4.13), 355 (4.52).
   5: Yellow needles, mp 204-205 °C, MS m/z 286 (M^++2, 4%), 285 (M^++1, 23%), 284 (M^+, base); IR (KBr) 3070, 1875, 1840, 1677, 1658, 1600, 1515, 1483 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.86 (2H, s, H-2,3), 7.53-7.71 (6H, m, meta- and para-positions of Ph), 8.53-8.77 (4H, m, ortho-positions of Ph); ^{13}C NMR (Fig. 1); UV-VIS (in MeCN) λ max nm (log ϵ) 223 (4.45), 228 sh (4.40), 233 sh (4.35), 238 sh (4.29), 258 (4.23), 305 sh (4.49), 315 (4.56), 348 (4.12).
   6: Pale yellow needles, mp 239-241 °C (dec), MS m/z 288 (M^++2, 4%), 287 (M^++1, 21%), 286 (M^+, base), 258 (M^+-CO, 7%), 230 (M^+-2CO, 38%); IR (KBr) 3050, 2910, 1821, 1640, 1488, 1455, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65 (4H, s, H-2,3), 7.50-7.77 (6H, m, meta- and para-positions of Ph), 8.60-8.87 (4H, m, ortho-positions of Ph); ^{13}C NMR (Fig. 1); UV (in MeCN) λ max nm (log ϵ) 227 (4.46), 253 sh (4.13), 263 (4.21), 327 (4.52).
5) The chemical shift assignments were made by proton off-resonance decoupling method, signal intensities, and comparison with the signals of structurally analogous compounds.
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