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CHARACTERIZATION OF 4-(2,3-DIPHENYLCYCLOPROPENYLIDENE)CYCLOHEXA-2,5-DIENONE.[1)]
HIGHLY POLARIZED 6,7-DIPHENYL[3.6]QUINAREN-3-ONE

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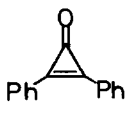
Summary: The title quinarenone 2 *has a pronounced contribution of the dipolar resonance structure to the ground state, and the three-membered ring of* 2 *is more diatropic than that of diphenylcyclopropenone. The quinarenone* 2 *exists in equilibrium with its oligomer in solution. The excited state properties of* 2 *have also been described.*

The title quinarenone 2,[2)] a benzene ring-inserted type compound of diphenylcyclopropenone 1, is one of the most fundamental key compounds in inserted type annulenones. Although 2 was synthesized by A. S. Kende for the first time in 1963,[3)] any physical data to clarify its electronic structure have not yet been known so far because of its intractability. We have now reinvestigated this undefined compound 2 and have characterized that 2 has the largest contribution of π charge transfer interaction to the ground state in the annulenone and inserted type annulenone series known so far. The kinetic properties closely related to difficulty in handling 2 have also been clarified. These are reported in the present article.

Cyclopropenium ion 3[4)] (5.4×10^{-3} mmol), conveniently available according to our improved procedure by treating 4-(diphenylcyclopropenyl)-t-butoxybenzene[5)] with triphenylmethyl fluoroborate in dichloromethane at -30 °C, followed by warming to room temperature, was allowed to react with an equimolar amount of diisopropylethylamine in dichloromethane-d_2 (0.3 ml) at -40 °C under argon atmosphere to afford a light orange solution (A). The solution (A) reproduced quantitatively 3 on treating with boric acid.



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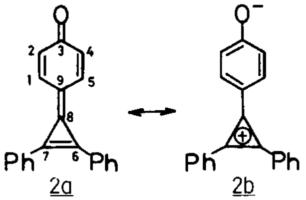
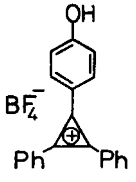


2a 2b

2



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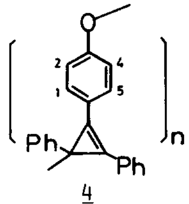


4

Attempts to isolate 2 having failed, the existence of 2 was clearly evidenced by 200 MHz ^{1}H NMR spectral determination of the above-described solution (A) at +5 °C, as given in Figure 1. Quinarenone 2 was shown to exist in equilibrium with oligomer 4,[6)] from the off-resonance decoupling and temperature variation experiments (vide post). Oligomer 4 separated out as a colorless solid when 3 was deprotonated in acetonitrile. On mass spectral analysis, 4 exhibited a $[M+2]^+$ peak characteristic to 2 at m/e 284 together with other peaks associated with the subsequent loss of CO and acetylene fragments, indicating that depolymerization occurred under conditions of mass analysis. The structural confirmation for 4 was also deduced from the ^{1}H NMR and IR spectra closely similar to those of 4-(diphenylcyclopropenyl)-t-butoxy-

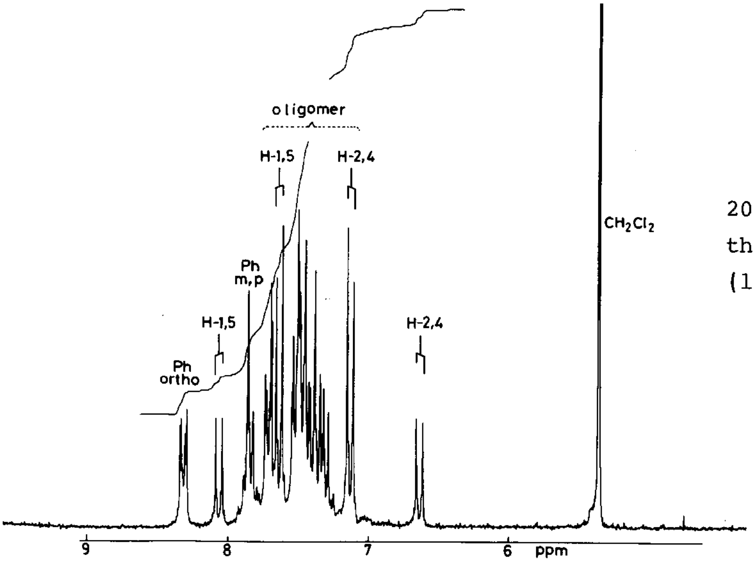


Figure 1.

200 MHz ^{1}H NMR Spectrum of the Solution (A) at +5.0 °C (1 : 2.5 mixture of 2 and 4) in CD_2Cl_2

Table 1. ^{1}H NMR Spectral Data of 1, 2, and 3. (200 MHz, δ in ppm, J in Hz)

		Six-membd. Ring			Phenyl Substituents			
Compd.	Solvent	H-2,4	H-1,5	J-vici.	ortho	meta,para	Δδortho	Δδmeta,para
1	CD_2Cl_2	——	——	——	8.00	7.63	-0.32	-0.22
2	CD_2Cl_2	6.63	8.07	9.5	8.32	7.85	0.00	0.00
3	MeCN	7.31	8.52	9.0	8.56	7.97	+0.24	+0.12

benzene except the signals originated from the t-butyl group.

The ^{1}H NMR parameters of 2 (Table 1) indicate a pronounced contribution of charge separated resonance formula 2b to the ground electronic strucutre. The signals for H-2,4 and H-1,5 appeared at relatively high and low fields, respectively, the chemical shift difference between them amounting to 1.44 ppm. The value of J1,2 (9.5 Hz) in 2 is 0.5 Hz less than the corresponding one of p-benzoquinone methide (10.0 Hz). The proton signals of 6,7-diphenyl groups of 2 appear substantially at lower field than the corresponding ones of 1,2-diphenylcyclopropene (Δδ for ortho-H is 0.62 ppm, Δδ for meta,para-H is 0.47 ppm). The chemical shifts of the former are not so different from those of 3 (Δδ for ortho-H is 0.24 ppm, Δδ for meta,para-H is 0.12 ppm). It is also noteworthy that the ortho and meta,para phenyl proton signals of 2 appear at lower field by 0.32 and 0.22 ppm than the corresponding ones of 1, respectively. This phenomenon is clearly responsible for a marked tendency for aromatization of the central six-membered ring which stabilizes significantly resonance formula 2b and destabilizes 2a.7) The chemical shifts of phenyl protons of 2 are 0.76~0.61 ppm downfield from those of tetraphenyltriafulvene.8) Thus the conjugative interaction between the carbonyl and the terminal odd-membered ring appears to be most significant in 2 among the annulenones and inserted type annulenones reported so far.9)

The quinarenone 2 is not considered to coexist with oligomer 4 in a highly dilute solution for electronic spectral measurements because of the high absorption intensity of the band (E2) at around 390 nm (Fig. 2).10) The two absorption bands E1 and E2 of 2 assigned to the $\pi_s \rightarrow \pi_a^*$

Table 2. Calculated Transition Energies, ΔE(eV) and Oscillator Strength f of 2

Method	Band	Theoretical ΔE (eV)	f	Assignment	Experimental (in dioxane) ΔE (eV)	λmax, nm	log ϵ
PPP-CI	E1	2.48	0.177	$\pi_{11} \rightarrow \pi_{12}$	2.30	540	3.3
	E2	3.35	1.607	$\pi_{11} \rightarrow \pi_{13}$	3.13	396	4.7

and $\pi_s \rightarrow \pi_s^*$ transitions, respectively, by the CNDO/S and PPP-CI methods (Table 2), showed blue shifts of about 60 nm and 12 nm, respectively, on changing the solvent from benzene to to acetonitrile.

By examining the π AO coefficients for the frontier orbitals concerned (Fig. 3),[11] the E1 band is considered to be a C-T band originated from the transition between the phenoxy chromophore as a donor and the diphenylcyclopropenium ion as an acceptor.[12] Thus the intense E1 band would be a good indication for the strong electron donating and electron accepting abilities of the three-membered ring.[13]

The strong conjugative interaction in 2 is also well reproduced by the MO energy diagram (π_a: -14.16, π_s: -8.30, π_a^* : +0.94, π_s^* : +2.11 eV) which resulted from the interaction between the anti-bonding MO's of the diphenylcyclopropenium ion (π_a^* : -3.12, π_s^* : -2.45 eV) and the bonding MO's of the phenoxy chromophore (π_a: -8.76, π_s: -2.87 eV), where the π_s^* of the diphenylcyclopropenium ion lies very closely to the π_s of the phenoxy chromophore.[14]

Figure 2. Electronic spectra of 2.

$1.0 \sim 1.5 \times 10^{-5}$ mol/l

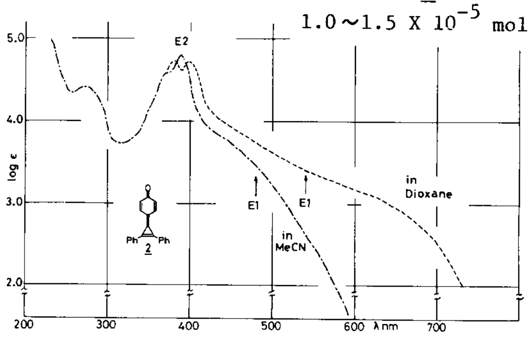
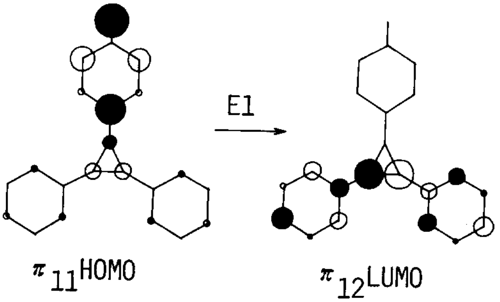
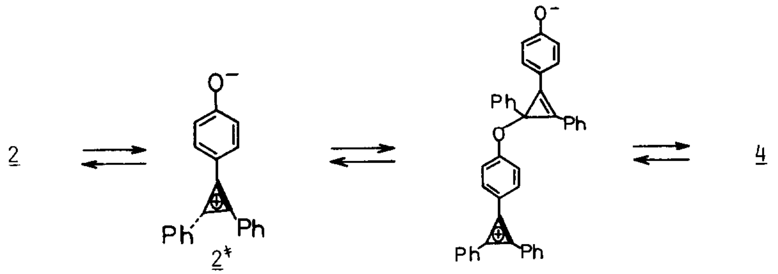


Figure 3.
The 2pπAO coefficients in the MO's responsible for the E1 transition of 2.



The compound 2 collapsed on heating above 30 °C in a dichloromethane solution. At lower temperatures in the same solution (1.8×10^{-2} mol/l), the ratio of 2 : 4 determined from the integration areas of the two doublets at 6.63 (H-2,4 of 2) and 7.13 ppm (H-2,4 of 4) were 1 : 1 at 25 °C, 1 : 1.8 at 15 °C, 1 : 2.5 at 5 °C, and 1 : 3.5 at -10 °C. The compound 4 became a major component below -60 °C. The enthalpy- ($\Delta H°$) and the entropy- ($\Delta S°$) changes for the oligomerization reaction of 2 are thus -5.06 Kcal/mol and -16.6 e.u., respectively. The activation energy (ΔH^*) for the oligomerization of 2 is too small to isolate monomeric 2 in solid state from the solution. Any steric reason raising the potential energy of the ground state is not conceivable in 2 because the molecule is assumed to be sufficiently planar. The observed high reactivity of 2 would be mainly attributable to the highly stabilized aromatic zwitterionic transition state 2^*, through which 2 oligomerizes in a solution of higher concentration, and also supplementarily attributable to the ground state of high dipolarity.



Acknowledgment: We thank Dr. Akio Tajiri, Chemical Institute of Non-aqueous Solutions, Tohoku University, for his help in using the PPP-CI program.

References and Notes

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2. The name "quinarenone" is used for the compound carrying a carbonyl group in a quinarene nucleus. For the name "quinarene", see K. Takahashi et al., Bull. Chem. Soc. Jpn., 47, 2272 (1974); Tetrahedron, 30, 2191 (1974).
3. A. S. Kende, J. Am. Chem. Soc., 85, 1882 (1963).
4. The compound 3: greenish yellow needles, mp. 214~5 °C (decomp.) from acetonitrile; IR (KBr) 3440~3280, 1835, 1600, 1580, 1410, 1290, 1163, and 1077 cm^{-1}; UV-VIS (MeCN) λ max 272 nm (log ϵ 4.27), 342 (4.78); ^{1}H NMR (Table 1); ^{13}C NMR 50.3 MHz (in CD_3CN) (δ ppm) 153.43 (C-6,7), 154.62 (C-8), 167.77 (C-3), 118.68 (C-2,4), 140.69 (C-1,5), 112.33 (C-9), 121.39 (Ph-ipso), 136.32 (Ph-ortho), 131.40 (Ph-meta), 138.74 (Ph-para); Anal. Found: C 68.03, H 4.15. Calcd. for $C_{21}H_{15}OBF_4$: C 68.14, H 4.08%.
5. Colorless oil MS m/e 340 (M^+, 3.3%), 320 (100%); ^{1}H NMR 60 MHz (in $CDCl_3$) (δ ppm) 1.35 (s, Bu^t), 3.19 and 3.52 (two s, 1H, cyclopropene), 6.87~7.70 (m, 14H). Preparation of this compound is as follows: p-Styryl-t-butoxybenzene [colorless oil, 82% yield, δ in $CDCl_3$ 1.30 and 1.33 (two s, Bu^t), 6.43~7.50 (m, 11H, other protons)], obtained by the Wittig reaction of the corresponding aldehyde, was allowed to react with 1.2 equiv. of chlorophenyldiazirine in benzene under reflux (1.5 h) to give p-(2-chloro-2,3-diphenylcyclopropyl)-t-butoxybenzene [colorless oil, 67% yield, δ in $CDCl_3$ 1.24, 1.33, and 1.36 (three s, Bu^t), 3.03~3.27 (m, 2H, cyclopropane), 6.73~7.67 (m, 14H, other protons)]. Dehydrochlorination of the cyclopropane was achieved by the treatment with 1.2 equiv. of potassium t-butoxide in THF at 0 °C (30 min), then at room temperature (15 min).
6. Oligomer 4: mp. 152~154 °C, MS (25 eV, 160 °C) m/e 284 (40%), 283 (5%), 256 (100%), 228 (69%); ^{1}H NMR 200 MHz (in CD_2Cl_2) (δ ppm) 7.13 (d, 2H, J=9.0 Hz, H-2,4), 7.64 (d, 2H, J=9.0 Hz, H-1,5), 7.72 (mc, 2H, Ph-ortho), 7.28~7.55 (mc, 8H, Ph-meta,para); IR (KBr) 3060, 1840, 1810, 1600, 1505, 1415, 1245, 1170, 1120, 960, 840, 765, 692 cm^{-1}; Anal. Found: C 87.65, H 5.10. Calcd. for $C_{21}H_{14}O \cdot 1/3H_2O$: C 87.47, H 5.18%.
7. This sort of conjugation enhancement induced by the inserted six-membered ring is seen also in the [3.6.5]- and [5.6.7]-quinarene systems: K. Takahashi, F. Ishikawa, and K. Takase, Tetrahedron Lett., 1976, 4655; K. Takahashi, and K. Takase, Tetrahedron Lett., 1975, 245.
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10. 2: UV-VIS (MeCN) λ max 275 nm (log ϵ 4.41), 372 sh (4.58), 388 (4.79), 476 sh (3.50).
11. There is no crucial difference in these MO descriptions between the PPP and CNDO/2 methods.
12. It has been reported that 1 shows an intramolecular C-T band: E. Ohsawa, K. Kitamura, and Z. Yoshida, J. Am. Chem. Soc., 89, 3814 (1967).
13. See also the subsequent paper in this series, Part XV.
14. Eigenvalues are calculated by the CNDO/2 method.

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