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ELECTRONIC STRUCTURE AND KINETIC BEHAVIOR OF 4-(CYCLOHEPTATRIENYLIDENE)CYCLOHEXA-2,5-DIENONE (OR [6.7]QUINAREN-9-ONE) AND ITS DERIVATIVES[1)]

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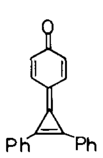
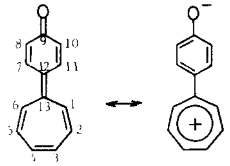
Summary: The conjugative interaction between the two terminal groups in title quinarenone 2 and its chloro- and methoxy-derivatives were evaluated, proving that the diatropicity of the seven-membered ring is a little larger in 2 than in tropone. Some of these quinarenones are also found to exist in equilibrium with their oligomers and show unexpectedly low barriers of rotation about the intercyclic bond.

Tropone has a resonance stabilization which has been considered to be slight judging from the pronounced bond alternation in its crystal structure[3)] and somewhat weak diatropic character observed in its spectroscopic data.[4)] Recently we have described that the benzene ring insertion into diphenylcyclopropenone, giving [3.6]quinarenone (1), enhances significantly the diatropicity of the three-membered ring.[5)] If such an effect of aromatic ring insertion is also responsible for tropone, an enhanced conjugative interaction in [6.7]quinaren-9-one (2) might be expected between the carbonyl and cycloheptatrienylidene groups. There have appeared many papers dealing with the synthesis of 2 over these twenty years,[6)] whereas no accurate physical and chemical data for 2, except its electronic spectral data, have been reported. In order to supply an information concerning the insertion effect, we now report the ground and excited state properties of 2 and its chloro and methoxy derivatives, together with some of their kinetic behavior derived from the ^{1}H NMR spectral data, the characterization of the electronic spectral absorption bands, and the energy barriers for rotation around the intercyclic bond.

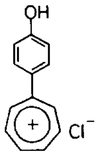


1

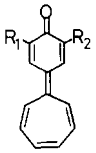


2a 2b

2



3



4: R_1=Cl, R_2=H
5: R_1=R_2=Cl
6: R_1=OMe, R_2=H
7: R_1=R_2=OMe

A dichloromethane solution of chloride 3[7)] (4 X 10^{-3} mol/l) was subjected to reaction with an equimolar amount of diisopropylethylamine at 0 °C under argon atmosphere to generate a deep violet solution, 200 MHz ^{1}H NMR analysis of which revealed the existence of 2 in equilibrium with its oligomer 8.[8)] Like the oligomer of 1,[5)] 8 yielded an intense ion peak at m/e 184, $[M+2]^+$ of the monomer, in its mass spectrum (25 eV, 180 °C). We could also successfully determined the 200 MHz ^{1}H NMR spectra of chloro and methoxy derivatives 4, 5, 6, and 7 in the solutions obtained by treating the corresponding conjugate acids[9,10)] with diisopropylethyl-

Table 1. ^1H NMR Spectral Data of 2, 3, 4, 5, 6, and 7. 200 MHz δppm, J in Hz

Compd.	Temp.(°C)	Solvent	H-8,10	H-7,11	J10,11	H-1,6	H-2∼5	J1,2
3	+5.0	CF_3CO_2H	7.28 d	7.93 d	9.0	9.20	8.87	——
2	+5.2	CD_2Cl_2	6.39 d	7.65 d	10.0	7.42 br.d	6.98	Ca.10
4	-4.6	CD_2Cl_2	6.53 d	7.68 dd 7.93 d	10.0	7.57 br.d	6.94	10
5	+5.7	CD_2Cl_2	——	7.80 s	——	7.57 d	6.97	10
6	-4.4	CD_2Cl_2	6.40 d	6.75 d 7.57 dd	10.0	7.19 br.d 7.34 br.d	6.54	11
7	+5.6	CD_2Cl_2	——	6.64 s	——	7.00 br.d	6.35	12
tropone	+21	CD_2Cl_2	——	——	——	H-2,7 7.11	H-4,5 6.97	

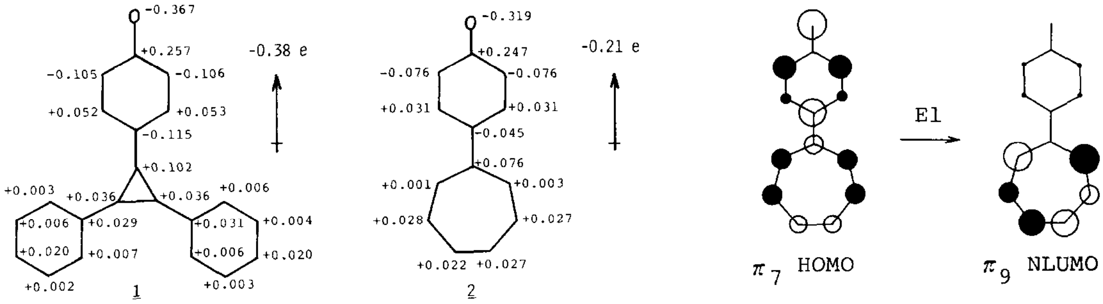
amine in similar manner to that for 2. In these cases, the equilibrium lies so far to the monomer.

The ^1H NMR parameters thus obtained are summarized in Table 1. The value of J10,11 of 2 is 1.0 Hz larger than that of conjugate acid 3 and the chemical shift of the seven-membered ring protons, H-2∼5, of 2 is 1.89 ppm highfield from that of 3. The value of J1,2 of 2 is less than the corresponding ones of tropone (J2,3 = 12 Hz) and heptafulvene (J1,2 = 12 Hz),4a) therefore the π-bond fixation of the seven-membered ring appears to be less in 2 than in the latters, revealing that the aromatic ring insertion into tropone does increase the diatropicity of the seven-membered ring, however the increasing extent appears to be slight, since the chemical shift difference between H-2∼5 of 2 and H-4,5 of tropone is hardly discernible, which is much less than that estimated from the difference between diphenylcyclopropenone and 1.5) Furthermore, the chemical shifts of H-2∼5 of the chloro derivatives 4 and 5 are still in line with that of 2, in addition, those of methoxy 6 and dimethoxy 7 derivatives shift 0.4 and 0.6 ppm upfield, respectively, as compared with that of 2. Thus it can be said that the conjugative overlap between the two terminal chromophores in 2 is readily perturbed by an electron donating substituent at the six-membered ring. In these quinarenones there appears to be a reasonable correlation between δH-2∼5 and J1,2, which would be a reflection of the slight variation in the bond alternation of the seven-membered ring.

The electronic spectral absorption bands at 488 nm of 2, 541 nm of 5, and 478 nm of 7 in acetonitrile11) showed hypsochromic shifts by 24 nm, 26 nm, and 17 nm, respectively, on changing the solvent to benzene.12)

According to the CNDO/2 calculations, the total electron densities on C-8,10 and O of 2 are less than those on C-2,4 and O of 1 (Fig. 1). Consequently, a net charge separation is decreased in 2 as compared with 1. Furthermore, the E1 band of 2 (shoulder at around 2.10 eV), assigned to an intramolecular C-T excitation from the HOMO (π_s) characteristic of a phenoxy chromophore to the NLUMO (π_a^*) characteristic of a tropylium ion, is weaker than the corresponding C-T band of 1 (Table 2).14) Indeed, the π-electron density difference between the two MO's associated with the C-T transition, i.e., the magnitude e which transfers from the phenoxy part to the odd-membered ring in the C-T process, is less in 2 than in 1. The observed relatively weak conjugative interaction in 2, as compared with that in 1, could also be rationalized due to a MO energy diagram yielded by the CNDO/2, where the energy difference

Figure 1.
Total Charge Densities and 2pπAO Coefficients Calcd. by the CNDO/2 Method.



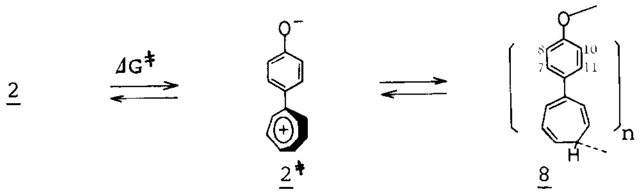
between the HOMO (π_s: -2.87 eV) of the phenoxy chromophore and the degenerate LUMO's (π_s^* , π_a^* : -5.48 eV) of the tropylium ion is larger than the difference between the π_s of the phenoxy chromophore and the π_s^* (-2.45 eV) of the diphenylcyclopropenium ion.[15)]

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

Method	Band	Theoretical			Experimental (in benzene)		
		ΔE (eV)	f	Assignment	ΔE (eV)	λmax, nm	log ϵ
PPP-CI	E1	2.61	0.02	$\pi_7 \rightarrow \pi_9$	Ca.2.10	590	Ca.2.5
	E2	2.93	1.54	$\pi_7 \rightarrow \pi_8$	2.67	464	4.3

In the derivatives 4 and 6, H-1,6 are non-equivalent below -20 °C, which coalesce to a broad signal at -4.6 and +5.6 °C, respectively, thus permitting calculation of the energy barriers for rotation about the intercyclic bond ($\Delta G_c^{\ddagger}$ = 13.4 Kcal/mol for 4, and $\Delta G_c^{\ddagger}$ = 14.0 Kcal/mol for 6). The rotation in 2 would be associated with a barrier having a similar value to that for 4, in regard to the similar structural situations of these compounds. To the best of our knowledge, these are the first determination of a rotational barrier for the cross-conjugated system containing an unsaturated seven-membered ring, and are quite impressively the lowest values recorded until now in the cyclic cross-conjugated compounds composed of C, H, and O. The barrier for 4 is lower by 4.6 Kcal/mol than that for formylcalicene,[16)] whereas the contribution of the corresponding charge separated resonance hybride is much more significant in the latter than in the former. The low barrier obtained here is attributable to the inserted aromatic ring which stabilizes the fully aromatic transition state $2^{\ddagger}$ and destabilizes the ground state contributed mainly by the quinonoid structure 2a.

The relative ratios of 2 to 8 at equilibrium are 1:5 at -5.2 °C, and 1:4 at +15.2 °C in a dichloromethane solution of 3.0 X 10^{-3} mol/l concentration, while 2 exists as a monomer in concentrations of the order of 10^{-5} mol/l. In the cases of 4 and 6, the equilibrium lies so far to the monomer, the oligomers being not detected in the ^{1}H NMR spectra above 0 °C, although they coexist with oligomers at lower temperatures, and their relative ratios of a monomer to an oligomer are 1:2 for 4 and 9:1 for 6 at -40 °C in a dichloromethane solution of 6.4 X 10^{-2} mol/l concentration. Thus the proportion of the monomer in equilibrium increases with decrease in concentration and with raise of temperature. A substituent adjacent to the carbonyl group is also very effective in increasing the monomer at equilibrium, which is best accounted for by steric hindrance for approach of the carbonyl oxygen to the seven-membered ring of an other molecule. No oligomer is detected for 5 and 7 even at low temperatures in solution. The degree of oligomerization n for 8 is not decisive but the oligomers appear to be composed of the species with n = 2~4 judging from the low melting point.



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7. The chloride 3 was prepared more conveniently by starting with the Grignard reaction of the magnesium derivative of 1-bromo-4(cyclohepta-1,3,6-trienyl)benzene with t-butyl perbenzoate, followed by treatment of the resulting butoxybenzene derivative with phosphorus pentachloride in carbon tetrachloride and recrystallization of the precipitate separated from 2N aqueous HCl.
8. Oligomer 8 was isolated as a colorless solid when 3 was treated with triethylamine in acetonitrile. 8: mp. 128~132 °C, MS (25 eV, 180 °C) m/e 184 ([M(monomer)+2]$^+$ 100%), 183 (56%), 182 (14%), 167 (19%), 155 (13%), 128 (14%); ^{1}H NMR 200 MHz (in $CDCl_3$) (δ ppm) 7.10 (d, H-8,10), 7.50 (d, H-7,11), 7.35, 7.0, 6.38, 5.80, 4.32 (tropyl); IR (KBr) 3040, 1605, 1500, 1245, 1180, 1060, 840 cm^{-1}; Anal. Found: C 83.40, H 5.71. Calcd. for $C_{13}H_{10}O \cdot 1/4H_2O$: C 83.62, H 5.66%.
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11. Electronic spectral data (in dry MeCN, 1~2 X 10^{-5} mol/l, at 25 °C, exists as the monomer) λ_{max} nm (log ϵ) 2: 250 (3.83), 270 (3.85), 282 sh (3.77), 320 sh (3.37), 488 (4.40); 4: 269 (3.83), 506 (4.33), 532 sh (4.30); 5: 278 (3.86), 310 (3.62), 541 (4.33); 6: 271 (3.79), 285 sh (3.62), 336 (3.37), 488 (4.32); 7: 353 (3.31), 478 (4.29).
12. The spectral properties of 5 mentioned here are incompatible with the proposed high dipolarity for 8,10-dibromo derivative of 2.[13] These dihalo compounds exhibit only very weak and indistinguishable carbonyl bands in IR spectra at around 1610~1630 cm^{-1}.
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14. The absorption coefficient e and the oscillator strength f of the E1 band for 2 are smaller by about one tenth than those for 1.
15. The CNDO/2 based eigen values for the frontier orbitals of 2 are as follows, π_s: -8.75, π_s^* : +0.22, and π_a^* : +0.94 eV.
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