SYNTHESIS AND PROPERTIES OF 7-(2,3-DIPHENYLCYCLOPROPENYLIDENE)-1,6-METHANO-2(7H)-
[10]ANNULENONE.
A [3.10]QUINAREN-5-ONE DERIVATIVE HAVING POLYOLEFINIC CHARACTER[1]

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The title quinarenone 2, in which the electron donating and
electron accepting groups are located at the separate sites
bisected by the 1,6-methano bridge, has been prepared. This
compound has a preferable contribution of quinonoid resonance
structure 2a to dipolar structure 2b in the ground state in order to
maintain the weak conjugation between the two terminal chromophores,
steming the C-1,6 overlap.

In the course of our study on quinarene[2] and quinarenone[3] systems, we
clarified that the extent of the conjugative interaction between two terminal
chromophores appears to be proportional to the aromatizability of the inserted
quinonoid system in qualitative sense. In bridged [3.10]quinarenone 1,[4] a 1,6-
methano[10]annulene ring inserted diphenylcyclopropenone, we found an apprecia-
ble degree of conjugative interaction between the 3-membered ring and carbonyl
group revealing a considerable extent of aromatizability of the methylene-1,6-
methano[10]annulenone moiety, and also found some transannular overlap between the
two bridgehead carbons inducing a homobenzene type ring current at the cyclohepta-
triene residue of the inserted ring. In order to get a further insight on the
aromatizability of a methylene-1,6-methano[10]annulenone system in the sense of the
proposed 10 π peripheral nature,[5] we have now prepared 2, a novel system carrying
the electron donating cyclopropenylidene group and the electron accepting carbonyl
group at the separate sites bisected by the bridgehead carbons of a 1,6-methano[10]-
annulene ring, in which the C-1,6 transannular overlap interferes the conjugative
interaction between the two terminal chromophores in contrast with 1.
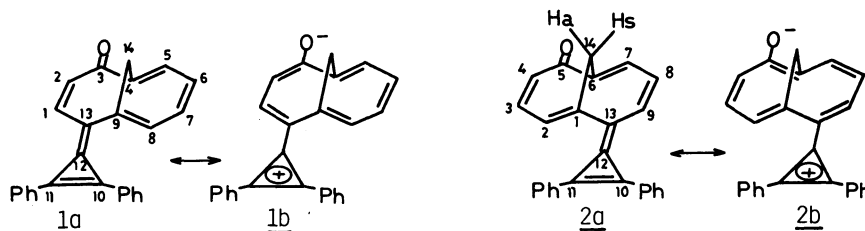
A starting key compound, 2-bromo-7-styryl-1,6-methano[10]annulene 3,[6] was
obtained by Wittig reaction of 2-bromo-7-formyl-1,6-methano[10]annulene[7] with
benzylidenetriphenylphosphorane. A dichloromethane solution of 2,3-diphenyl-1-(6-
hydroxy-2,7-methano[10]annulenyl)cyclopropenium ion 8 (1.47 X 10^{-2} mol/l), obtained

from $\underline{3}$ according to the following scheme,[6] was then treated with an equimolar amount of triethylenediamine at -40 °C under argon atmosphere to afford a reddish violet solution, which was submitted immediately to the 200 MHz ^{1}H NMR spectral analysis. By off-resonance decoupling and temperature variation experiments, $\underline{2}$ was shown to exist in equilibrium with its oligomer $\underline{9}$.[8] Compound $\underline{2}$ was not isolable as a solid state. In dichloromethane solution of the above concentration, $\underline{2}$ was stable below 0 °C but collapsed at room temperature within a half day.
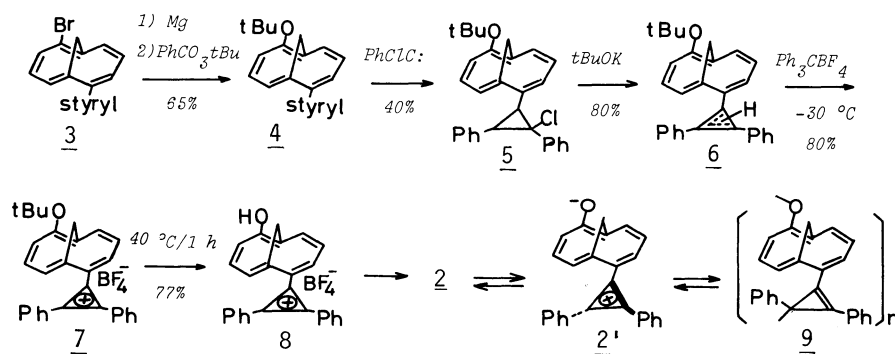
The ^{1}H NMR chemical shifts of the 10-membered ring protons of $\underline{2}$ are found at higher field than those of the corresponding protons of $\underline{1}$[4] and the difference (1.18 ppm) in the average chemical shifts of the 10-membered ring protons between $\underline{2}$ and its conjugate acid $\underline{8}$ is twice as large as that (0.51 ppm) between $\underline{1}$ and its conjugate acid $\underline{10}$. The vicinal coupling constants $J3,4$ and $J2,3$ of $\underline{2}$ are 1.7 Hz larger and 0.9 Hz smaller, respectively, than the $J6,7$ and $J7,8$ values of $\underline{1}$, revealing a noticeable bond fixation in the 10-membered ring of $\underline{2}$. The bridged methylene protons H-s and H-a of $\underline{2}$ are found 2.2 — 2.6 ppm downfield from those of $\underline{8}$ indicating decrease in induced diatropic ring current on the 10-membered ring of $\underline{2}$. The chemical shift difference in the phenyl protons between $\underline{2}$ and $\underline{8}$ (0.3 — 0.45 ppm) is greater than the difference in the corresponding protons between $\underline{1}$ and $\underline{10}$ (0.18- 0.26 ppm), which is ascribable to a less contribution of $\underline{2b}$ to $\underline{2}$ than that of $\underline{1b}$ to $\underline{1}$. Thus $\underline{2}$ is characterized to be a polyolefinic compound having a slight conjugative interaction between the terminal chromophores. This conclusion on $\underline{2}$ is supported also by such electronic spectral solvent effect on the $\pi - \pi^*$ transition at around 520 nm which showed a red shift by 18 nm on going from benzene to acetonitrile.[9] Quite impressively $\underline{2}$ is the first example to show a solvent effect

Table 1. ^{1}H NMR spectral data of $\underline{2}$ and $\underline{8}$ at +10 °C; $\underline{2}$ in CD_2Cl_2, $\underline{8}$ in CD_3CN (200 MHz, δ:ppm, J:Hz)

Compd.	H-a	H-s	H-2	H-3	H-4	H-7	H-8	H-9	Phenyl protons ortho-H	m,p-H
$\underline{2}$	3.08 ddd	2.01 ddd	5.44 ddd	6.94 dd	6.25 d	6.86 ddd	6.16 dd	7.44 d	8.17 mc	7.71 mc
	$Ja,s=10.0$, $Js,2=0.8$, $Js,7=0.5$, $J2,3=5.5$, $J3,4=12.0$, $J7,8=6.0$, $J8,9=11.0$									
	$Ja,2=0.4$, $Ja,7=0.2$									
$\underline{8}$	0.49 dd	-0.16 dd	7.21 dd	7.48 dd	6.96 d	8.29 dd	7.60 dd	8.62 d	8.62 mc	8.01 mc
	$Ja,s=10.5$, $Js,2=1.2$,		$J2,3=8.5$, $J3,4=10.5$, $J7,8=8.5$, $J8,9=10.0$							
	$Ja,7=0.1—0.2$									
Δб	-2.59	-2.17	1.77	0.54	0.71	1.43	1.44	1.18	0.45	0.30

of red shift in the cross-conjugated compounds such as fulvenes, fulvalenes, quinarenes, and quinarenones carrying a highly electron donating diphenylcyclo-propenylidene group. Coplanarity of the 3-membered ring to the 10-membered ring of 2 is not markedly destroyed because no significant hypochromic effect is seen in the electronic spectral 1st excitation band of 2 (log ϵ = 4.40) as compared with that of 1 (log ϵ = 4.54).[4,10]

A useful information to rationalize the reason for the polyolefinic character of 2 has been provided by the PPP-SCF MO calculations on 2. As shown in Fig. 1 ($\beta_{1,6}$ = -0.48 eV),[11] the π-HOMO of 2 exhibits antibonding orbitals on C-1,6 and considerably large $2p\pi$ AO's on the oxygen atom, the 3-membered ring, and the [10]-annulene residue, while the π-NHOMO exhibits bonding orbitals on C-1,6 and $2p\pi$AO's only on the [10]annulene residue. The π-HOMO and the π-NHOMO are destabilized and stabilized, respectively, with the increase of cross ring resonance integral, $\beta_{1,6}$, and the stabilization extent of the π-NHOMO is apparently greater than the destabilization extent of the π-HOMO. In addition, the electron densities at the left side and the right side of the bridge progressively increase and decrease, respectively, with the increase of $\beta_{1,6}$.

Fig. 1.

The $2p\pi$ AO coefficients in the occupied MO's of 2 calcd. by the PPP·SCF MO method.

HOMO   NHOMO
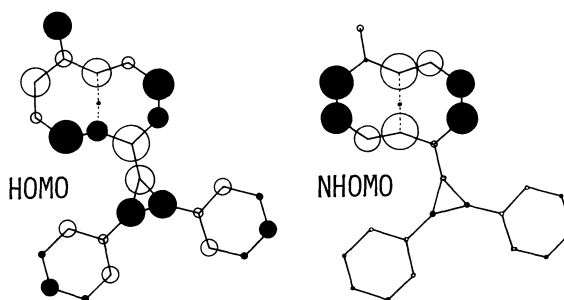
Therefore, it follows that the C-1,6 overlap is inevitably developed in the charge separated structure 2b. The C-1,6 overlap reasonably interferes the conjugative stabilization interaction between the oxygen atom and the cyclopropenium ion, whereas stabilizes only the 1,6-methano[10]annulene residue, thereby making 2b markedly destabilized, in contrast to the conjugate acid 8 having an hydroxyl group instead of the oxygen anion,[12] because the highly negatively charged oxygen atom on the left homobenzene residue of 2b conjugates only sluggishly with the cyclo-propenium ion on the right homobenzene residue due to the increased C-1,6 overlap. Whereas the strain energy of the bridged 10-membered ring appears to increase with the contribution of the quinonoid structure 2a, 2 nevertheless exists in the strained structure in the ground state.[13] This is probably due to the fact that the development of the transannular overlap in 2 is stemed to a minimum extent only in a quinonoid-like structure such as 2a which maintains the weak conjugation between the two terminal chromophores. This reveals the relatively weak and critical nature of 10π peripheral conjugation in 1,6-methano[10]annulene residue of 2.

Compound 2 exists in equilibrium with its oligomer 9 in a dichloromethane solution of 1—2 X 10^{-2} mol/l concentration, while 1 exists as a monomer, not forming an oligomer, in dichloromethane solution of the same concentration. This is quite reasonable because the ground state of 2 is considered to be destabilized

due to the strained polyolefinic character and because of the increased basicity of the oxygen atom in the zwitterionic twisted conformer 2'. The nucleophilicity of 2' would be large enough to get into intermolecular reaction due to the difficult intramolecular electronic interaction.

References

1) Cyclic Cross-conjugated Hydrocarbons Having an Inserted p-Quinonoid Ring XVII. Part XVI: K. Takahashi, K. Ohnishi, and K. Takase, Tetrahedron Lett., 25, 5685 (1984).

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5) H. J. Dewey, H. Degar, W. Frölich, B. Dick, K. A. Klingensmith, G. Hohlneicher, E. Vogel, and J. Michl, J. Am. Chem. Soc., 102, 6412 (1980); R. Boschi, W. Schmidt, and J.-C. Gfeller, Tetrahedron Lett., 1972, 4107.

6) 3: Yellow oil, (trans : cis = 8 : 5), 94% yield; ^{1}H NMR (CDCl$_3$) δ -0.26 and -0.08 (two dd, J = 10.0 and 1.0 Hz, H-11, trans), -0.42 and -0.22 (two dd, J=10.0 and 1.0 Hz, H-11, cis), 6.58 —7.70 (m, 13H, other protons).

   4: trans:cis = 2:1, Orange oil, ^{1}H NMR (CDCl$_3$) δ -0.26 (br.s, H-11 of trans isomer), -0.47 and -0.36 (two dd, J=10 and 1.0 Hz, H-11 of cis isomer).

   6: Yellow orange solid, mp 46.5 —57.0 °C.

   7: Orange needles, mp 143 °C (decomp.), IR (KBr) 3030, 2980, 1815, 1600 cm^{-1}.

   8: Deep orange needles, mp 211— 212 °C (decomp.), 63% yield; IR (KBr) 3400, 3070, 1832, 1600, 1488, 1428, 1400, 1076 cm^{-1}; λ max (MeCN) nm (log ϵ) 239 (4.34), 263 (4.36), 304 (4.46), 342 (4.19), 480 (4.28); ^{1}H NMR (Table 1).

7) K. Takahashi, K. Ohnishi, and K. Takase, Chem. Lett., 1985, 1079.

8) Oligomer 9: Yellow powder, mp 200 —210 °C, IR (KBr) 3030, 2940, 1838, 1800, 1600, 1485, 1441, 1315, 1230, 1180, 1080 cm^{-1}; MS (170 °C, 25 eV) m/e (%) 346 (M^{+}-monomer, 83), 32 (12), 105 (100); ^{1}H NMR (CD$_2$Cl$_2$) δ -0.90 (dd, J=10.0 and 1.0 Hz, H-s or H-a), -0.80 (dd, J=10.0 and 0.5 Hz, H-s or H-a), 6.42 (d, J=9.5 Hz, H-4), 6.48 (1H, br.d, H-2), 6.70 (1H, dd, J=9.5 and 9.2 Hz, H-3), 7.15 (2H, m, H-9,8), 7.39 (1H, br.d, J=8.0 Hz, H-7), 7.52 (mc, 6H, Ph-meta, para), 7.81 (mc, 2H, Ph-ortho), 7.42 (mc, Ph-ortho).

9) Quinarenone 2 exists as a monomer in a dilute solution for electronic spectral measurements (1— 5 X 10^{-5} mol/l): λ max (MeCN) nm (log ϵ) 270 (4.27), 296 (4.13), 372 (3.72), 520 (4.40).

10) K. Takahashi, T. Sakae, and K. Takase, Chem. Lett., 1978, 237.

11) The orbital symmetry behavior of the frontier orbitals of 2 remains unchanged with the variation of $\beta_{1,6}$ in the range of 0— -0.96 eV.

12) The charge separation extent is greater in 8 than in 10, the conjugate acid of 1, since the ^{13}C NMR chemical shifts of the 3-membered ring carbons (C-10,11) and C-5 of 8 are 2.4 ppm downfield and 10.6 ppm upfield, respectively, from those of the corresponding carbons of 10.

13) The strained structure of the bridged 10-membered ring of 2 is revealed by the unusual large syn-type long range couplings between H-s and H-7, and H-a and H-2 in ^{1}H NMR spectrum of 2 (Table 1).