

[3.3]Orthocyclophanes having *vis-à-vis* Benzene RingsShuntaro Mataka,^{a,b} Kazufumi Takahashi,^{a,b} Toshizumi Hirota,^b Keisuke Takuma,^{a,b} Hiroshi Kobayashi,^{a,b} and Masashi Tashiro^{*a,b}^a Research Institute of Industrial Science, and ^b Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University 86 6-1, Kasuga-kohen, Kasuga-shi, Fukuoka 816, JapanBy the modification of the bridging carbonyl group, dibenzobicyclo[4.4.1]undecan-11-one (**3**) was converted into [3.3]orthocyclophanes having facing aromatic rings.

Because of their unique structures, *para*- and *meta*-cyclophanes have been extensively studied.¹ However, relatively little is known about orthocyclophanes having *vis-à-vis* aromatic rings; the [3.3]orthocyclophane system with two facing benzene rings is incorporated in janusene (**1**)² and the related compound (**2**).³

Recently, we found[†] that (**3**) inverts between two equivalent chair-boat conformers. We reasoned that trans-

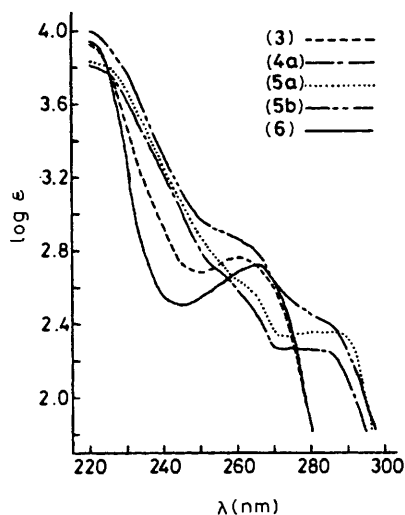
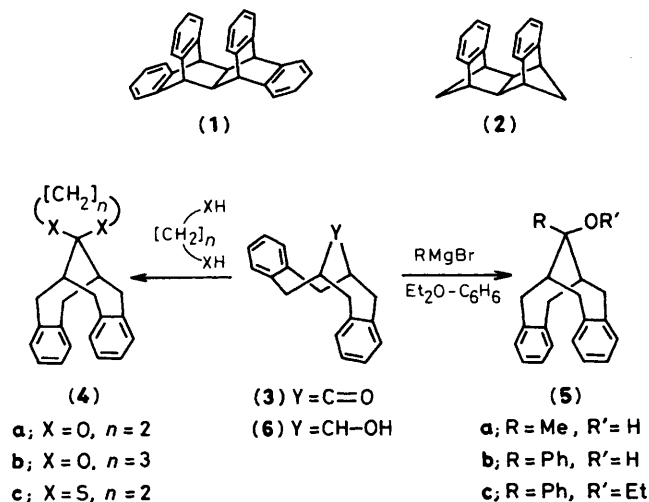


Figure 1. Electronic spectra of (**3**), (**4a**), (**5a**), (**5b**), and (**6**) (in EtOH).

[†] Unpublished work. The 1,6-bis(methoxycarbonyl) derivative (m.p. 184–186 °C) of (**3**) was prepared by the reaction of α,α' -dibromo-*o*-xylene with dimethyl 3-oxoglutarate under phase-transfer catalysed conditions. Hydrolysis of the ester followed by pyrolytic decarboxylation at 300 °C afforded (**3**) (m.p. 132–135 °C).

formation of the bridging carbonyl group of (**3**) into a substituted methylene bridge would induce steric hindrance and the resulting repulsion between the substituent(s) and the benzene rings may confine the structure to a twin-chair conformation which is a [3.3]orthocyclophane with facing aromatic rings.

This expectation is realized in the present communication.

The transformation of the carbonyl group was achieved by the reaction of the ketone (**3**) with ethylene and propylene glycol, ethane-1,2-dithiol, and Grignard reagents. The acetals, (**4a**) (m.p. 221–222 °C) and (**4b**) (m.p. 236–237 °C) and dithioacetal (**4c**) (m.p. 263–267 °C) were obtained in 79, 89, and 96% yields, respectively,[‡] by a standard method. Methylmagnesium bromide yielded the alcohol (**5a**) (m.p. 203–204 °C) in 79% yield, while phenylmagnesium bromide gave (**5b**) (m.p. 203–205 °C) in 48% yield, along with the ethyl ether (**5c**) (m.p. 239–240 °C) in 7% yield.[‡]

The ¹H n.m.r. spectra of (**4**) and (**5**) showed no line broadening due to conformational motion over the temperature range from –50 to +25 °C, thus indicating their fixed conformation. Benzylic signals were observed as an ABX pattern with $|J_{gem}| = 15–16$ and $|J_{vic}| = 0–3$ and 5–6 Hz, respectively. The observed J_{vic} values are in accord with $J_{a,e}$ (<2 Hz) and $J_{e,e}$ (6.0–6.7 Hz) of 1,1-disubstituted 4,5-benzocycloheptenes⁴ but differ from $J_{a,a}$ (11.6–13.0 Hz), disclosing the twin-chair conformation of (**4**) and (**5**). Aromatic protons appeared as a closely split multiplet(s) (δ 6.5–6.8) in a region 0.3–0.5 p.p.m. higher than that of (**3**) (single peak, δ 7.10), owing to the shielding effect of the opposite benzene ring.

Electronic spectra of (**4**) and (**5**) (Figure 1) show bands at 285–290 nm with ϵ 200–300, indicating an intramolecular 'through-space' interaction between the two facing benzene rings. A similar band was observed in the spectra of (**1**) and (**2**), but not in those of (**3**) and the alcohol (**6**).

These results strongly suggest that the compounds (**4**) and (**5**) are [3.3]orthocyclophanes with *vis-à-vis* benzene rings, though their definite structures await X-ray crystallographic determination.

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[‡] Compounds (**4**) and (**5**) gave satisfactory elemental analyses.