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STERIC CROWDING IN A HIGHLY POLARIZED [5.6.7]QUINARENE1)

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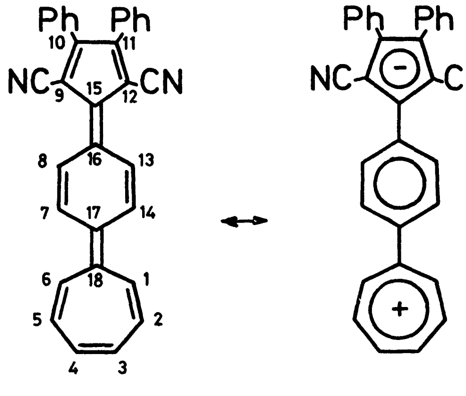
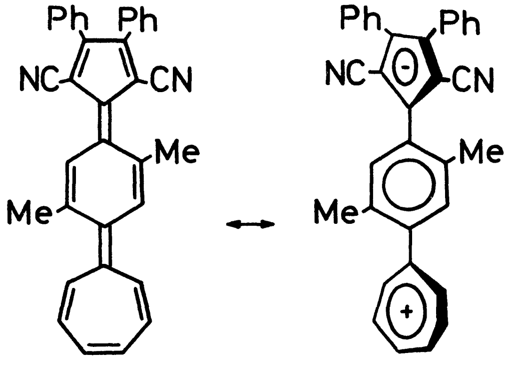
Sterically hindered 9,12-dicyano-7,13-dimethyl-10,11-diphenyl [5.6.7]quinarene (2) was spectroscopically investigated in order to clarify the effect of steric crowding on the structure of highly polarized [5.6.7]quinarenes. It has proved that the steric crowding caused a twisting of the molecule around the intercyclic bonds resulting in a further increase of charge separation and a decrease of electronic interaction among the three rings.

We synthesized previously 9,12-dicyano-10,11-diphenyl [5.6.7]quinarene (1) and indicated that the dipolar structure (1b) makes a larger contribution to its ground state rather than to the excited state.2) In such a compound, it is supposed that the increased contribution of the dipolar structure will reduce the bond order of the intercyclic pivot bonds and consequently the coplanarity of the three rings will be markedly influenced by steric and electronic factors. In order to clarify this point we have now synthesized and studied spectroscopically the 7,13-dimethylquinarene (2).



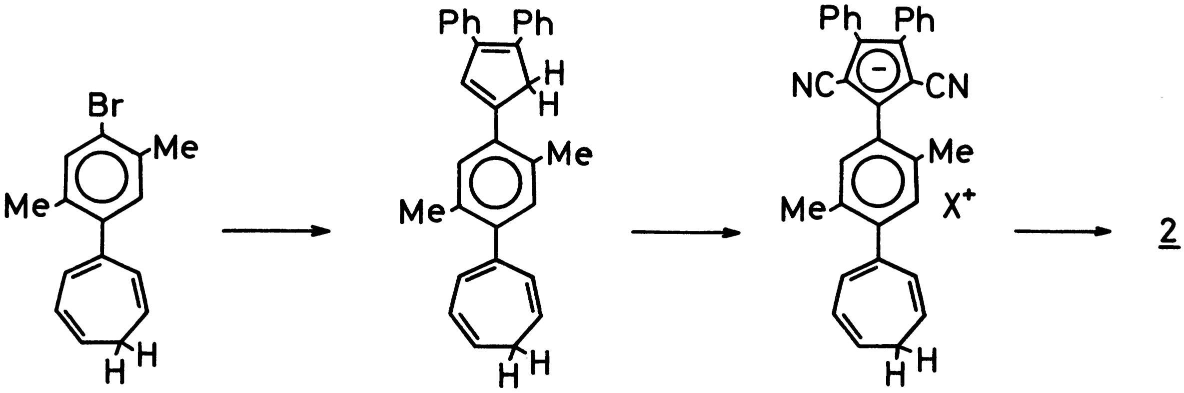
1a 1 1b



2a 2 2b

Grignard reaction of the magnesium derivative of 2,5-dibromo-p-xylene with 7-methoxycycloheptatriene in ether, followed by the thermal isomerization of the product gave tropylbromoxylene (3 : a colorless oil, 58%), and the successive

Grignard reaction of the magnesium derivative of 3 with 3,4-diphenylcyclopent-2-enone in tetrahydrofuran gave a hydrocarbon (4 : mp 122°C, 38%). The quinarene (2) was prepared from 4 by cyanation with cyanogen chloride in the presence of sodium hydride leading to cyclopentadienide (5, $X=NMe_4$: colorless needles, mp 177 °C ; λmax (MeCN) 285 nm(log ε 4.57), 326(4.27), 36%) and subsequent hydride abstraction from 5 to 2 by using trityl salt (2 : blue black needles, mp > 350°C ; νmax (KBr) 2170, 1595 cm^{-1}).



3 4 5

As can be seen from the electronic spectrum of 2, as well as 1, (Table 1), the solvent effect on the longest wavelength absorption maximum (1st band) showed a red shift on going from polar to less polar solvent indicating a larger contribution of the dipolar structure 2b to the ground state rather than the excited state. Furthermore, in the nmr spectrum of 2 (Table 2), the chemical shift of the 7-membered ring protons (H-2,5,3,4) appeared at relatively lower field and in a more narrow range (9.20 ± 0.08 ppm in 100 MHz) than those of the corresponding protons of 1 showing that the 7-membered ring of 2 is more electron-deficient with a decreased bond alternation in comparison with that of 1. Thus it can be said

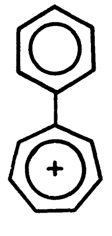
Table 1 : The Solvent Effect on the 1st Bands of 2 and 1. λmax, nm (log ε)

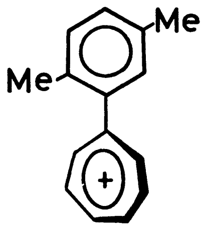
Compd.	DMSO	MeCN	Acetone
2	605 (3.62)	609 (3.73)	630 —
1	672 (4.23)	687 (4.26)	733 (4.23)

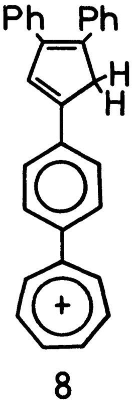
Table 2 : H-nmr Spectral Data of 2 and 1 (100 MHz, δ ppm in DMSO-d_6)

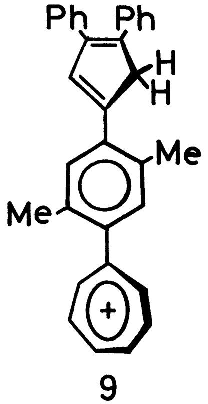
Compd.	7-Membered ring	Central ring	Substituent
2	9.37, m, 2H, H-1,6 9.20, m, 4H, H-2,5, 3,4	7.56, s, 1H 7.48, s, 1H	7.18, br.s, 10H, Ph 2.41, s, 3H, Me 2.50, s, 3H, Me
1	9.41, m, 2H, H-1,6 8.89, m, 2H, H-3,4 8.72, m, 2H, H-2,5	8.22, d, 2H 7.96, d, 2H J=8.3 Hz	7.15, br.s, 10H, Ph

that the contribution of 2b to 2 is more significant than that of 1b to 1 in the ground state. A further nmr spectral comparison of 2 with 1 revealed that the chemical shift of the central ring protons of 2 appeared at higher field by 0.66-0.48 ppm than that of 1. This δ value difference between 2 and 1 is still large, even if the chemical shift difference between benzene (7.37 ppm) and xylene (7.05 ppm) is taken into account. This would be mainly due to the fact that the 5- and 7-membered rings of 2 are twisted out of the plane of the central ring to minimize the steric hindrance resulting in a decrease of diamagnetic anisotropies and hence in an increase of shielding for the central ring protons. The molecular twisting of 2 was more distinctly evidenced by the 1st band of the electronic spectrum[3] which showed both a hypochromic effect (a decrease in transition probability) and a hypsochromic shift (an increase in transition energy) relative to that of less hindered quinarene (1). The twisting angle (θ) of 2 was calculated from $\varepsilon/\varepsilon_0 = \cos^2\theta$ (where ε_0 refers to εmax of 1) to give 57° (in MeCN) and 60° (in DMSO). This indicates that the 5- and 7-membered rings of 2 are twisted 57-60° more, out of the plane of the central ring, than 1. Similar calculation of the twisting angle gave 49° for 7 (ε_0 refers to εmax of 6) and 34° for 9 (ε_0 refers to εmax of 8).[4] If only an electronic effect were taken into consideration, 2 should be less twisted than 9 because the resonance interaction between the electron donating 5-membered ring and the electron accepting 7-membered ring would be more effective in 2. Therefore the observed large twisting angle of 2 would be caused by the serious hindrance of C-9,12 cyano groups with C-13 methyl group rather than the hindrance of the C-1,6 protons with C-7 methyl group.







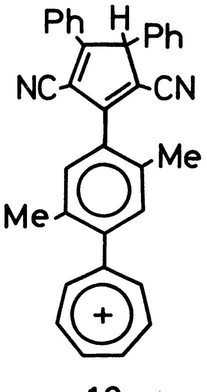


	6	7	8	9
λ_{max}^{MeCN}	366	364	543	519
(log ϵ)	(4.18)	(3.82)	(4.20)	(4.04)

The steric interference in 2 raises the potential energies of both the ground and the excited states, and the interference is probably more effective in the latter state because the intercyclic bond order (p) is larger in the latter one $[(p^*-p) > 0]$. This is the reason for a marked hypsochromic shift in 2, and is fully consistent with the result obtained from the electronic spectral solvent effect of 2 (vide supra).

Deviation from coplanarity in 2 would increase the basicity of the 5-membered ring especially at C-15, and this was evidenced by the fact that 2 was protonated at C-10 and C-15 to give a 5:1 mixture of 10 and 11[5] whereas 1 was protonated only at C-10 position.

The structural features of 2 mentioned here are entirely in contrast to other sterically crowded compounds in the cyclic cross-conjugated system. For examples, the 7-membered ring of 1,6-dimethyl-8,8-dicyanoheptafulvene (12) takes a boat form as those of in cycloheptatrienes,[6] and the 7-membered ring of 1,6-dimethyldibenzosesquifulvalene (13) takes a norcaradiene form.[7] Contrary to these examples, the steric crowding in the [5.6.7]quinarene (2) caused an increased charge separation in the ground state but a reduced interaction of each ring by twisting out the rings around the intercyclic pivot bonds. This is the first observation so far in the non-alternant cross-conjugated systems.



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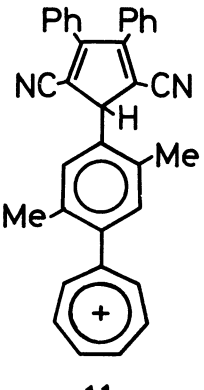

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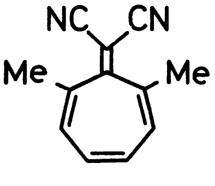

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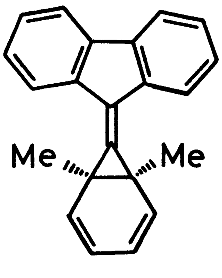

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References and Notes

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