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# SYNTHESIS AND PROPERTIES OF 2-CYCLOHEPTATRIENYLIDENE-5-DICYANOMETHYLIDENE-2,5-DIHYDROTHIOPHENE (A THIOPHENE ANALOG OF [1.6.7]QUINARENE)[1]

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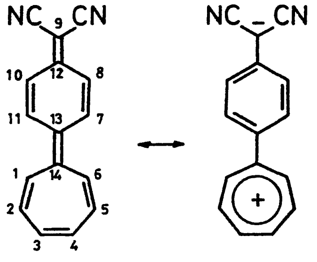
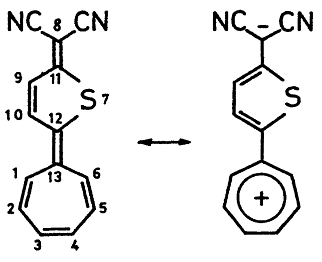
The title compound 2 was prepared in 7 steps starting from 2-bromo-5-(cycloheptatrienyl)thiophene. While the [1.6.7]quinarene derivative 1 can not be isolated in a monomeric solid due to easy and reversible oligomerization, the thiophene analog 2 is stable as a monomer both in solid and in solution. The responsible factors for the oligomerization reaction were discussed based on the chemical and physical properties of these quinarenes 1 and 2.

In the course of our study on the quinarene system[2] (the cyclic cross-conjugated hydrocarbons having an inserted quinonoid ring between the dipole centers of fulvene- or fulvalene-like hydrocarbons), we reported previously the synthesis of the 8,8-dicyano derivative 1 of [1.6.7]quinarene, which is stable both in a dilute solution in polar solvents and in a solid state absorbed on a silica gel but is unable to be isolated in a monomeric form due to easy and reversible oligomerization on concentration.[3] Thus we trended toward the investigation on a hetero analog of 1 expecting the successful isolation of the monomeric compound and a further insight into the oligomerization mechanism. The present paper describes the synthesis of 2, as the first example of a [1.6.7]quinarene analog isolable in a monomeric form, and the comparison of chemical and physical properties of 2 with those of 1 in order to know how the properties, especially in the ground state, of 2 will be influenced by changing the type of the $\pi$-conjugated central ring.

2-Bromo-5-(cyclohepta-1,3,6-trienyl)thiophene[4] was first lithiated with n-butyllithium in ether and then formylated with DMF to give the aldehyde 3 (pale yellow needles, mp 38-39 °C, 81%, $\nu$max (KBr) 3040-2850, 1600, 1450, 1215, 1045 cm$^{-1}$ ; $\delta$($CDCl_3$) 7.17 (d, H-4, J=4.0 Hz), 7.64 (d, H-3), 9.83 (s, CHO)). The aldehyde 3

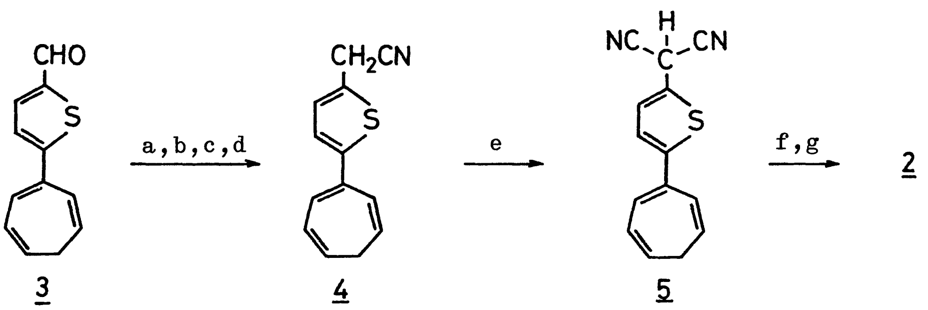


1a 1 1b



2a 2 2b

was condensed with rhodanine, the product hydrolyzed and the resulted thiopyruvic acid converted to the oximino acid, which was then simultaneously dehydrated and decarboxylated to 4$^{5)}$ (pale yellow plates, mp 64-65 °C, 51% from 3, $\nu$max (KBr) 3040-2840, 2240, 1614, 1467, 1433, 1405, 1393 cm$^{-1}$; $\delta$(CDCl$_3$) 3.83 (s, CH$_2$CN), 6.93 (s, H-3,4)). The dicyanomethyl derivative 5 (pale yellow crystals, mp 92-93 °C, 13%,$^{6)}$



a: Rhodanine, AcOH-AcONa, refl. (30 min); b: 15% aq NaOH, refl. (30 min); c: aq NH$_2$OH, EtOH, refl. (2 h); d: in Ac$_2$O, 100 °C (25 min); e: 1.2 eq n-BuLi, in ether, 0 °C (15 min), 1.0 eq Me(CN)NC$_6$H$_5$, in ether, room temp. (2 h); f: Ph$_3$CBF$_4$, in CH$_2$Cl$_2$, 0 °C (5 min); g: H$_2$O.

$\nu$max (KBr) 2290 cm$^{-1}$; $\delta$(CDCl$_3$) 5.28 (s, CH(CN)$_2$), 7.05 (d, H-4, J=4.0 Hz), 7.23 (d, H-3)), prepared from 4, was finally dehydrogenated to the quinarene 2$^{7)}$ (dark violet needles, mp 234-237 °C, 67%, $\nu$max (KBr) 2190, 1540, 1478-1457, 1410, 1265, 1250, 1240, 1165, 1145, 1092 cm$^{-1}$; $\lambda$max (MeCN) 312 (log $\varepsilon$ 3.63), 388 (3.22), 556 (4.55); m/e (%) 237 (17), 236 (100) M$^+$, 210 (13) M$^+$-CN, 209 (11), 171 (16)). The quinarene 2 is quite stable in solid state on exposure to air and/or light at room temperature and in solution in commonly used hydrous or anhydrous organic solvents, showing no tendency for oligomerization in contrast to 1.

The electronic spectral first excitation band of 2 showed a bathochromic shift on going from acetone to more polar DMSO, indicating that the quinonoid structure 2a is preferable to the dipolar structure 2b at the ground state in analogy with 1 (Table 1). On comparing the $^1$H NMR chemical shifts of the corresponding protons with each other, H-2~H-5 of 2 are found at lower field by about 0.9 ppm than H-3~H-6 of heptafulvene, but at higher field by about 0.52 ppm than H-3~H-6 of 8,8-dicyanoheptafulvene 6, while H-2~H-5 of 1 are in nearly the same low field as H-3~H-6 of 6 (Table 2). This evidence suggests that the insertion of a thiophene ring, instead of a benzene ring, between the dipole centers of 6 reduces the diatropic

Table 1: Solvent Effect on the 1st Excitation Band of the Quinarenes 1 and 2 $\lambda$ nm (log $\varepsilon$)

| Compd. | DMSO | MeCN | Acetone | Shift |
|---|---|---|---|---|
| 2 | 586<br>(4.55) | 556<br>(4.55) | 554<br>(4.56) | + |
| 1 | —— | 668<br>(4.47) | 660<br>(4.40) | + |

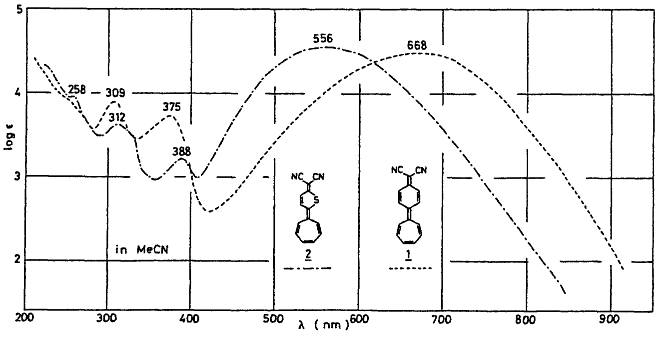


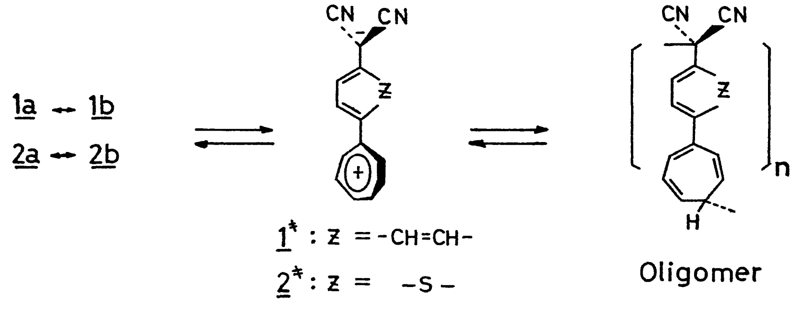
Fig. 1 Electronic Spectra of 1 and 2

Table 2: $^1$H NMR Data of the Quinarenes 1 and 2, and 8,8-Dicyanoheptafulvene 6 ( $\delta$ from TMS, at 100 MHz)

| Compd. | Solvent[14] | H-1, H-6 | H-2～H-5 | H-9 | H-10 |
|---|---|---|---|---|---|
| 2 | $(CDCl_2)_2$ | 6.98～7.18<br>m | 6.37～6.58<br>mc 6.48 | 6.96<br>d | 7.47<br>d |
| | | $J_{1,2}=J_{5,6}$=12.0 Hz | | $J$=5.7 Hz | |
| 1 | DMSO-$d_6$ | 7.80～7.90<br>m | 6.80～7.15<br>m | 7.67 ～ 7.85<br>m | |
| 6[15] | MeCN-$d_3$ | 7.28<br>(H-2,7) | 7.05 (H-3,6)<br>6.96 (H-4,5) | — | — |
| | | $J_{2,3}=J_{6,7}$=12.0 Hz | | | |

character of the 7-membered ring. The 6- and 7-membered rings in 1 are assumed to be insufficiently coplanar because of the steric interaction between H-1,6 and H-7,11. The two rings in 2 are in the same situation, but to a lesser extent judging from a molecular model. Nevertheless the contribution of 1b in 1 is not diminished compared with that of 2b in 2 in the ground state, as seen in the above $^1$H NMR data,[8)] suggesting that the electronic factor to induce the dipolar structure is more significant in 1 rather than 2. The electronic spectrum of 2 is closely similar in band shape to that of 1 (Fig. 1), but a remarkable hypthochromic shift by 112 nm in the 1st excitation band of 2 was observed. These $^1$H NMR and electronic spectral phenomena are reasonably attributable to the smaller resonance energy of thiophene residue,[9)] stabilizing the quinonoid ground state and destabilizing the dipolar excited state as compared with the corresponding benzene analog 1.

As reported in our previous communication,[3)] the oligomerization of 1 is suppressed in the solvent of high ionizing power and the deoligomerization rate reproducing 1 was enhanced with an increase in the solvent polarity. This fact is interpreted in terms of an extensively solvated transition state, which in turn reflects that the zwitterionic structure[10)] such as $1^*$ or $2^*$ is essential for the transition state of the equilibrium process (Eq. 1). Thus the energy barrier $\Delta G^*$ for 2 is considered so high that no oligomerization occurs at temperatures handled. The reasons for the easy oligomerization of 1 would be given as follows: firstly, the transition state is potentially stabilized by the effective presence of a benzene ring (in $1^*$) rather than a thiophene ring (in $2^*$);[9)] secondly, the nonbonding interaction between H-1,6 and the ortho-protons of the central ring, which rises the energy of the ground state and thus lowers the energy barrier ($\Delta G^*$), is larger in 1 than in 2, and thirdly, the nucleophilicity of the exo-methylene carbanion in the transition state is large enough to attack the cationic center. The fact that 9,12-dicyano-7,13-dimethyl-10,11-diphenyl[5.6.7]quinarene is quite stable as a monomer and shows no tendency for oligomerization although it exists in a twisted zwitterionic structure,[11)] would be explained in terms of the poor nucleophilicity of the dicyanocyclopentadienide anion moiety.[12)] Interestingly the quinarene 1 is not oligomerized in phenol even in a very high concentration, Eq. 1



(1)

shifting substantially to the left, presumably because of a hydrogen-bond formation between the phenolic OH and the exo-methylene carbanion resulting in weakening of the nucleophilicity of this anionic center.13)

## References and Notes

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2) K. Takahashi, S. Takenaka, and T. Nozoe, Tetrahedron, 30, 2191 (1974); K. Takahashi, S. Takenaka, Y. Kikuchi, K. Takase, and T. Nozoe, Bull. Chem. Soc. Jpn., 47, 2272 (1974).
3) K. Takahashi, N. Hirata, and K. Takase, Tetrahedron Lett., 1970, 1285.
4) K. Takahashi, T. Sakae, and K. Takase, Chem. Lett., 1980, 179.
5) The more convenient synthetic route to 4 using 5-cycloheptatrienyl-2-thenyl chloride was impractical since the chlorination of the corresponding 2-thenyl alcohol failed.
6) Attempts to improve the yield were unsuccessful.
7) All new compounds gave satisfactory elemental analyses.
8) H-2∼H-5 of 2 are by about 0.4 ppm more up-field than those of 1.
9) The resonance energy of thiophene is by 31.8 KJ/mol less than that of benzene.
10) Based upon the electronic spectral solvent effect, both 1 and 2 were proved to have a larger contribution of the quinonoid structure to the ground state. Therefore somewhat more ionic species such as $1^*$ or $2^*$, which have an ability to form an ion pair with the solvent molecule, should exist as the transition state of Eq. 1. Although the exact geometry of the transition state is not clear, it would be more twisted compared with the ground state of the quinarenes since the pivot bonds should be single bonds in the zwitterionic structure. Such a twisted zwitterionic structure has been proposed for the transition state of rotation about the exo-cyclic bond in triafulvenes and heterofulvenes, or rotation about the pivot bond in calicene: M. J. S. Dewar and M. C. Kohn, J. Am. Chem. Soc., 94, 2699 (1972); G. Seitz, Angew. Chem. int. Ed. Engl., 8, 478 (1966); A. S. Kende, P. T. Izzo, and W. Fulmore, Tetrahedron Lett., 3697 (1966); I. Belsky, H. Dodiuk, and Y. Shvo, J. Org. Chem., 42, 2734 (1977).
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13) It has been reported by Evans that the high ionization power of phenol for trityl chloride is responsible for the solvation of the chloride ion by the acidic hydroxyl group of phenol rather than the solvation of the trityl cation by the basic oxygen: A. G. Evans, I. H. McEvan, A. Price, and J. H. Thomas, J. Chem. Soc., 1955, 3098. We thus regard that the nucleophilicity of the carbanion would be more responsible for the oligomerization rather than the lewis acidity of the cycloheptatrienyl cation in $1^*$.
14) The effect of these different solvents on the chemical shift of H-2∼H-5 would not be so serious as to make erroneous evaluation, judging from the $^1$H NMR examination of other related quinarenes.
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