

Medium-sized Cyclophanes. Part XIX.¹ Bridged Naphthalenes: Structural Aspects, Carbon-13 Nuclear Magnetic Resonance, and Benzoperylene Formation

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'*cis*'-[2.2](2,7)Naphthalenophane has been isolated from the reaction of 2,7-bisbromomethylnaphthalene with sodium. The structure was assigned by comparing the spectra with those of Baker's '*trans*'-compound and acyclic models. The carbon-13 n.m.r. spectrum revealed an anomalous downfield shift of the inner aryl carbon resonances for the '*trans*'-compound as compared with the '*cis*'-isomer. This was attributed to *p* orbital compression. The attempted preparation of an extremely distorted bridged $\alpha\alpha'$ -binaphthyl, [2.0](7,1)naphthalenophane, by the Wurtz reaction gave dehydrogenation products (benzoperylenes). The homologue incorporating a sulphur atom in a three-membered bridge, 3-thia[3.0](7,1)naphthalenophane, has a rigid structure with considerable strain as evidenced by u.v. and n.m.r. spectra.

IN 1951, Baker and his co-workers² prepared [2.2]-(2,7)naphthalenophane † (1) by the action of sodium on 2,7-bisbromomethylnaphthalene in dioxan. This com-

† For nomenclature see F. Vögtle and P. Neumann, *Tetrahedron*, 1970, **26**, 5847.

¹ Part XVIII, T. Sato and T. Takemura, *J.C.S. Perkin II*, 1976, 1195.

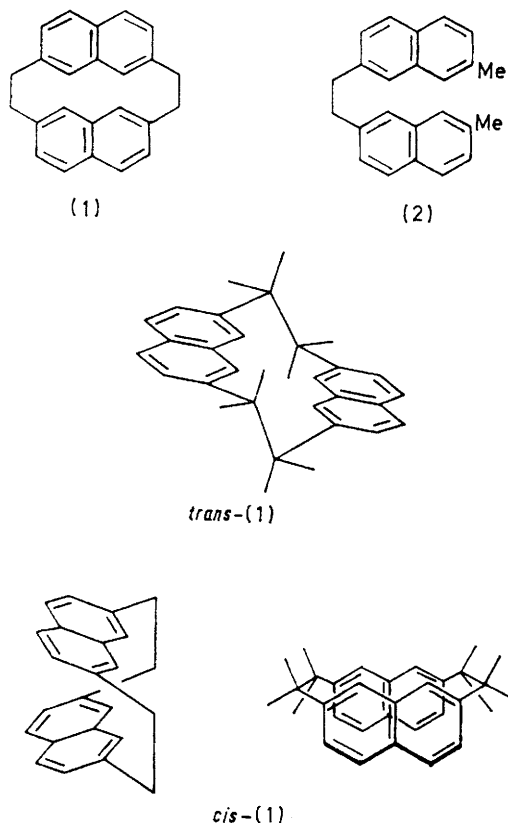
pound, m.p. 237—238°, underwent dehydrogenation to coronenes² and nitration at an inner aryl position.³

We have become interested in the ¹³C n.m.r. spectra of

² W. Baker, F. Glockling, and J. F. W. McOmie, *J. Chem. Soc.*, 1951, 1118.

³ R. W. Griffin, jun., and N. Orr, *Tetrahedron Letters*, 1969, 4567.

such strained molecules. For structure (1) no stereochemistry has been established rigorously. Moreover, models indicate the possibility of the existence of two



stereoisomers, '*cis*-' and '*trans*'-forms. From a similar condensation reaction we isolated three compounds after chromatography and mechanical separation: (A), m.p. 234–236°, (B), m.p. 247–249°, and (C), m.p. 208–212°. Compound (C) was 1,2-bis-(7-methyl-2-naphthyl)ethane (2).² Both compounds (A) and (B) showed the same parent peak in the mass spectrum at *m/e* 308 and analysis agreed with the formula C₂₄H₂₀.

Compounds (A) and (B) are identified as the '*trans*-' and '*cis*-' isomers of (1), respectively, on the basis of ¹H n.m.r. data (Table). The '*trans*-' isomer showed a

¹H Chemical shifts (δ values; solvent CDCl₃)

| Compd. | M.p. (°C) | Outer ArH | Inner ArH | CH ₂ |
|-------------------|-------------|-------------|-----------|----------------------|
| <i>trans</i> -(1) | 234–236 | 7.79 (d) | 5.01 (d) | 3.19, } AA'BB' |
| | | 7.25 (dd) | | 2.21 } |
| <i>cis</i> -(1) | 247–249 | 7.63 (d) | 6.95 (d) | 3.14 (s) |
| | | 7.22 (dd) | | |
| (7) | 153.5–154.5 | 7.3–8.1 (m) | 6.20 | 3.53 (d) 3.88 (d) |

characteristic '*inner*' aryl proton resonance at δ 5.01, together with an AA'BB' pattern for the bridging methylene protons. These data are expected from a stepped *transoid* geometry having two parallel naphthalene nuclei, since the '*inner*' aryl protons are in-

⁴ J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972.

fluenced by the diamagnetic ring current of the opposite aromatic ring and the ethylene bridges exist in a *gauche* geometry (synclinal). On the other hand, the '*cis*'-isomer showed the '*inner*' aryl resonance in the normal position, and a singlet for the methylene protons. As illustrated, '*cis*-(1)' has the ethylene bridges in the synperiplanar conformation. Baker's compound corresponds to '*trans*-(1)'.

Figure 1 shows the u.v. spectra of *cis*- and *trans*-(1) together with those of models. The *cis*-isomer has spectral features similar to those of acyclic models, in accord with the presence of less π - π interaction between the two naphthalene rings which are almost perpendicular. The spectrum of *trans*-(1), however, has less defined absorptions, with general red shifts. Again, this is typical of stepped cyclophanes with two chromophores in parallel planes.

Whereas *trans*-(1) has rigid stepped geometry, *cis*-(1) appears to have geometric freedom resulting from the conformational mobility of the 14-membered ring, as indicated by the equivalence of the methylene protons. Interconversion of the *cis*- and *trans*-forms must involve a high energy barrier, since the n.m.r. spectra determined in hexachlorobutadiene at 180 °C are almost unchanged. This high energy barrier is presumably due to severe non-bonded interactions between the '*inner*' aryl protons.

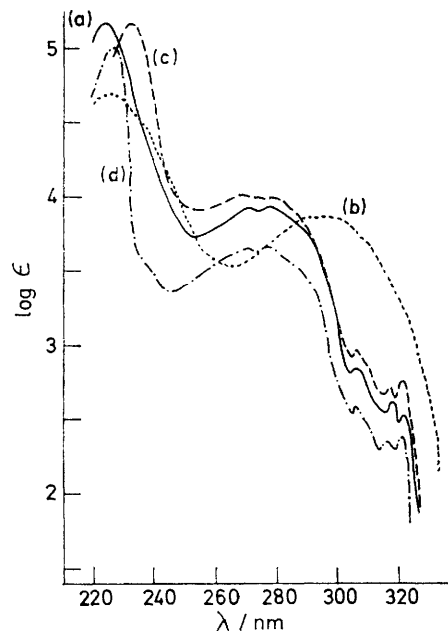


FIGURE 1 U.v. spectra (solvent tetrahydrofuran) of (a) *cis*- and (b) *trans*-isomers of compound (1), (c) the dinaphthylethane (2) and (d) 2,7-dimethylnaphthalene

The proton-noise decoupled ¹³C n.m.r. spectra were determined in CDCl₃ (Varian XL-100 spectrometer). The assignments (Figure 2) are based on calculation⁴ and comparison with models.⁵ Protonated aryl carbon

⁵ L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra,' Wiley, New York, 1972.

resonance occur in a narrow range, 126–127 p.p.m. downfield from Me_4Si for *cis*-(1) and 2,7-dimethylnaphthalene. With *trans*-(1), however, one of the three protonated aryl carbon signals is shifted to 130.8 p.p.m. It is assignable to the 'inner' aryl carbon atoms (Δ) on the basis of residual coupling comparison in the continuous wave off-resonance spectra, and utilizing the chemical shift difference of the 'inner' aryl proton resonances between the two isomers [$\Delta\delta$ 1.9 (Table)].

In [2.2]metacyclophanes the 'inner' aryl carbon resonance is shifted downfield by 6–7 p.p.m. in comparison with simple arenes.⁶ We attributed this to a decreased electron density at the sp^2 carbon atoms as a result of direct p orbital compression. The downfield shift (3.6 p.p.m.) of *trans*-(1) in comparison with *cis*-(1) is caused by a similar effect. Ring current effects appear to be small and would operate in the opposite direction.

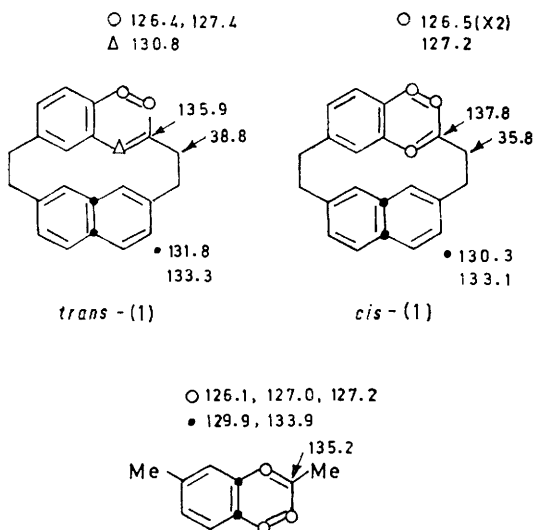


FIGURE 2 ^{13}C N.m.r. data

Whereas two p orbitals on the 'inner' aryl carbon atoms interact severely in the stepped *trans*-conformation, no such interaction is expected in the *cis*-conformation since the two p orbitals are almost perpendicular. No doubt a part of the upfield shift of the 'inner' aryl proton resonance in *trans*-(1) and also in [2.2]metacyclophanes arises from polarization along the carbon-hydrogen axis caused by electron migration from a carbon p orbital, although the diamagnetic ring current effect dominates.

In comparison with *trans*-(1), the methylene carbon resonance of *cis*-(1) is shifted to high field by 3 p.p.m. This reflects the conformation of the ethylene bridge (synclinal *vs.* synperiplanar).

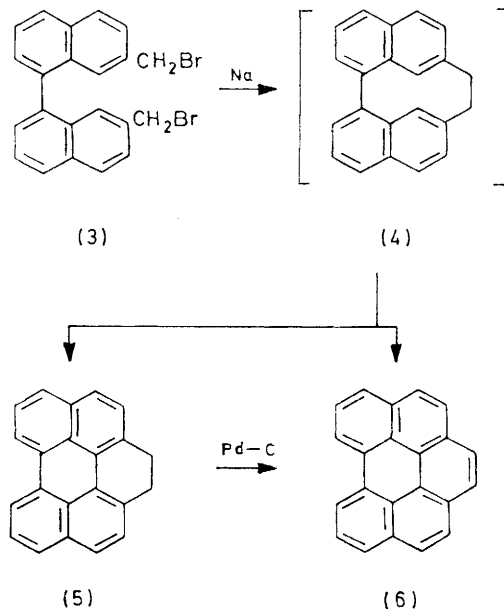
We also attempted the preparation of the more distorted bridged $\alpha\alpha'$ -binaphthyl, [2.0](7,1)naphthalenophane (4), by treatment of 7,7'-bisbromomethyl-1,1'-binaphthyl (3) with sodium. The product, however,

⁶ T. Sato and T. Takemura, *J.C.S. Chem. Comm.*, 1974, 97.

⁷ E. Clar and M. Zander, *Ber.*, 1932, **65**, 846.

⁸ E. Clar, U. Sanigok, and M. Zander, *Tetrahedron*, 1967, **24**, 2817.

was a mixture of benzo[ghi]perylene (6) and (probably) its 1,2-dihydro-derivative (5). The formation of the latter (5) is suggested by a u.v. band at 450 nm and by



mass and ^1H n.m.r. spectra. The u.v. and ^1H n.m.r. data agreed with reported values.^{7,8} The formation of compounds (5) and (6) suggests the intermediacy of the naphthalenophane (4), and may proceed *via* the derived anion radical.⁹

Treatment of the dibromide (3) with sodium sulphide in ethanol gave the sulphur analogue (7). This showed peripheral aromatic proton resonances at δ 7.3–8.1 and an inner aryl proton signal at δ 6.2 (Table). No spectral changes of the methylene AB pattern were noticed at 180 °C, indicating a high barrier for inversion. The ^{13}C data are shown in Figure 3. Comparison with the

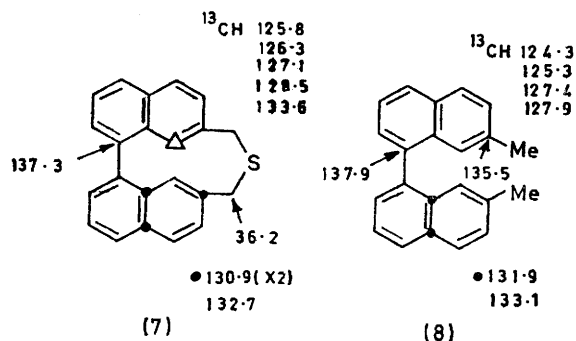


FIGURE 3 ^{13}C N.m.r. data

binaphthyl (8) reveals that one of the protonated carbon signals of (7) is shifted downfield to 133.6 p.p.m.; this is probably due to the 'inner' aryl carbon (Δ) (p orbital compression). Whereas 7,7'-dimethyl-1,1'-binaphthyl (8) showed u.v. absorptions at 286, 292, and 322 nm,

⁹ W. B. Martin and F. Gerson, *J. Amer. Chem. Soc.*, 1969, **91**, 1883; H. Kowata, M. Hoshino, and M. Koizumi, Abstracts, 24th Annual Meeting of the Chemical Society of Japan, Osaka, 1971.

compound (7) showed a broad band at 306 nm indicative of considerable strain and π - π interaction.

EXPERIMENTAL

2,7-Bisbromomethyl-naphthalene.—A mixture of 2,7-dimethylnaphthalene (10 g), *N*-bromosuccinimide (26 g), benzoyl peroxide (0.2 g), and carbon tetrachloride (75 ml) was heated under reflux for 3 h. Succinimide was then filtered off and the dibromide was isolated by evaporation; m.p. 144–146° (40%) (Found: C, 45.45; H, 3.2. Calc. for $C_{12}H_{10}Br_2$: C, 46.0; H, 3.2%).

'*cis*'- and '*trans*'-[2.2](2,7)*Naphthalenophane* (1).—A mixture of the foregoing dibromide (6.5 g), sodium (2.0 g), sodium iodide (0.05 g), and dioxan (100 ml) was refluxed for 4 h, filtered, and evaporated. Benzene extracts were subjected to repeated chromatography on alumina. With the aid of mechanical separation three fractions were obtained: *trans*-(1), m.p. 234–236°,² *cis*-(1), m.p. 247–249°, and the dinaphthylethane (2), m.p. 208–212°.

Both isomers of (1) showed *m/e* 308 (Found: C, 93.0; H, 6.7. $C_{24}H_{20}$ requires C, 93.45; H, 6.55%).

7,7'-Bisbromomethyl-1,1'-binaphthyl (3).—7,7'-Dimethyl-1,1'-binaphthyl was brominated with *N*-bromosuccinimide as above to give plates, m.p. 154–157° (65.8%). Treatment of the dibromide with sodium as above gave yellow plates, m.p. 206–210°, found to be a 1:1 mixture of benzoperylene(5) and (6) from u.v. (450 nm) and ¹H n.m.r. data. Dehydrogenation over Pd-C gave pure benzo[*ghi*]perylene(6), *m/e* 276.

2-Thia[3.0](7,1)*naphthalenophane* (7).—To a stirred mixture of sodium sulphide nonahydrate (2.4 g), ethanol (150 ml), and water (5 ml) was added a solution of 7,7'-bisbromomethyl-1,1'-binaphthyl (2 g) in benzene (150 ml) during 25 h under reflux. Chromatography of the product gave light yellow *needles*, m.p. 153.5–154.5° (18%) (Found: C, 84.55; H, 5.15. $C_{22}H_{18}S$ requires C, 84.6; H, 5.15%).

[6/303 Received, 12th February, 1976]