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CYCLIC CROSS-CONJUGATED HYDROCARBONS HAVING INSERTED p-QUINOID RING. V.[1)]

HIGHLY POLARIZED [5.6.7] QUINARENE DERIVATIVES.

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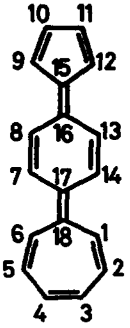
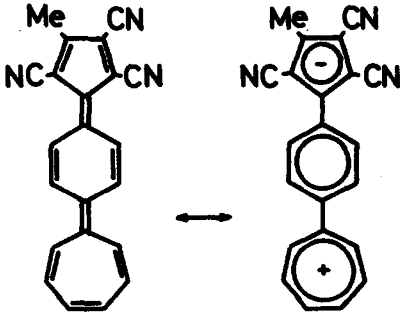
The ppp-type SCF-π-MO calculation has predicted[2)] that [5.6.7] quinarene (I) (R_E/π =2.6 Kcal) is comparable in stability to sesquifulvalene (R_E/π =2.47 Kcal) which is known to be a reactive polyolefin rather than an aromatic compound.[3)] After fruitless attempts to synthesize a 10,11-diphenyl derivative of I,[4)] we have recently succeeded to synthesize II,[1)] but very little is known concerning the electronic properties of the three-ring cross-conjugated hydrocarbon having an inserted p-quinoid ring. New quinarene (V) has now been synthesized and the spectroscopic data of V, as well as II, have been discussed, proving that the ground state of V and II should be dipolar, which will be reported here.

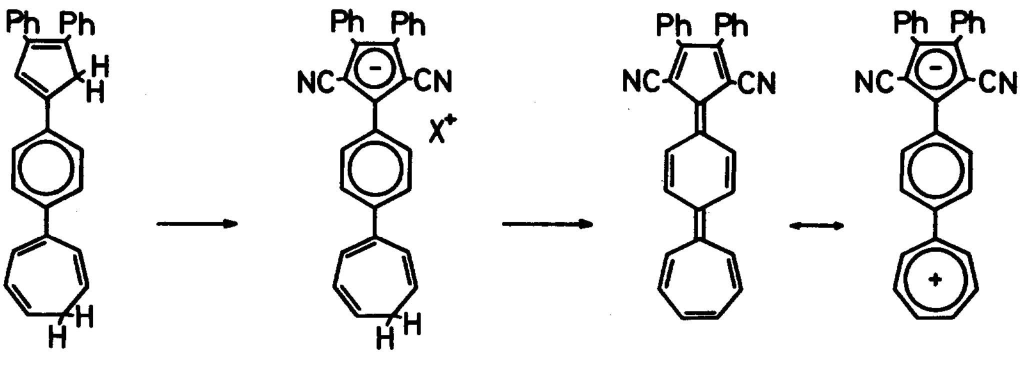
1,2-Diphenyl-4-(p-tropylphenyl)cyclopentadiene (III)[4)] reacted with cyanogen chloride in the presence of sodium hydride to give the sodium salt of dicyano compound (IV, X=Na, mp. 303-305°C, 56%), which is transformed into the tetramethyl-



I



II IIa



III IV V Va

ammonium salt (IV, X=NMe_4, greenish-yellow prisms, mp. 239-240°C), 5) and then treated with trityl perchlorate to give the quinarene (V, blue black needles, mp. 313-315°C, 66%). The compound (V) is slightly soluble in DMSO, acetonitrile, acetone, and insoluble in dichloromethane, benzene, or acetic acid. It is noticeable that V is quite stable as a monomer, while 9,9-dicyano[1.6.7]quinarene6) oligomerizes with ease.

In the ir spectrum of V, νmax (KBr) 3000w, 2180s, 1594s, 1503s, 1486s, 1425s, 1333s, 1250s, 1194s, 1132s, 839m, 762m, 713m, 697m cm^{-1}, the absorption at 1503 cm^{-1} is very intense and characteristic.7) The electronic spectrum of V, λmax (MeCN) 233 nm(log ε 4.54), 284(4.53), 348(4.18), 687(4.26), is closely similar in band shape to that of II, but a remarkable bathochromic effect by 130 nm in the longest-wavelength band of V was observed. As seen in Table 1, the longest-wavelength bands of V and II showed the red shift on going from polar to less polar solvent. Such type of solvent effect suggests a significant contribution of charge-separated polar forms (Va) and (IIa) to the ground state of these quinarenes. This polarization is also reflected in the nmr spectra of V and II as

Table 1 : Effect of the solvent polarity on the longest-wavelength transition of the quinarenes, V and II, nm (log ε).

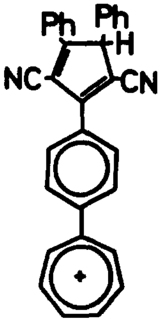
Solvent	V	II
DMSO	672 (4.23)	534 (4.11)
MeCN	687 (4.26)	552 (4.09)
Acetone	733 (4.23)	577 (4.02)

shown in Table 2. The signals of 7-membered ring protons of V and II appeared at quite lower field: the H-2,5,3,4 8) of V showed much the same δ values but slight upfield shift of 0.4 ppm compared with those of its conjugate acid (VI, vide infra) and a similar upfield shift of about 0.3 ppm was observed between II and its conjugate acid. This fact indicates an appreciable positive character of the 7-membered ring. The 5-membered ring of II, however, would be less negative compared to sodium 1-(p-tropylphenyl)3-methyl-2,4,5-tricyanocyclopentadienide 1) because the methyl proton of II are found to be about 0.23 ppm downfield from those of the cyclopentadienide. 9) The δ value difference between H-1,6 and H-2,5, 3,4 is larger in V and II than in VI, suggesting that 6- and 7-membered rings in the quinarenes would be more coplanar.

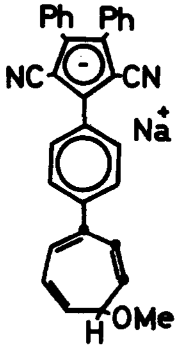
V is more basic than II, e.g., although II is not protonated, V is easily protonated in trifluoroacetic acid to give yellow VI; λ max (CF_3CO_2H) 367 nm(log ε 4.39). 10) Appreciable electrophilicity of V is revealed, like II, by the facile reaction at 7-membered ring with methanol in the presence of aqueous sodium hydrogencarbonate to give a mixture of methoxy tropilidenes (VII, mp. 272-277°C), 11)

Table 2 : NMR spectral data of V, II, IV, and VI (ppm, 100 MHz, TMS).

Compound	Solvent	H-1,6	H-2,5	H-3,4	H-7,8,13,14	Substituent
V	DMSO-d_6	9.41 m	8.72 m	8.89 m	8.09 AA'BB'-q JAB=8.3 Hz $\Delta\delta$AB=0.18 ppm	7.15 br. s $W_{\frac{1}{2}}$=4.0 Hz
II	CF_3CO_2H	9.41 m	8.85 m	9.17 m	8.09 br. s $W_{\frac{1}{2}}$=8.0 Hz	2.50 s
VI	CF_3CO_2H	9.48 m	9.20 m		8.17 s	7.15-7.85 m 5.50 s (methine)
IV	DMSO-d_6	7.04, m	6.7-6.25, m	5.7-5.4 m	7.60 AA'BB'-q JAB=8.1 Hz $\Delta\delta$AB=0.18 ppm	7.17 br. s



VI



VII

λ max (MeCN) 246 nm(log ε 4.43), 291(4.54), 365(4.37), δ (acetone-d_6) 3.48, 3.42, 3.13 (three s, OMe in the 1.4:2:1 ratio), 3.42(m, methine), 6.7-5.45(m, tropyl), 7.34-7.01(m, Ph), 7.66-7.64(two or three AA'BB'-q, para disubstituted benzene).

From these findings, it has proved that the [5.6.7]quinarene having electron-withdrawing substituents on 5-membered ring, V and II,12) show a considerable degree of cycloheptatrienium-phenylene-cyclopentadienide aromatic character.

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8) These protons are not effected by anisotropic effect.
9) The similar behavior has been observed with 2,3-dicyano-5,6-diphenylpentatriafulvalene by H. Prinzbach and E. Woishnik, Helv. Chem. Acta, 52, 2472 (1969).
10) This electronic spectral data exclude the possible C-9 protonated structure for VI, see ref. 4).
11) VII turned quantitatively to the original quinarene (V) in acetic acid.
12) Dipole moment of these quinarenes (V) and (II) could not measured owing to the poor solubility and the low vapor pressure.