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Synthesis and structure of novel [2.*n*](4,4′)binaphthylophanes: a new family in cyclophane chemistry

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Abstract

[2.*n*](4,4′)Binaphthylophanes (*n*=6 and 7) were first synthesized as cyclophanes possessing binaphthyl nuclei and composed of carbon and hydrogen atoms alone. Their structure in crystal and behavior in solution were analyzed by X-ray crystallography and NMR spectroscopy, respectively. © 1999 Elsevier Science Ltd. All rights reserved.

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Since the first preparation of [2.2]paracyclophane in 1949, cyclophane chemistry has been extensively and energetically developed, together with the addition of many members possessing various aromatic nuclei.[1] Although 1,1′-binaphthyl nuclei have attracted great interest as a component of chiral materials,[2] there have been limited examples at binaphthylophanes, cyclophanes possessing binaphthyls, according to our literature survey.[3] Several binaphthylophanes with substituents at the 2- and 2′-positions are known, whereas no parent binaphthylophanes without substituents or heteroatoms have been reported. Since unsubstituted 1,1′-binaphthyl itself permits racemization even at room temperature,[4] examination of the behavior of two 1,1′-binaphthyl moieties incorporated in cyclophanes as macrocyclic ring systems is an intriguing and important subject of research.

We have successfully synthesized various [2.*n*]cyclophanes, including biphenylophanes and naphthalenophanes, by intramolecular [2+2] photocycloaddition of α,ω-bis(vinylaryl)alkanes.[5] Thus, we were prompted to apply this photochemical method to the preparation of [2.*n*]binaphthylophanes. In this communication, we report the successful synthesis of [2.*n*](4,4′)binaphthylophanes **5** and their structures and conformational behavior.

The oligomethylene tether length (*n*) suitable for the formation of **5** was first estimated by the MM2 calculation and found to be around 6 or 7.[6] Hence, we prepared precursor olefins **4** with *n*=5, 6, and 7.

The synthetic sequence is summarized in Scheme 1. Bromides **1**[7,8] were allowed to react with 1-naphthylmagnesium bromide in the presence of bis(triphenylphosphine)nickel(II) dichloride to give **2**.[9]

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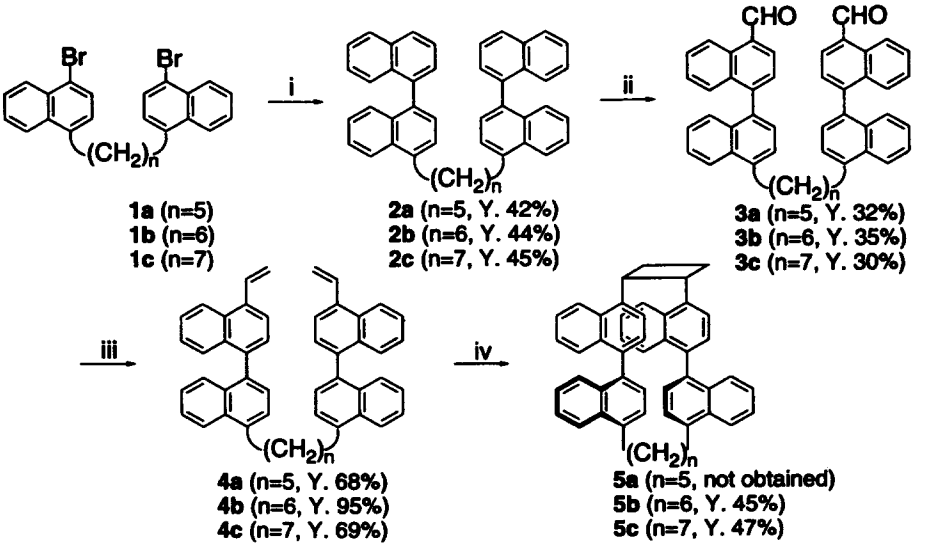
Dialdehydes **3** were regioselectively prepared by Friedel–Crafts formylation of **2** with dichloromethyl methyl ether and tin(IV) chloride.[10] The substitution of the formyl groups at the 4′-position of the binaphthyl rings was confirmed by ^{1}H NMR spectroscopy, including a COSY experiment. Precursor olefins **4** were obtained from **3** by a conventional Wittig reaction.[11] The intramolecular [2+2] photocycloaddition of **4** was carried out in benzene (2 mM) with a 400 W high-pressure mercury lamp through a Pyrex filter for 40 min. In the case of **4a** possessing a pentamethylene tether, none of the desired cyclophane was obtained and a small amount of a polymer was obtained with recovery of **4a**, probably due to the high strain loaded in the transition state.



Scheme 1. (i) 1-Naphthylmagnesium bromide, $NiCl_2(PPh_3)_2$, THF; (ii) CH_3OCHCl_2, $SnCl_4$, CH_2Cl_2; (iii) Ph_3PCH_3Br, BuLi, THF; (iv) hν, benzene

On the other hand, **4b** and **c** successfully led to the corresponding cyclophanes **5b** and **c** in reasonable yields of 45 and 47%, respectively, as a single isomer. The ^{1}H NMR spectra of **5b** and **c** exhibit a quite similar pattern to each other and give only 12 peaks in the aromatic region,[12] indicating that they have similar structures with two binaphthyl moieties equivalent in solution.

Recrystallized from benzene–hexane, binaphthylophane **5b** gave a pertinent single crystal, which was subjected to X-ray crystallographic analysis.[13] As Fig. 1 shows, one of the two binaphthyl moieties adopts the (*R*)-configuration and the other (*S*)-configuration in each molecule. The two naphthalene rings (upper-pair) attached to the cyclobutane ring are of *syn*-conformation, resulting from the rigid *exo*-conformation of the vinyl groups in the 1-vinylnaphthalene moieties of precursors **4**,[5] while those (lower-pair) attached to the oligomethylene tether are of *anti*-conformation with a quite small overlap. The dihedral angles between the two naphthalene planes of the binaphthyl moieties are ca. 71° and 108°, which are close to the value observed for the *cis* and *trans* form of 1,1′-binaphthyl itself in the crystal,[14] respectively. This structure is seemingly inconsistent with the results in the NMR spectroscopy; in crystals, the two binaphthyl moieties have different conformations in contrast with the observation in solution. This discrepancy can be rationalized by considering the dynamic behavior of the lower naphthalene rings. As far as can be judged from the space inside these rings,[15] it is possible that they are not fixed in solution at the conformation determined by X-ray analysis, but have some rotational or swinging freedom around the 1,1′-axis within a small angle (ca. ±40°), though interconversion between the (*R*)- and (*S*)-configurations

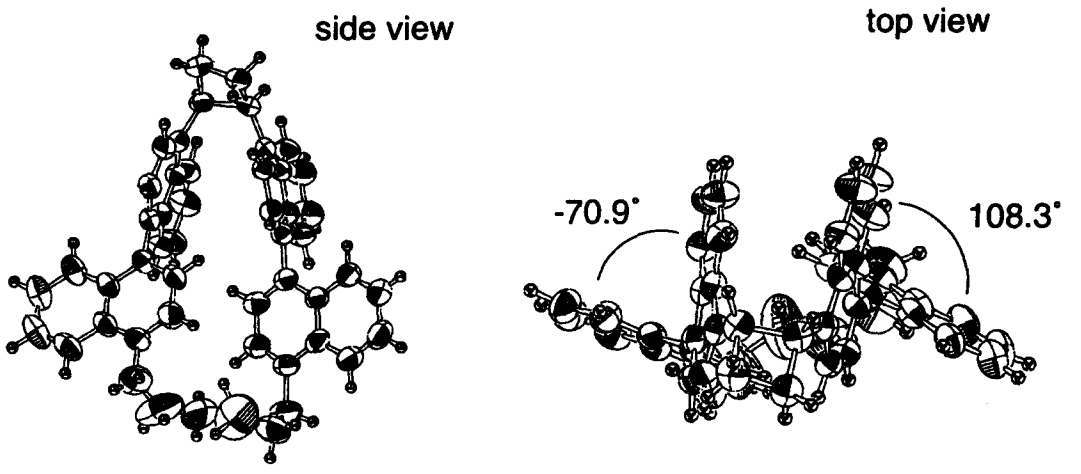
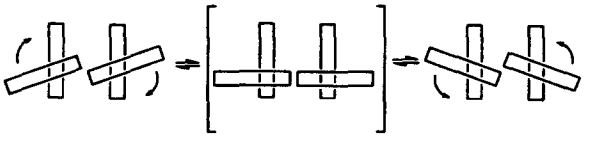


Figure 1. ORTEP drawing of **5b**

should be impossible. Such pendulous motion, which probably proceeds cooperatively, can make the two binaphthyl moieties equivalent, leading to symmetrical structures in solution (see Scheme 2).



Scheme 2. Conformational interconversion of [2.*n*](4,4′)binaphthylophanes **5**. The schematic view from the oligomethylene chain is depicted. The rectangles represent the naphthalene rings

In order to study its dynamic behavior, **5b** was subjected to a VT NMR experiment in the range of 50 to −90°C. With both increasing and decreasing temperature, slight shifts within 0.07 ppm were observed for all aromatic protons. Some peaks became slightly broad with lowering temperature. These observations suggest the motion mentioned above. Since no aromatic peaks were further split even at −90°C, the rotation barrier seems to be rather small, although precise kinetic data could not be obtained.

Further investigation, including the introduction of some substituents at the 2- and 2′-positions, is now in progress and will be reported elsewhere.

Acknowledgements

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12. Analytical and spectroscopic data for **5b**: mp 213–215°C. ^{1}H NMR ($CDCl_3$) δ 8.10 (2H, d, *J*=8.6), 7.86 (2H, m), 7.60 (2H, d, *J*=8.2), 7.47 (2H, dd, *J*=7.1, 8.2), 7.26 (2H, dd, *J*=7.3, 8.0), 7.22 (2H, d, *J*=7.3), 7.12 (2H, d, *J*=7.3), 7.02 (2H, m), 6.90 (4H, m), 6.85 (2H, d, *J*=7.1), 6.48 (2H, d, *J*=7.0), 5.20 (2H, bs), 3.14 (4H, t, *J*=3.5), 2.91 (2H, m), 2.76 (2H, m), 1.95 (4H, m), 1.47 (4H, m). ^{13}C NMR ($CDCl_3$) δ 136.66, 136.55, 136.28, 135.71, 132.77, 132.32, 132.05, 131.53, 129.25, 127.39, 126.33, 126.21, 125.39, 125.19, 125.14, 124.49, 123.99, 123.94, 123.91, 123.04, 41.27, 31.59, 28.07, 27.69, 21.58. Anal. calcd for $C_{50}H_{42}$: C, 93.42, H, 6.58, found: C, 93.07, H, 6.78%. HRMS calcd 642.3287, found 642.3300. For **5c**: mp 162–164°C. ^{1}H NMR ($CDCl_3$) δ 8.10 (2H, d, *J*=8.5), 7.86 (2H, d, *J*=8.0), 7.56 (2H, d, *J*=8.5), 7.45 (2H, dd, *J*=7.1, 7.9), 7.23 (2H, dd, *J*=8.6, 6.1), 7.18 (2H, d, *J*=7.4), 7.09 (6H, m), 6.92 (4H, m), 6.68 (2H, d, *J*=7.0), 5.17 (2H, bs), 3.16 (4H, m), 2.88 (2H, m), 2.72 (2H, m), 1.88 (4H, m), 1.48 (6H, m). ^{13}C NMR ($CDCl_3$) δ 136.74, 136.73, 136.51, 135.67, 132.96, 132.47, 132.06, 131.86, 128.44, 127.37, 126.38, 126.28, 125.30, 125.24, 125.14, 124.49, 123.91, 123.80, 123.79, 123.00, 41.26, 30.67, 27.94, 27.37, 26.95, 22.01. HRMS calcd 656.3443, found 656.3442.
13. Crystal data for **5b**: $[C_{50}H_{42}]$, M=642.88, monoclinic, crystal dimensions 0.20×0.20×0.30 mm^3, space group $P2_1/n$, *a*=14.377(1) Å, *b*=12.659(2) Å, *c*=19.7677(8) Å, β=99.646(5)°, *V*=3546.9(5) Å^3, *Z*=4, μ (CuKα)=5.10 cm^{-1}. Of total 5812 collected reflections, 3653 were observed. The final *R* (*Rw*) values were 0.061 (0.039).
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