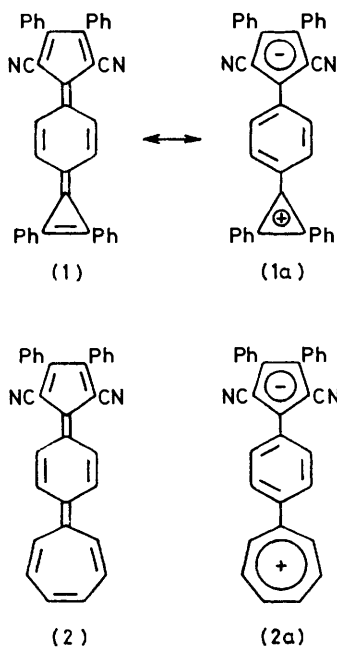


Cyclic Cross-conjugated Hydrocarbons having an Inserted *p*-Quinonoid Ring. Part 8.¹ Quinarenes containing Naphthalene Residues

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2'',5''-Dicyano-3'',4''-diphenyl derivatives (6) and (7) of 1-cycloheptatrienyliidene-4-cyclopentadienyliidene-1,4-dihydronaphthalene and 1-cycloheptatrienyliidene-5-cyclopentadienyliidene-1,5-dihydronaphthalene have been synthesized.

LONG-CONJUGATED three-ring quinarenes (1) and (2) have recently been synthesized,^{2,3,4} the main contributions in the ground state being shown to be polar [structures (1a) and (2a)] rather than quinonoid. In order to know how changes in the central ring will affect the properties of the quinarenes, we have now synthesized the new quinarenes (6) and (7) containing 1,4- and 1,5-naphthoquinonoid moieties.



4-Bromo-1-naphthylmagnesium bromide⁵ was first allowed to react with 7-methoxycycloheptatriene in ether and the product was thermally isomerized⁶ to give a bromide (3) (40%). Grignard reaction of the magnesium derivative of (3) with 3,4-diphenylcyclopent-2-enone in ether gave a hydrocarbon (4) (53%) *via* dehydration of the intermediate followed by migration of the double bond. The hydrocarbon (4) was treated with sodium hydride and then with cyanogen chloride at 0 °C. The resulting sodium salt was treated with tetramethylammonium chloride in acetonitrile to produce the stable ammonium salt (5) (85%). Hydride abstraction of (5) with a trityl salt in dichloromethane gave a quinarene (6).

Quinarene (7) was similarly obtained in four steps from 1,5-dibromonaphthalene.⁷ Quinarenes (6) and

(7) are stable on exposure to light and air at room temperature in the solid state.

The electronic spectrum of (6) showed the absorption maximum of longest wavelength (1st band) at 625—684 nm, assignable to the π - π^* transition along the long molecular axis. The absorption maximum showed a blue shift on going from less polar to polar solvents (Table) indicating a larger contribution of the dipolar

Effect of solvent on the transitions of longest wavelength for the quinarenes (6) and (2)

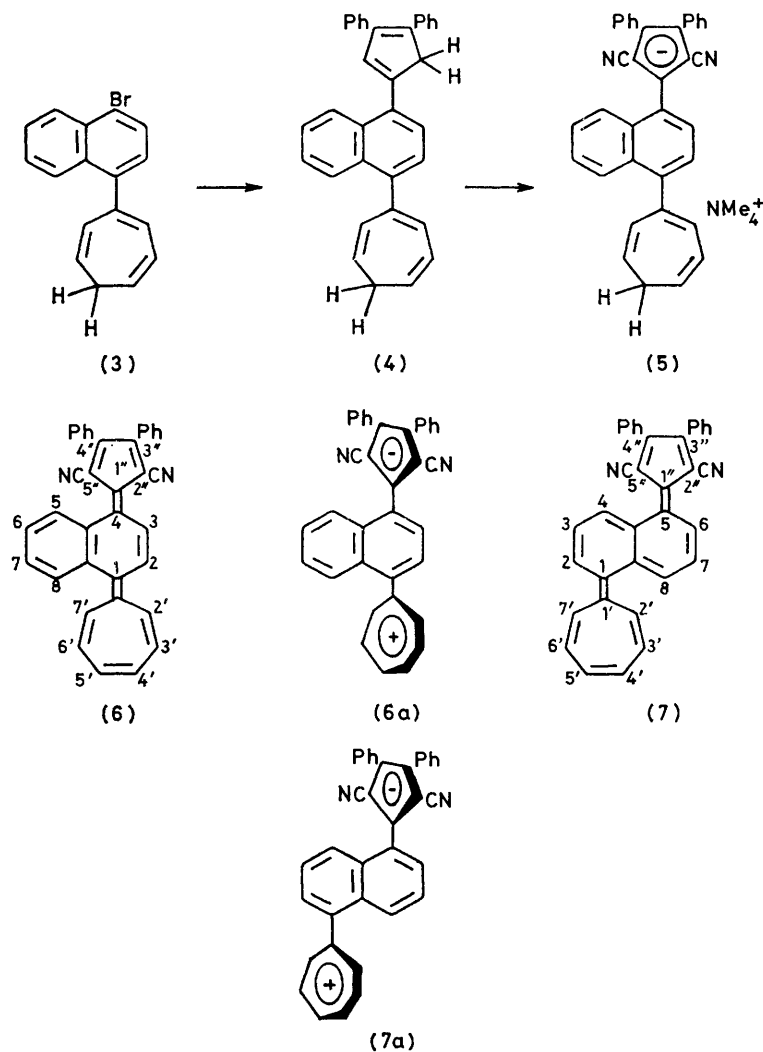
Solvent (dielect. const.)	DMSO (46.7)	MeCN (37.5)	Me ₂ CO (20.7)	Sign of shift
Quinalene (6)	625 (3.48)	644 (3.81)	684 (3.00)	—
(2)	672 (4.23)	687 (4.26)	733 (4.23)	—

structure (6a) to the ground state rather than the excited state, by analogy with the quinarene (2). In the n.m.r. spectrum the chemical shifts of the 7-membered-ring protons (H-3', 4', 5', 6') of (6) appeared at lower field by 0.40—0.49 p.p.m. and in a narrower range (9.36—9.16 p.p.m.) than those of the corresponding protons of (2).³ This evidence suggests that the contribution of (6a) to (6) is more significant than that of (2a) to (2) in the ground state. However in the electronic spectrum the absorption intensity of the 1st band of (6) [644 nm; log ϵ 3.81 (MeCN)] is smaller than that of (2) (687 nm; log ϵ 4.26 in MeCN) showing the diminished electronic interaction between the 5- and 7-membered rings in (6). This would be due to the twisting of the molecule around the intercyclic bonds,⁸ rather than the bending † of the rings, to relieve the steric interactions of the *peri*-hydrogens of the annelated ring with 5- and 7-membered rings in (6) since the dipolar structure is highly favoured in the ground state. This kind of annelation effect is different from that observed in the cyclic cross-conjugated hydrocarbons.⁹ As the quinarene (7) is insoluble in all common organic solvents, the i.r. spectrum (KBr disc) only was determined. Nevertheless, we could not find any plausible reasons why (7) should not exist in the twist conformation (7a), this being favoured on steric grounds as in (6) and, moreover, by the instability of a 1,5-naphthoquinonoid system.¹⁰

† X-Ray analysis of 10-(hepta-2,4,6-trienyliidene)anthracen-5(10*H*)-one reveals that the 7-membered ring exists in the boat form with angles of 20° (stern) and 27° (bow) (Y. Kitahara and C. Kabuto, to be published).

Contrary to the predominant C-3'' protonation in (2), both (6) and (7) were reversibly protonated at C-3'' and C-1'' positions in a 1:1 ratio by dissolving in trifluoroacetic acid. Protonation at C-1'' in the twist quinarenes

room temperature, the resulting solution was hydrolyzed with 2*N*-hydrochloric acid and extracted with ether. The ether extract was washed with saturated aqueous sodium bicarbonate, dried (Na₂SO₄), and concentrated. The



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(6) and (7) would be due to increase in electron density at this position by the lack of through-ring conjugation and to liberation from steric hindrance between the *peri*-hydrogen of the naphthalene ring and the cyano-groups of the 5-membered ring.

EXPERIMENTAL

Spectral data were measured on Shimadzu IR-27G (i.r.), Varian HA-100 and A-60 (n.m.r.), and Hitachi 323 (electronic) spectrometers.

1-Bromo-4-(cyclohepta-2,4,6-trienyl)naphthalene.— To a solution of 4-bromo-1-naphthylmagnesium bromide in dry ether (200 ml) [from 1,4-dibromonaphthalene (1.0 g, 3.49 mmol) and magnesium ribbon (112 mg, 4.6 mmol)] was added dropwise a solution of 7-methoxycyclohepta-1,3,5-triene (419 mg, 3.43 mmol) in dry ether (10 ml) with stirring at room temperature. After being stirred overnight at

residual brown oil was chromatographed on silica gel (n-hexane as an eluant) to afford an *oil* (45.2%); ν_{\max} (neat) 3 030, 1 594, 1 370, and 930 cm^{-1} ; $\delta(\text{CCl}_4)$, cyclohepta-trienyl: 3.35 (1 H, br t, *J* 5.0 Hz, H-7), 5.45 (2 H, dd, *J* 9.0 and 5.0 Hz, H-1,6), 6.20 (2 H, m, H-2,5), and 6.70 (2 H, t, *J* 4.0 Hz, H-3,4); naphthalenyl: 8.27 (1 H, m, H-5), and 7.20–8.05 (5 H, m, others) (Found: C, 68.5; H, 4.2. C₁₇H₁₃Br requires C, 68.70; H, 4.41%).

1-Bromo-4-(cyclohepta-1,3,6-trienyl)naphthalene (3).—A solution of 1-bromo-4-(cyclohepta-2,4,6-trienyl)naphthalene (340 mg, 1.14 mmol) in xylene (10 ml) was refluxed for 4 h. The solvent was evaporated off under reduced pressure and the oily residue chromatographed on silica gel (n-hexane as eluant) to give (3) as an *oil* (312 mg, 92%); ν_{\max} (neat) 3 030, 1 585, 1 371, and 951 cm^{-1} ; $\delta(\text{CCl}_4)$, cycloheptatrienyl: 2.42 (2 H, t, *J* 6.5 Hz, H-7), 6.09 (2 H, m, H-1,6), 6.19 (1 H, dd, *J* 9.0 and 5.5 Hz, H-5), 6.29 (1 H,

d, *J* 9.0 Hz, H-2), and 6.69 (1 H, dd, *J* 5.5 and 1.0 Hz, H-4); naphthalenyl: 8.15—7.15 (6 H, m) (Found: C, 68.6; H, 4.2. C₁₇H₁₃Br requires C, 68.70; H, 4.41%).

1-(Cyclohepta-1,3,6-trienyl)-4-(3,4-diphenylcyclopenta-1,3-dienyl)naphthalene (4).—Finely cut magnesium ribbon (471 mg, 19.4 mmol) was heated on a luminous flame for 30 min under nitrogen. A solution of the bromide (3) (4.03 g, 13.6 mmol) and 1,2-dibromoethane (1.09 g, 5.80 mmol) in dry ether (40 ml) was then added dropwise with stirring. After the Grignard reagent had been formed, a solution of 3,4-diphenylcyclopent-2-enone (3.18 g, 13.6 mmol) in ether (100 ml) was added and the mixture was stirred at room temperature overnight. After work-up, the reaction mixture was chromatographed on silica gel [*n*-hexane-dichloromethane (5:1)] to separate *plates* (4) (3.15 g, 53%), m.p. 169—170 °C (from methanol); ν_{\max} (KBr) 3 030, 1 600, 832, 760, and 700 cm⁻¹; δ (CCl₄), cycloheptatrienyl: 2.49 (2 H, t, *J* 6.5 Hz, H-7), 5.38 (2 H, m, H-1,6), 6.21 (2 H, m, H-2,5), and 6.66 (1 H, d, *J* 6.0 Hz, H-4); cyclopentadienyl: 3.98 (2 H, s, H-5) and 6.85 (1 H, s, H-2); aromatic: 7.83—8.01 (1 H, m) and 8.30 (1 H, m) (H-5 and -8 of naphthalenyl) and 7.00—7.50 (14 H, m, others); λ_{\max} (MeCN) 310 (log ϵ 4.17) and 352 nm (4.28) (Found: C, 93.85; H, 5.95. C₃₄H₂₆ requires C, 93.97; H, 6.03%).

Tetramethylammonium 1-(Cyclohepta-1,3,6-trienyl)-4-(2,5-dicyano-3,4-diphenylcyclopentadienylidene)naphthalene (5).—Sodium hydride (50% dispersion in oil; 960 mg, 20 mmol) was washed with dry benzene (3 × 5 ml) and then suspended in dimethoxyethane (15 ml). To this was added dropwise at 0 °C the cyclopentadienyl derivative (4) (1.74 g, 4.0 mmol) in dimethoxyethane (30 ml). The deep red solution was stirred for 1 h at 0 °C and then for 10 min at room temperature. Cyanogen chloride was condensed into the system over 1 h at 0 °C and stirring was continued at 0 °C overnight. The mixture was then filtered and evaporated and the residue was dissolved in acetonitrile (10 ml). Tetramethylammonium chloride (440 mg, 4.0 mmol) was added and, after standing at room temperature for 1 h, the acetonitrile was evaporated off. The residue was dissolved in dichloromethane and washed with water. After evaporation of the solvent, the residue was chromatographed on alumina (dichloromethane as eluant) to give the ammonium salt (5) (1.89 g, 85%), m.p. 119—120 °C (decomp.) (from dichloromethane-*n*-hexane); ν_{\max} (KBr) 3 030, 2 180, 1 600, and 1 475 cm⁻¹; δ (CD₃CN) 2.91 (12 H, s, Me) and 7.05—7.35 (10 H, m, Ph); cycloheptatrienyl: 2.54 (2 H, t, *J* 7.0 Hz, H-7), 5.37—5.70 (2 H, m, H-1 and -6), 6.33 (1 H, d, *J* 9.0 Hz, H-2), 6.36 (1 H, dd, *J* 9.5 and 5.5 Hz, H-5), and 6.84 (1 H, d, *J* 5.5 Hz, H-4); naphthalenyl: 7.90—8.06 (1 H, m) and 8.15—8.30 (1 H, m) (H-5 and -8), and 7.38—7.63 (4 H, m, others); λ_{\max} (MeCN) 270 (log ϵ 4.54) and 366 nm (4.06) (Found: C, 86.45; H, 6.6; N, 7.15. C₃₆H₃₅N₃ requires C, 86.14; H, 6.33; N, 7.54%).

1-Cycloheptatrienylidene-4-(2'',5''-dicyano-3'',4''-diphenylcyclopentadienylidene)-1,4-dihydronaphthalene (6).—Triphenylmethyl fluoroborate (59 mg, 0.18 mmol) was added to a stirred solution of the cyclopentadienide (5) (100 mg, 0.18 mmol) in dry dichloromethane (1 ml) at 0 °C. After 20 min, ether (15 ml) was added to form a precipitate which was filtered and washed successively with ether, ethyl acetate, and 1*N*-hydrochloric acid to give (6) (23 mg, 26%). Recrystallization from trifluoroacetic acid-acetic acid gave pure (6) as black *needles*, m.p. 273—276 °C (decomp.); ν_{\max} (KBr) 2 180, 1 598, 1 570, 1 480, and 1 440 cm⁻¹; δ ([²H₆]DMSO) 9.68—9.38 (2 H, m, H-2' and 7'), 9.38—9.12

(4 H, m, H-3'—6'), 8.45 (1 H, m, H-5), 8.04—7.66 (5 H, m, H-2, -3, -6, -7, and -8), and 7.24 (10 H, br s, Ph); δ (CF₃CO₂H) 9.66—9.43 (2 H, m, H-2' and -7'), 9.42—9.19 (4 H, m, H-3'—6'), 8.27—8.02 (1 H, m, H-8), 7.99—7.74 (5 H, m, H-2, -3, -5, -6, and -7), 7.99—7.20 (10 H, m, Ph), 5.71 (0.5 H, s), and 5.65 (0.5 H, s); λ_{\max} (MeCN) 268 (log ϵ 4.58), 370 (3.92), and 644 nm (3.81); λ_{\max} (CF₃CO₂H) 470 nm (log ϵ 3.87) (Found: C, 89.45; H, 4.35; N, 5.65. C₃₆H₂₂N₂ requires C, 89.60; H, 4.59; N, 5.81%). (6) is slightly soluble in DMSO, acetonitrile, and acetone.

1-Bromo-5-(cyclohepta-2,4,6-trienyl)naphthalene.—A solution of 1-bromo-5-naphthylmagnesium bromide was prepared from 1,5-dibromonaphthalene (10.0 g, 35.0 mmol), dibromoethane (1.0 g, 5.8 mmol), magnesium ribbon (1.0 g, 41.4 mmol), and dry THF (70 ml). This solution was added dropwise to a cooled solution of 7-methoxycyclohepta-1,3,5-triene (4.32 g, 35.2 mmol) in dry ether (300 ml). The mixture was worked up as described for the preparation of 1-bromo-5-(cyclohepta-2,4,6-trienyl)naphthalene to give an *oil* (5.46 g, 52%); δ (CCl₄), cycloheptatrienyl: 3.31 (1 H, br t, *J* 5.0 Hz, H-7), 5.43 (2 H, dd, *J* 9.0 and 5.0 Hz, H-1 and -6), 6.20 (2 H, m, H-2 and -5), and 6.65 (2 H, t, *J* 4.0 Hz, H-3 and -4); naphthalenyl: 8.15 (1 H, dd, *J* 8.0 and 3.0 Hz, H-4) and 6.95—7.90 (5 H, m, others) (Found: C, 68.4; H, 4.2. C₁₇H₁₃Br requires C, 68.70; H, 4.41%).

1-Bromo-5-(cyclohepta-1,3,6-trienyl)naphthalene.—Prepared as for (3), this was an *oil* (89%); δ (CCl₄), cycloheptatrienyl: 2.42 (2 H, t, *J* 6.5 Hz, H-7), 5.45 (2 H, m, H-1 and -6), 6.12 (2 H, dd, *J* 9.0 and 6.0 Hz, H-2 and -5), and 6.61 (1 H, d, *J* 6.0 Hz, H-4); naphthalenyl: 8.15 (1 H, dd, *J* 6.0 and 3.5 Hz, H-4), and 6.96—7.91 (5 H, m, others) (Found: C, 68.55; H, 4.25. C₁₇H₁₃Br requires C, 68.70; H, 4.41%).

1-(Cyclohepta-1,3,6-trienyl)-5-(3,4-diphenylcyclopenta-1,3-dienyl)naphthalene.—The preparation of this hydrocarbon was carried out by the method described for the preparation of (4), utilizing 1-bromo-5-(cyclohepta-1,3,6-trienyl)naphthalene and 3,4-diphenylcyclopent-2-enone to afford *plates* (46.7%); m.p. 146—147 °C (from dichloromethane-methanol); δ (CCl₄), cycloheptatrienyl: 2.50 (2 H, t, *J* 7.0 Hz, H-7), 5.39 (2 H, m, H-1 and -6), 6.24 (2 H, m, H-2 and -5), 6.66 (1 H, d, *J* 6.0 Hz, H-4); cyclopentadienyl: 3.97 (2 H, s, H-5), 6.84 (1 H, s, H-2); aromatic: 7.80 (1 H, dd, *J* 7.0 and 3.0 Hz) and 8.25 (1 H, m) (H-4 and -8) and 7.00—7.20 (14 H, m, others); λ_{\max} (MeCN) 310sh (log ϵ 4.15) and 347 nm (4.24) (Found: C, 94.15; H, 5.9. C₃₄H₂₆ requires C, 93.97; H, 6.03%).

Tetramethylammonium 1-(Cyclohepta-1,3,6-trienyl)-5-(2,5-dicyano-3,4-diphenylcyclopentadienylidene)naphthalene.—A procedure identical with that described for (5) gave yellow *needles* (48%), m.p. 160—163 °C (decomp.) (from dichloromethane-*n*-hexane); ν_{\max} (KBr) 2 180, 1 600, and 1 485 cm⁻¹; δ (CD₃CN) 2.87 (12 H, s, Me), 7.02—7.40 (10 H, m, Ph); cycloheptatrienyl: 2.55 (2 H, t, *J* 7.0 Hz, H-7), 5.52 (2 H, m, H-1 and -6), 6.31 (1 H, d, *J* 10.0 Hz, H-2), 6.34 (1 H, dd, *J* 9.1 and 6.0 Hz, H-5), 6.84 (1 H, br d, *J* 6.0 Hz, H-4); naphthalenyl: 7.99 (1 H, ddd, *J* 7.2, 2.5, and 1.0 Hz) and 8.22 (1 H, ddd, *J* 7.1, 3.0, and 1.0 Hz) (H-4 and -8), and 7.40—7.65 (4 H, m, others); λ_{\max} (MeCN) 271 (log ϵ 4.54) and 370sh nm (3.97) (Found: C, 86.45; H, 6.4; N, 7.45. C₄₀H₃₅N₃ requires C, 86.14; H, 6.33; N, 7.54%).

1-Cycloheptatrienylidene-5-(2'',5''-dicyano-3'',4''-diphenylcyclopentadienylidene)-1,5-dihydronaphthalene (7).—Dehydrogenation of tetramethylammonium 1-(cyclohepta-

1,3,6-trienyl)-5-(2,5-dicyano-3,4-diphenylcyclopentadienido)naphthalene, as described for (6), gave (7) as a black powder (25%), m.p. 265 °C (decomp.); ν_{\max} (KBr) 2 180, 1 600, 1 576, and 1 485 cm^{-1} ; $\delta(\text{CF}_3\text{CO}_2\text{H})$ 9.60—9.35 (2 H, m, H-2' and -7'), 9.35—9.15 (4 H, m, H-3'—6'), 8.33—8.12 (1 H, m, H-8), 8.10—7.66 (5 H, m, H-2, -3, -4, -6, and -7), 8.10—7.10 (10 H, m, Ph), 5.68 (0.5 H, s), and 5.61 (0.5 H, s); λ_{\max} ($\text{CF}_3\text{CO}_2\text{H}$) 464 nm ($\log \epsilon$ 3.87) (Found: C, 89.9; H, 4.6; N, 5.55. $\text{C}_{36}\text{H}_{22}\text{N}_2$ requires C, 89.60; H, 4.60; N, 5.81%).

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