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THE INSERTION OF A p-QUINOID STRUCTURE INTO FULVENE-TYPE NONBENZENOID AROMATICS

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In nonbenzenoid aromatic hydrocarbon chemistry, there have been many studies of annelated systems having a condensed benzene or naphthalene ring1). A novel approach to these problems, however, could be to introduce a benzene ring between the two dipole centers2), thus producing long conjugated systems such as V.

This communication will describe the synthesis and properties of 1-cycloheptatrienylidene-4-dicyanomethylidene-2,5-cyclohexadiene (V). p-Tropylbenzyl cyanide (I) and p-tropylphenylmalononitrile (II)2) were prepared3) starting from p-tropylaniline (III)4). On treatment with triphenylmethyl perchlorate in an acetonitrile solution, compound II afforded a stable cation (IV, X=$1/2PtCl_6$), orange yellow prisms, mp > 290°C (Found: C, 44.63; H, 2.96; N, 6.66; Pt, 22.03%); $\lambda_{max}^{concH_2SO_4}$ nm (log ε): 224 (4.62), 269 (4.42), 354 (4.23); ν_{max}^{KBr} : 2262, 1605, 1522, 1484, 1410, 1370, 1267, 1004, 844, 761 and 725 cm^{-1}; $\delta_{CF_3COOH}^{TMS}$: 5.77 (1H, s, benzyl methine), 8.07 (4H, AA'BB'-q, J=8.5 Hz, δ_A=8.18, δ_B=7.98, phenyl), 9.18~9.52 (6H, m, tropylium). Proton abstraction from IV was effected with sodium hydrogen carbonate in an aqueous solution; subsequent extraction with hot chloroform gave a deep blue solution of V. On treatment of V with a stronger base such as sodium ethoxide, however, the base attacked the seven-membered ring to give VI; $\lambda_{max}^{0.1N\ NaOEt-EtOH}$ nm (log ε): 225 (4.28), 295 (4.02), 356 (4.12); $\delta_{DMSO-d_6}^{NaOD}$: 1.23, 3.64 (J=6.9 Hz, ethyl), 1.27, 3.66 (J=6.9 Hz, ethyl), 3.5 (1H, m, allylic H of 3- and 2-substituted tropyl), 5.66, 6.43, 7.0 (5H, m, tropyl vinyl), 7.62 (4H, br.s, phenyl). VI regenerated V in a reaction with acid. V was protonated in formic acid, but not in acetic acid, suggesting that one of the approximate pKa values is 3.8~4.5. The pKa-value determination of the two steps, IV ⇄ V and V ⇄ VI, is now in progress.

The dicyano derivative, V, was quite stable in acetonitrile, methanol, or chloroform in a dilute solution, but it was polymerized in a concentrated solution. The evaporation of the solvent afforded colorless crystals (VII, mp 225° (decomp)) in a quantitative yield. VII has the empirical formula of $(C_{16}H_{10}N_2)n$ (Found: C, 83.09; H, 4.48; N, 11.73%), and its nmr spectrum in deuteriochloroform showed tropyl proton resonance at 5.40~5.82, 6.25~6.65, 6.92~7.08 ppm (three m, vinyl), and 2.50 ppm (br.t, allylic H). The integration of the vinyl to the allylic proton gave the expected 5:1 ratio. No benzyl proton resonance was observed. The infrared spectrum having a weak unconjugated nitrile band[2,3] at 2247 cm^{-1} and the ultraviolet spectrum showing absorption maxima at λ_{CH_3CN} nm (log ε): 240 (4.25), 280 (3.99), at 0°C[5] gave further structural evidence. The addition of cyclohexane or water to the concentrated chloroform solution of VII caused the immediate isolation of colorless prisms, whose elemental analysis agreed with the formula $(C_{16}H_{10}N_2)_2 \cdot C_6H_{12}$ (Found: C, 83.46; H, 5.55; N, 10.65%) or $(C_{16}H_{10}N_2)_4 \cdot H_2O$ (Found: C, 82.24; H, 4.51; N, 11.67%). These solvents, captured in crystals, were vaporized, with the degradation of the crystal lattice, on heating in vacuo at 120°C/0.2 mmHg. VII is presumably a dimer or trimer, judging from its low melting point. On mass analysis, VII exhibited a strong fragmentation peak at 230 (M^+ of V) and several weak ion peaks in the higher-mass region, indicating that the compound depolymerizes mainly under conditions of mass analysis (2.0~2.5 KV, 190~250°C). Similar polymerization reactions have also been noticed in heptafulvene[6] and its alkyl derivatives[7]. It is of interest that 8,8-dicyanoheptafulvene (VIII)[8] is quite stable, while V polymerizes with ease, as has been described above. This is because V, a benzologue of VIII, has two remote dipole centers and a large dipole moment which facilitate molecular association.

The VII polymer was stable on exposure to light or air at room temperature in the solid state and in a concentrated solution, but it dissociated quantitatively to V in a hot dilute solution in polar solvents. The dissociation rate was enhanced as the polarity of the solvents and the temperature of the solution increased. A solution of monomeric V can be obtained by dissolving it at 60~70°C in acetonitrile, methanol, chloroform, dichloromethane, acetic acid, and acetone in a concentration less than $1 \times 10^{-3} \sim 1 \times 10^{-5}$ mole/l.

It is noteworthy that V does not polymerize, even in the solid state, on silica gel. The treatment of a chloroform solution of V with silica gel,

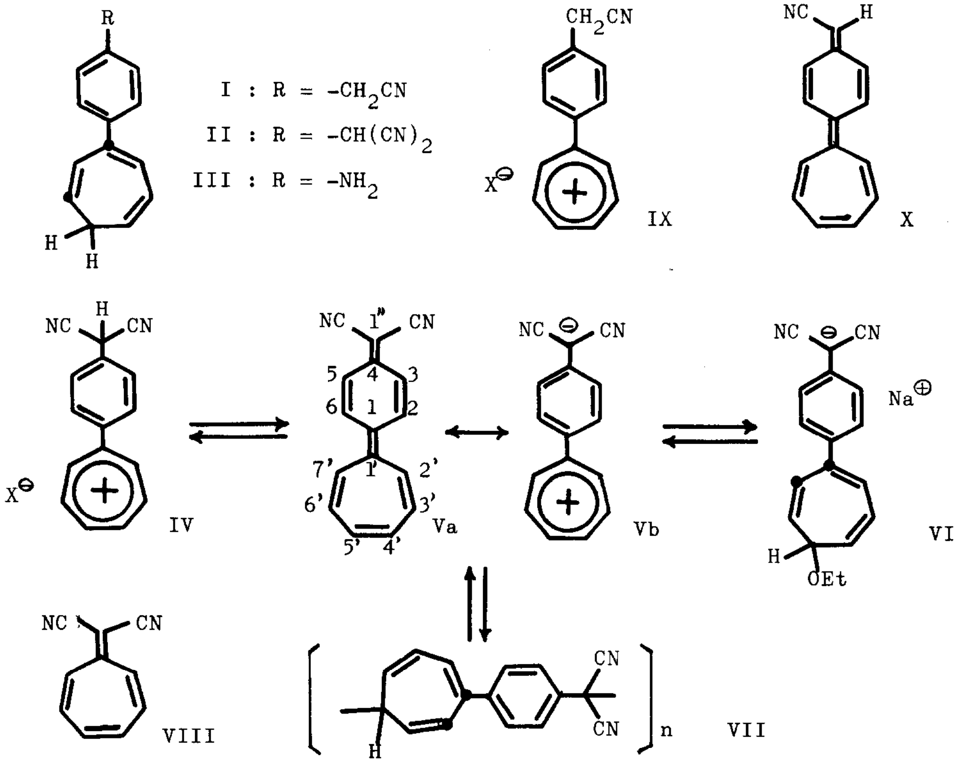

TABLE 1 : ELECTRONIC SPECTRA of V (at 60°C)

Solvents	Absorption Maxima, nm (log ε)				Δ nm
methanol	235(4.08)	302(3.98)	360(3.89)	672(4.25)	+62
acetonitrile	—— †	312(3.67)	375(3.72)	668(4.39)	+58
acetic acid	——	——	380(3.54)	662(4.28)	+52
acetone	——	——	382(3.69)	660(4.37)	+50
dichloromethane	241(4.30)	272(4.47)	390(3.66)	655(4.26)	+45
chloroform	——	275(3.93)	395(3.85)	640(4.23)	+30
benzene	——	——	402 *	627 *	+17
carbon tetrachloride	——	——	407 *	610 *	0

† : not observed owing to the interference by solvent absorptions

* : exact ε values were not obtained owing to the poor solubility

followed by the absolute evaporation of the solvent in vacuo, gave a deep blue absorbate of monomeric V, which was stable over the temperature range of + 170°~ -40°C and in prolonged storage at room temperature in a sealed tube.

The solvent effect on the electronic spectrum of V furnished evidence for the significant contribution of a less polar form such as Va to the ground state of this dicyano derivative. As is shown in the table, an increase in the solvent polarity resulted in a shift of the absorption maxima to a longer wavelength. This is due to the transition to a more polar excited state$^{9)}$.

The nmr spectrum of V in deuterio dimethyl sulfoxide at 80°C showed two peaks at 7.71 ppm (6H, br.s, half height width 4.5 Hz) and at 6.82 ppm (4H, m); these peaks are tentatively assigned to H-2,3,5,6,2',7' and H-3',4',5',6' respectively$^{10)}$. The hydride abstraction of I gave the stable cation (IX, X=ClO_4), greenish yellow needles, mp 123~124°C (Found: C, 58.65; H, 4.05; N, 4.47%), $\lambda_{max}^{concH_2SO_4}$ nm (log ε): 227 (4.59), 272 (4.15), 374 (4.21); ν_{max}^{KBr} : 1603, 1529, 1477, 1266, 1087, 845 and 757 cm^{-1}; $\delta_{CF_3COOH}^{TMS}$: 4.09 (2H, s, benzyl), 7.90 (4H, AA'BB'-q J=8.5 Hz, δ_A=8.04, δ_B=7.76), 9.10~9.47 (6H, m, tropylium). However further proton abstraction failed to afford X.

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