Tetrahedron Letters No. 50, pp 4655-4658. 1976. Pergamon Press. Printed in Great Britain.

CYCLIC CROSS-CONJUGATED HYDROCARBONS HAVING INSERTED p-QUINOID RING. VI.1) SYNTHESIS AND SOME PROPERTIES OF A 1-CYCLOPENTADIENYLIDENE-4-CYCLOPROPENYLIDENE-2,5-CYCLOHEXADIENE (OR [3.6.5] QUINARENE) DERIVATIVE.

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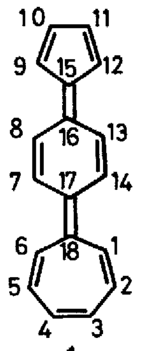
(Received in Japan 23 October 1976; received in UK for publication 11 November 1976)

In a preceding paper, we have reported the synthesis of some derivatives of [5.6.7] quinarene 1 as the first example of a cyclic cross-conjugated three-ring system. Our interest has been centered in a hitherto unknown ring system, [3.6.5] quinarene 2, since this compound has been anticipated to have a relatively large dipole moment (μ_π = 12.85 D) and an appreciable value of resonance energy (R_E/π = 3.2 Kcal/mol) from SCF-π-MO calculation.2) We now report the synthesis and some properties of this type of a new quinarene, 2',5'-dicyano-2",3',3",4'-tetraphenyl-1-cyclopentadienylidene-4-cyclopropenylidene-2,5-cyclohexadiene, or 1,4-dicyano-2,3,7,8-tetraphenyl [3.6.5] quinarene 6.



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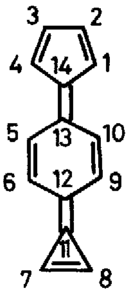

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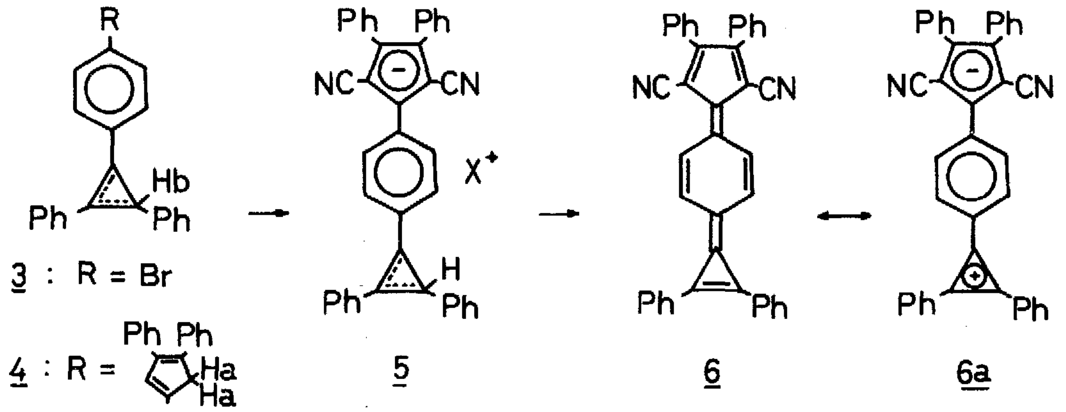
The quinarene 6 was synthesized starting with the addition of p-bromotolan3) with phenylcarbene4) and the treatment of the adduct with hydrogen bromide to give 1-(p-bromophenyl)-2,3-diphenylcyclopropenium bromide5) (mp. 244-5°C ; νmax (KBr) 1410, 1385 cm^{-1}). Lithium aluminum hydride reduction of the cyclopropenium bromide gave a 2:1 mixture of 1-(p-bromophenyl)-2,3-diphenyl- and 3-(p-bromophenyl)-1,2-diphenyl-cyclopropene 3 (mp. 98-111°C ; νmax (KBr) 1820 cm^{-1} ; δ ($CDCl_3$) 3.24(s, 2H), 3.21(s, 1H). After being lithiated with an equi-molar amount of n-butyllithium in ether, the mixture was allowed to react with 2,3-diphenyl-2-cyclopentenone and the product was hydrolyzed with 2N sulfuric acid to produce 4 (mp. 128-135°C ; 38% yield ; ν max (KBr) 1825 cm^{-1} ; λ max (MeCN) 390 nm(log ϵ 4.54) ;



δ (CDCl$_3$) 3.96(Ha), 3.28(Hb)). Deprotonation of 4 with sodium hydride in DME provided a deep red solution of the corresponding cyclopentadienide. The solution was directly submitted to the action of cyanogen chloride, the resulting crude 5a (X=Na) was treated with tetramethyl ammonium chloride and then purified by chromatography over alumina, affording yellow needles 5b (X=NMe$_4$)(mp. 269-270°C ; 10% yield ; νmax (KBr) 2180, 1828 cm^{-1} ; λmax (MeCN) 265 nm(log ε 4.38), 311(4.47), 406 (4.48)). Hydride abstraction of 5b with trityl salt in acetonitrile yielded the quinarene 6 as reddish violet needles (mp.> 300°C ; 97% yield ; νmax (KBr) 3050w, 2180s, 1835w, 1592vs, 1500m, 1489m, 1455m, 1405vs, 1320s, 1300s cm^{-1} ; λ max (MeCN) 274 nm(log ε 4.58), 301(4.58), 315sh(4.55), 540(4.60)).

6 is stable in solid state and in an absolutely dry solvent such as acetonitrile, acetone, chloroform or DMSO. However it is extremely unstable in a wet

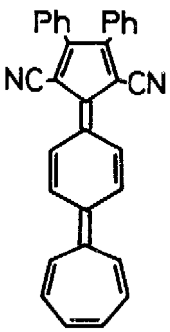
Table 1 : NMR spectral data of 6, 10, 5b, 8, and 7 (δ, ppm, 100 MHz, TMS).

Compound	Solvent	Central 6-mem. ring		Phenyls at C-7,8		Phenyls at C-2,3
		H-5,10	H-6,9	ortho-H	m,p-H	
6	(CDCl$_2$)$_2$	8.58 J=8.3 Hz	8.68	8.51	7.95	7.25
10	CF$_3$CO$_2$H	8.41 J=8.2 Hz	8.82	8.61	8.02	7.20-7.84 5.57(H-2)
5b	DMSO-d$_6$	7.72 J=8.2 Hz	7.82	7.70 (2H), 7.48 (3H), 7.38 (5H)		7.18
8	DMSO-d$_6$	———		8.32 (Ph at C-5)	7.85 (Ph at C-6)	7.75 (H-1,4)
7	DMSO-d$_6$	8.00 (H-8,13) J=8.3 Hz	8.18 (H-7,14)	9.41 (H-1,6) 8.72 (H-2,5) 8.89 (H-3,4)		7.15 (C-10,11)

Table 2 : Effect of the solvent polarity on the longest wavelength transition of the quinarenes 6, 7, and calicenes 8, 9 (nm).

Solvent (Dielect. const.)	DMSO (46.7)	MeCN (37.5)	Me_2CO (20.7)	CH_2Cl_2 (8.9)	$(CHCl_2)_2$ (8.2)	C_6H_5Br (5.4)	C_6H_6 (2.3)
6	537	540	564	592	606	632	-
7	672	687	733	840	908	934	-
8	-	347	-	352	-	-	358
9	-	371	-	-	-	-	379

solvent, because of the high electrophilicity of the three-membered ring, and affords a yellow solution of the corresponding hydroxycyclopropene derivative. The nmr signal (Table 1) of the phenyl protons ortho to the three-membered ring appeared at quite lower field, which is upfield only by 0.1 ppm compared with that of 10 (vide infra). 6 has a characteristic intense band in the infrared at 1405 cm^{-1} which may be mostly ascribable to C-C ring expansion of the three-membered ring. From these findings it has proved that the three-membered ring of 6 has an appreciably positive character and hence the polar structure 6a contributes predominantly to the ground state. This fact is also demonstrated by such a solvent effect on the electronic spectrum (Table 2) that 6 shows a blue shift of the 1st band on going from polar to less polar solvents. Although the direction of the shift is parallel to those of calicenes 8 6)and 9, 7) it is of outstanding interest that the solvent polarity produced a big change in λ values of the absorption maxima in the case of the quinarenes 6 and 7. A further comparison of the nmr spectrum of 6 with that of cation 10 reveals that H-5 and H-10 in 6 are diamagne-



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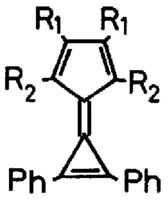
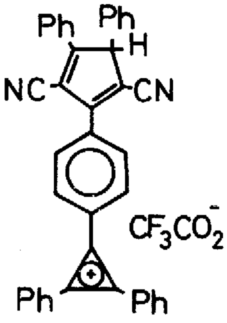


8 : R_1=CN, R_2=H

9 : R_1=R_2 =Ph



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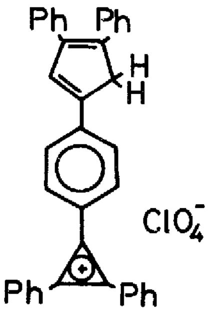

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tically shifted by 0.17 ppm while H-6 and H-9 in 6 are shifted paramagnetically by 0.14 ppm. This would be mainly due to the diamagnetic anisotropy of the 5-membered ring, oriented in good co-planarity with the central 6-membered ring, of 6. The chemical shift of the C-7 and C-8 phenyl protons in 6 appears at relatively lower field than that of the corresponding protons of dicyanocalicene 8,[6] indicating that the contribution of the polar structure would be more significant in 6 than in 8. This may be due to the enhanced stabilization of the central 6-membered ring, which trends to be a cyclic 6π system, of 6a. Although the quinarene 6 is quite sensitive to base, it is rather stable to acid and was not protonated in acetic or formic acid,[8] but was protonated reversibly in trifluoroacetic acid affording a yellow salt 10 (λ max (CF_3CO_2H) 259 nm(log ε 4.34), 324(4.75)). The protonation of 6 to the salt 10 took place presumably at C-2,[9] because the electronic spectrum showed the long wavelength absorption maximum at much shorter wavelength reagion compared with the conjugated cation 11[10](mp. 230-231°C ; λ max (MeCN) 230 nm(log ε 4.47), 300(4.50), 310(4.51), 458(4.49) ; ν max (KBr) 1592, 1400, 1075 cm^{-1} ; δ (CF_3CO_2H) 8.52-8.37(H-6,9 and ortho-H of Ph at C-7,8), 8.08-7.91(H-5, 10 and m,p-H of Ph at C-7,8), 7.59(H-4), 7.41-7.27(Ph at C-2,3), 4.11(H-1) and the nmr spectrum showed (Table 1) the C-2 and C-3 phenyl signals over a wide range of 7.20-7.84 ppm.

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8) The [5.6.7]quinarene 7 is easily protonated in formic acid.
9) 10 is possibly contaminated with about 10-15% of the compound protonated at other position than C-2 (probably at C-14) because a very weak singlet was observed at 5.41 ppm along with 5.57 ppm.
10) A similar phenomenon was observed between the protonated species of 7 and p-(3,4-diphenyl-1,3-cyclopentadien-1-yl)phenyl tropylium ion.[11]
11) K. Takahashi, S. Takenaka, Y. Kikuchi, K. Takase, and T. Nozoe, Bull. Chem. Soc. Japan, 47, 2272 (1974).