Tetrahedron Letters,Vol.25,No.49,pp 5685-5688,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

SYNTHESIS AND PROPERTIES OF 5-(2,3-DIPHENYLCYCLOPROPENYLIDENE)-1,6-METHANO-2(5H)-[10]-ANNULENONE (OR 10,11-DIPHENYL-4,9-METHANO[3.10]QUINAREN-3-ONE). CONTRIBUTION OF A HOMOBENZENE STRUCTURE ANNELATED ON [3.6]QUINAREN-3-ONE[1]

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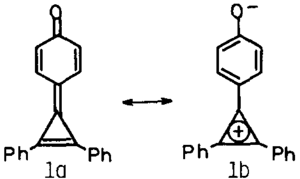
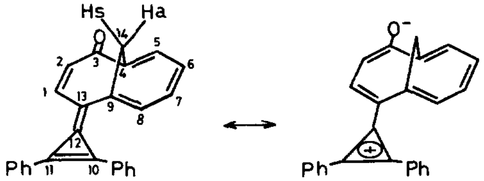
Summary: The title quinarenone 2 has been prepared and proved that the three-membered ring possesses a larger diatropicity than diphenylcyclopropenone and the seven-membered ring exists in a cycloheptatriene (not norcaradiene) tautomer having a contribution of a homobenzene structure. The rotational barrier about the intercyclic bond of 2 is 13.3 Kcal/mol.

We have recently clarified that 6,7-diphenyl[3.6]quinaren-3-one (1),[2] a benzene ring-inserted type diphenylcyclopropenone, has the largest contribution of a π-charge transfer interaction to the ground state in the annulenone and quinarenone (inserted type annulenone) siries known so far, and such a conjugation enhancement is regarded to be developed by the significant aromatizability of the inserted quinonoid ring which stabilizes the charge separated resonance structure 1b. Therefore, through the changes in the π-charge transfer interaction that occur on going from 1 to its 5-methylene-1,6-methano-2(5H)-[10]annulenone analog 2, it appears to be possible to evaluate how the 10-membered cyclic π-system could stabilize the charge separated resonance structure 2b as compared with a benzene ring. It is also fruitful to disclose how the peripheral or transannular interaction in the bridged 10-membered ring[3] could be affected on insertion of this ring system into a cyclopropenone system. From these viewpoints we have now synthesized 4,9-methano[3.10]quinaren-3-one 2, the first one of 10-membered quinonoid ring inserted type cyclopropenones, and compared its properties with those of 1 and mother diphenylcyclopropenone, which are reported herein.

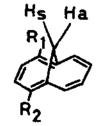


1a 1b

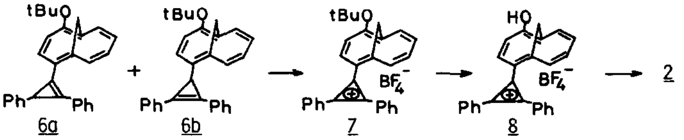


2a 2b

Both of a carbonyl oxygen atom and a cyclopropenylidene moiety were introduced into 1,6-methano[10]annulene according to the procedure as follows: 2-bromo-5-styryl derivative 3,[4] obtained through the highly regiospecific bromination of 2-styryl-1,6-methano[10]annulene[5] with NBS, was first allowed to react with magnesium and then with t-butylperbenzoate to give 4.[6] Treatment of 4 with chlorophenyldiazirine provided cyclopropane 5[7] which upon dehydrochlorination with potassium t-butoxide in THF afforded a 5 : 4 mixture of 6a[8] and 6b,[9] in 92% yield. The mixture can be separated into its components on silica gel column chromatography. Hydride abstraction of the mixture with triphenylmethyl fluoroborate in



3 : R_1=Br, R_2=styryl
4 : R_1=tBuO, R_2=styryl
5 : R_1=tBuO, R_2=Ph_2cyclopropylchloride



dichloromethane at -30 °C gave t-butylated cyclopropenium ion 7,[10] which was easily de-t-butylated *in situ* by warming the reaction solution to room temperature to give conjugate acid 8.[11] When treated with an equimolar amount of pyridine in dichloromethane at -40 °C under argon atmosphere, 8 yielded quantitatively a deep red solution of 2[12] (7.6 X 10^{-2} mol/l), which was evidenced by 200 MHz ^{1}H NMR spectral analysis of the solution (Figure 1). In such a concentration of dichloromethane solution, 2 is stable below 0 °C, whereas decomposed at room temperature within 30 min.[13]

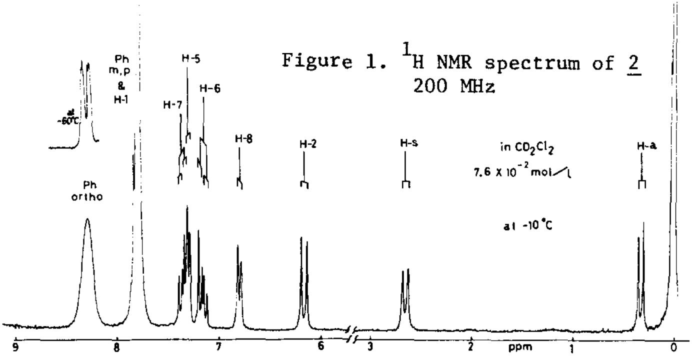
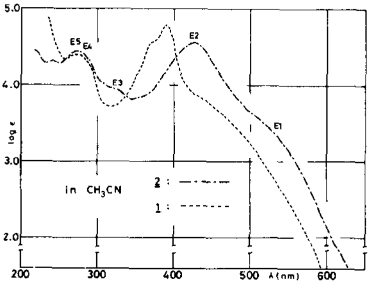


Figure 1. ^{1}H NMR spectrum of 2 200 MHz

Figure 2. Electronic spectra of 1 and 2



According to the geminal coupling constant of the bridge protons (*J*a,s = 10.0 Hz) and the vicinal coupling constant *J*6,7, which is larger than the *J*5,6 and *J*7,8 (Table 1), 2 is considered to exist in a cycloheptatriene tautomer rather than in a norcaradiene tautomer.[14]

The chemical shift difference between H-2 and H-1 of 2 ($\Delta\delta$ = 1.65 ppm) is almost consistent with that of 8 ($\Delta\delta$ = 1.62 ppm). The chemical shifts of the phenyl protons of 2 are 0.5 ~ 0.6 ppm lower than those of 6b, whereas they are 0.18 (Ph-m,p)~0.25 ppm (Ph-o) higher than those of 8, and the latter $\Delta\delta$ values between 2 and 8 are not so different from the $\Delta\delta$ values (0.12 ppm for Ph-m,p, 0.24 ppm for Ph-o) between 1 and its conjugate acid.[2] These observations indicate an appreciable contribution of the dipolar structure 2b to the ground state of 2. Furthermore, the chemical shifts of phenyl protons of 2 are by about 0.2~0.3 ppm lower than those of diphenylcyclopropenone 9, revealing that the diatropicity of the

Table 1. ^{1}H NMR of 2, 8, 4, 9, and 1. 200 MHz *J* (Hz), δ (ppm)

Compound	Solvent	Bridge Protons		[10]Annulene Ring Protons						Phenyl Protons	
		H-a	H-s	H-8	H-5	H-6	H-7	H-1	H-2	ortho-H	m,p-H
2	CD_2Cl_2	0.31	2.67	6.80	7.30	7.19	7.35	7.80	6.15	8.25(2H) 8.34(2H) W/2=12 Hz	7.81 (6H)
		d	ddd	dd	dd	dd	dd	d	d		
		Ja,s=10.0, Js,5=Js,8=0.2, J5,6=J7,8=6.4, J6,7=10.3, J1,2=11.2									
8	CD_3CN	-0.14	0.95	7.40	7.81	7.49	7.62	8.46	6.84	8.56 (4H)	7.95 (6H)
		Ja,s=10.0, Js,5=Js,8=1.0, J5,6≃J7,8=6.4, J6,7=10.0, J3,4=10.0									
4	$CDCl_3$			H-10	H-7	H-8,9		H-3	H-4	——	——
		-0.55	0.26	7.67	7.61	7.20~7.47		7.13	6.61		
		Ja,s=9.8, Js,7=Js,10=1.1						J3,4=10.0			
9	CD_2Cl_2									8.00	7.63
1	CD_2Cl_2									8.35	7.88

3-membered ring is surely enhanced by the insertion of a 1,6-methano[10]annulene ring into 9.

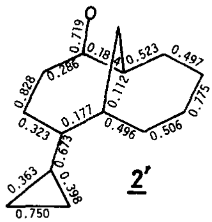
The chemical shifts of H-6,7 of 2, being by 0.82$\sim$0.98 ppm downfield from those of H-3,4 of 1,6-methanocyclodeca-1,3,5-triene, lie in an aromatic region and the difference between the coupling constants J6,7 and J5,6 (J7,8) of 2 is nearly the same as those of 8. Although the signals of both bridge protons H-a and H-s of 2 appear relatively downfield from those of the corresponding protons of 8, the shift of H-a is smaller by about one fourth than the shift of H-s. Thus the $\Delta\delta$ value between H-a and H-s is significantly increased in 2 (2.36 ppm) relative to the corresponding $\Delta\delta$'s for 4 (0.81 ppm) and 8 (1.09 ppm). These facts suggest that an induced homobenzene type ring current[3] is appreciably maintained in the C-4,5,6,7,8,9 region of 2, which results in a deshielding and shielding anisotropic effect on the outer (H-s) and inner (H-a) protons, respectively refered to the homobenzene moiety.

This proposal is further confirmed by the analysis of electronic spectrum of 2. A variety of PPP-CI calculations on 2[15] were thus performed by introducing cross ring resonance integrals, $\beta_{4,9}$ being varied from 0 to -1.5 eV. By comparing the theoretical transition energies obtained in this way with the experimental ones, the most likely value of $\beta_{4,9}$ for 2 was found to be -0.48 $\sim$ -0.72 eV (Table 2), which corresponds to 20 $\sim$ 30 % of the resonance integral for benzene. The occupied orbitals (π_{13} and π_{12}) and the unoccupied orbitals (π_{15} and π_{16}) of 2 are stabilized and destabilized, respectively with the increase of $\beta_{4,9}$, thus resulting in the blue shifts of the E2, E3, and E4 bands. These findings also correlate well with the π-bond orders in 2' (unphenylated) calculated by the CNDO/2 (Figure 3). The broad E1 band of 2 assigned to the $\pi_{13} \rightarrow \pi_{14}$ transition, is regarded to be an intramolecular C-T band, since the π_{13} exhibits large 2pπAO's on C-13, 2, 4, 9, and oxygen atom and the π_{14} is characteristic of one of the degenerate LUMO's (π_a^*) of diphenylcyclopropenium ion. The symmetry behavior of these two orbitals resembles closely that of the π-HOMO and the π-LUMO of 1, respectively.[2]

Table 2. Calculated transition energies ΔE (eV) and oscillator strength f of 2

Theoretical						Experimental(in MeCN)		
Band	Assignment	$\beta_{4,9}$= -0.48		$\beta_{4,9}$= -0.72				
		ΔE	f	ΔE	f	ΔE	λnm	log ϵ
E 1	$\pi 13 \rightarrow \pi 14$	2.38	0.146	2.39	0.148	2.38	520sh	3.36
E 2	$\pi 13 \rightarrow \pi 15$	2.98	0.970	3.04	1.044	2.92	425	4.54
E 3	$\pi 12 \rightarrow \pi 15$	3.70	0.147	3.79	0.109	3.81	325sh	3.92
E 4	$\pi 12 \rightarrow \pi 14$	4.30	0.305	4.39	0.392	4.35	285sh	4.36
E 5	$\pi 11 \rightarrow \pi 14$	4.62	0.598	4.63	0.530	4.52	274	4.44

Figure 3. π-Bond orders of 2' calcd. by the CNDO/2



2'

The ^{1}H NMR signals of the ortho phenyl protons of 2 were consisted of two broad lines (W1/2 = 12 Hz) separated by Ca. 20 Hz with equal areas below -40 °C, and coalesced into a single broad resonance at 8.30 ppm (4H) at -10 °C, giving a rotational barrier about the intercyclic bond $\Delta G_c^{\ddagger}$ = 13.3 Kcal/mol. This value is nearly as low as that for 1. The potential energy of the twisted, zwitterionic, and fully aromatic transition state $2^{\ddagger}$ for the rotation about the intercyclic bond is assumed to be much higher in the case of 2 than 1, since the resonance energy of 1,6-methano[10]annulene (17.2 Kcal/mol) is about 9 Kcal/mol less than that of benzene.[16] Therefore the potential energy of the ground state of 2 has to be higher by nearly the same value than that of 1.

Another feature of interest is the observation that the quinarenone 2 exists as a monomer *in a dichloromethane solution of the concentrations of* $1\sim7$ X 10^{-2} mol/l *at the* temperature which the intramolecular rotation is possible, while 1[2] exists in equilibrium with its oligomer under the same conditions. This difference could be attributable to the poor nucleophilicity of the oxygen atom in the transition state 2^* relative to that of 1, which is just expectable in regard to the fact that the keto form of 2-hydroxy-1,6-methano[10]annulene[17] is sufficiently stable to be isolated whereas the enol form preponderates in DMSO.

References and Notes

1) Cyclic Cross-conjugated Hydrocarbons having an Inserted p-Quinonoid Ring XVI. Part XV: K. Takahashi, T. Nozoe, K. Takase, and T. Kudo, Tetrahedron Lett., 25, 77 (1984).

2) K. Takahashi, K. Ohnishi, and K. Takase, Tetrahedron Lett., 25, 73 (1984).

3) H. J. Dewey, H. Degar, W. Frolich, B. Dick, K. A. Klingensmith, G. Hohlneicher, E. Vogel, and J. Michl, J. Am. Chem. Soc., 102, 6412 (1980).

4) 3: Yellow orange solid, mp. $85\sim106$°C, 70% yield; IR (KBr) 3030, 2950, 1600, 1445 cm^{-1}; MS m/e (%) 324 (M+2, 47), 322 (M^+, 47), 243 (96), 228 (100); ^1H NMR ($CDCl_3$) δ -0.36 (d, J=10 Hz, 1H, H-a), 0.12 (dm, J=10 Hz, H-s), $7.03\sim7.86$ (m, 13H). The appearance of H-a as a sharp doublet while H-s as broad doublet due to long range coupling with H-7 and H-10 reject any other isomers than 3.

5) This compound was obtained by the Wittig reaction of 2-formyl-1,6-methano[10]annulene.

6) 4: Orange oil, 42% yield; IR (neat) 2980, 1600, 1530, 1490, 1450, 1380, 1355 cm^{-1}; MS m/e (%) 316 (M^+, 22), 260 (100).

7) 5: Orange solid, 87% yield, MS m/e (%) 440 (M^+, 6), 384 (39), 349 (100); ^1H NMR ($CDCl_3$) δ -0.68, -0.75, -0.81 (three d, J=10 Hz, 1H, H-a), -0.05, -0.41, and -0.24 (three dm, J=10 Hz, 1H, H-s), 1.42, 1.37, and 1.14 (three s, 9H, tBu, 8:1:5), $3.36\sim3.73$ (m, 2H, cyclopropane), $6.27\sim7.83$ (m, 16H, other protons).

8) 6a: Orange solid, IR (KBr) 1800, 1600 cm^{-1}; MS m/e (%) 404 (M^+-56, 100); ^1H NMR ($CDCl_3$) δ -0.46, -0.48 (two d, J=10 Hz, 1H, H-a), 0.26, 0.36 (two dm, J=10 Hz, 1H, H-s), 1.43 (s, 9H, tBu), 3.33, 3.22 (two s, 1H, cyclopropene, 3:8), 6.69, 6.63 (two d, J=10 Hz, 1H, H-2), $7.08\sim7.95$ (m, 15H).

9) 6b: Orange solid, IR (KBr) 1820, 1600 cm^{-1}; MS m/e (%) 404 (M^+, 4), 348 (M^+-56, 100); ^1H NMR ($CDCl_3$) δ -0.70 (d, J=10 Hz, 1H, H-a), -0.06 (dm, J=10 Hz, 1H, H-s), 1.32 (s, 9H, tBu), 3.77 (s, 1H, cyclopropene), 6.47 (d, J=10 Hz, 1H, H-2), 6.57 (d, J=10 Hz, 1H, H-4), $7.08\sim7.97$ (m, 4H, other protons).

10) 7: Yellow needles, mp. 112°C (decomp.), 66% yield; IR (KBr) 1828, 1600, 1485, 1453, 1430, 1333 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.11 (d, J=10.4 Hz, 1H, H-a), 1.04 (ddd, J=10.4, 0.9, and 0.9 Hz, 1H, H-s), 1.60 (s, 9H, tBu), 7.25 (ddd, J=7.7, 1.6, and 0.9 Hz, 1H, H-8), 7.28 (d, J=10.2 Hz, 1H, H-2), 7.40 (dd, J=9.5 and 7.7 Hz, 1H, H-6), 8.73 (d, J=10.2 Hz, 1H, H-1), 7.52 (dd, J=9.5 and 7.7 Hz, 1H, H-7), 7.69 (ddd, J=7.7, 1.6, and 0.9 Hz, 1H, H-5), $7.86\sim7.94$ (m, 6H, Ph-m,p), $8.50\sim8.59$ (m, 4H, Ph-ortho).

11) 8: Orange needles, mp. $217\sim218$°C (decomp.), 49% yield; IR (KBr) 1828, 1600, 1580, 1503, 1492, 1458, 1432, 1350, 1337 cm^{-1}; ^1H NMR (Table 1).

12) 2 can not be isolated in a monomeric solid due to the instability.

13) In a dilute solution for electronic spectral measurements ($1\sim5$ X 10^{-5}mol/l), 2 is stable at room temperature.

14) 5-(Methyl-1,3-benzodithiolylidene)-1,6-methano-2(5H)-[10]annulenone also was reported to exist in the cycloheptatriene tautomer; R. Neidlein and H. Zeiner, Angew. Chem. Int. Ed. Engl., 20, 1032 (1981).

15) The geometry of 2 is defined by reference to the X-ray parameters of bicyclo[4.4.1]-undeca-3,6,8,10-tetraen-2,5-dion-2-phenylhydrazone and 2,3-diphenyl-4,4-dicyanotriafulvene.

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(Received in Japan 24 July 1984)