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[2.2](2,6)BIPHENYLENOPHANE AND [2](2,6)BIPHENYLENO[2](2,6)NAPHTHALENOPHANE

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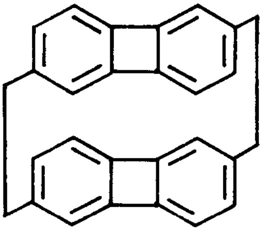
Summary: Two cyclophanes, [2.2](2,6)biphenylenophane and [2](2,6)biphenyleno[2](2,6)naphthalenophane, were prepared.

A various type of cyclophanes has been prepared to date which contain two $(4n+2)\pi$-electron systems of benzenoid, hetero, and nonbenzenoid aromatic compounds.[1,2] In these cyclophanes through-space interaction between the superposed π-electron systems has drawn much attention. In connection with this, layered cyclophanes[3] and intramolecular charge-transfer complexes of cyclophanes[4] were prepared. However, there has been little investigation concerned with interaction between two $4n\pi$-electron systems or between $4n\pi$- and $(4n+2)\pi$-electron systems because of the instability of the $4n\pi$ anti-aromatic system. Recently, synthesis of a cyclophane containing s-indacene (planar 8π-electron system) was tried[5] and some cyclophanes containing cyclooctatetraene (non-planar 8π-electron system) were prepared.[6] We wish to report the synthesis and some properties of cyclophanes (**1**) and (**2**) containing a biphenylene component, which has a potentially paratropic, 4π-electron system in the central four-membered ring.



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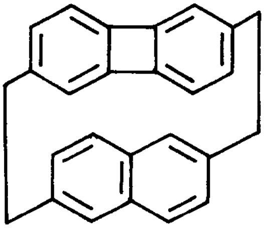
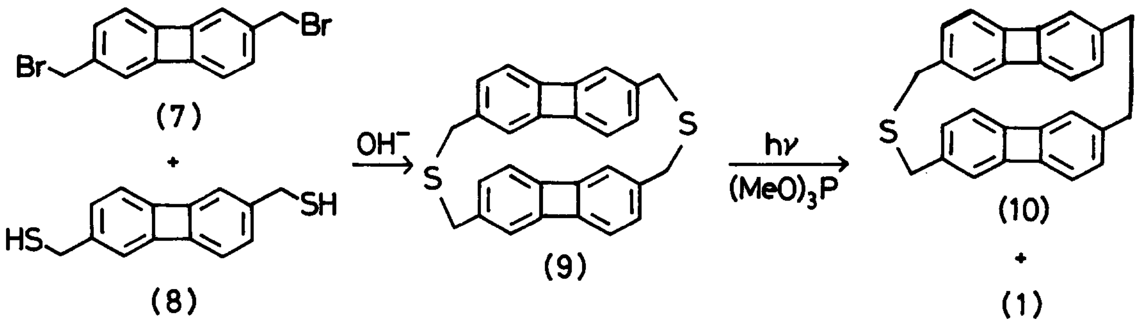


(2)

Biphenylene (**3**) reacted with N,N-dimethylcarbamoyl chloride and anhydrous aluminum chloride to give 2,6-bis(N,N-dimethylcarbamoyl)biphenylene (**4**)[7] in 82.3% yield, in which the position of the functional groups was confirmed by converting **4** to the authentic 2,6-diacetylbiphenylene[8] through the reaction

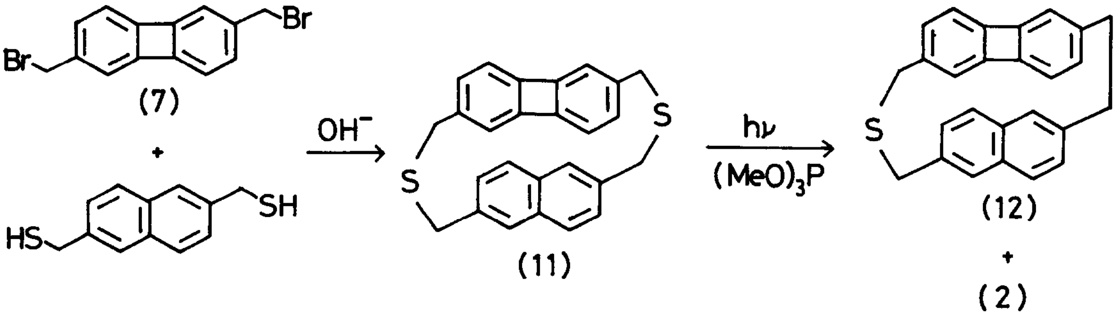


of **4** with methyl lithium in tetrahydrofuran. Compound **4** was submitted to ethanolysis in the presence of sulfuric acid to afford 2,6-bis(ethoxycarbonyl)-biphenylene (**5**) as yellow needles (m.p. 89-90°C) in good yield. Reduction of **5** with lithium aluminum hydride produced 2,6-bis(hydroxymethyl)biphenylene (**6**) (m.p. 213-213.5°C) in quantitative yield, which was brominated with phosphorous tribromide in refluxing benzene to give 2,6-bis(bromomethyl)biphenylene (**7**) as pale yellow plates (m.p. 184.5-184.6°C) in 70% yield. Compound **7** was allowed to react with thiourea and subsequently hydrolyzed to give 2,6-bis(mercaptomethyl)biphenylene (**8**)[9] as yellow crystals in 82% yield.

The reaction of 2,6-bis(bromomethyl)biphenylene (**7**) with disodium salt of 2,6-dimercaptobiphenylene (**8**) in boiling ethanol under high dilution conditions afforded 2,13-dithia[3.3](2,6)biphenylenophane (**9**) as pale yellow crystals [(m.p. 185-190°C(dec.)] in 70% yield. The structure of **9** was determined by elemental analysis, mass [m/e 420 (M^+)] and ^{1}H-NMR spectrum, which contained two sets of aromatic signals, [δ 5.89(bs, 2H) and 6.49-6.62 (m, 4H)] and [6.33 (bs, 2H), and 6.29 (dd, J=5.8 and 1.0 Hz, 2H), and aromatic signals at δ 6.37 (dd, J=5.8 and 0.8 Hz, 2H)], along with complex methylene signals (δ 3.25-3.69). The ^{1}H-NMR spectrum indicates that **9** is a 1:1 mixture of two orientational isomers (vide infra). Irradiation (100W high pressure Hg-lump, Pyrex filter) of **9** in trimethylphosphite for 5 days gave [2.2](2,6)biphenylenophane (**1**) and 2-thia[3.2](2,6)biphenylenophane (**10**) in 22.4% and 16.8%, respectively. The ^{1}H-NMR spectrum of **10** was very complex [δ ($CDCl_3$) 5.42-6.50 (m, 12H), 2.20-2.90 (m, 8H) and 3.49-3.83 (m, 8H)] but was not inconsistent with the assigned structure. The ^{1}H-NMR spectrum of **1** [δ ($CDCl_3$) 5.55 (s, 4H), 6.49 (s, 8H), and 2.15-2.18 (m, 8H)] offered the confirmation for the assigned structure and some further inquisitive information about this compound. Biphenylenophane 1, like [2.2](2,6)naphthalenophane,[10] exists as two orientational isomers, the crossed and fully overlapped forms. In the ^{1}H-NMR spectrum of **1**, one of the α-protons of a biphenylene moiety resonated at considerably upfield (δ 5.55). This can be explained only by the crossed form, in which one of the α-protons is held over the benzene ring of the opposite biphenylene nucleus suffering mainly from a shielding effect by the benzene ring.[11] The electronic spectrum of **1** showed a blue shift of the β-band, a red shift of the α- and p-bands and an appearance of a new band at 265-285 nm, compared with a reference compound (2,6-diethylbiphenylene), suggesting obvious transannular π-electronic interaction. This spectral feature is quite similar to that observed for [2.2](2,6)naphthalenophane,[10] which would suggest that the central four-membered ring of **1** adds no novel character to this cyclophane.

Compound **7** reacted with disodium salt of 2,6-bis(mercaptomethyl)naphthalene in boiling ethanol under high dilution conditions to give 2,13-dithia[3](2,6)-biphenyleno[3](2,6)naphthalenophane (**11**) as yellow cubes (m.p. 232-234°C) in 35% yield. The elemental analysis, mass [m/e 396], and ^{1}H-NMR spectra [δ($CDCl_3$) 6.13 (s, 2H), 6.11 (d, J=7.1 Hz, 2H), 6.50 (d, J=7.1 Hz, 2H), 6.94 (s, 2H), 7.37 (s, 2H), 7.38 (s, 2H), 3.56 (d, J=14.1 Hz, 4H), 3.76 (d, J=14.1 Hz, 4H), 3.56 (d, J=15.2 Hz, 4H) and 3.95 (d, J=15.2 Hz, 4H)] supported the assigned structure of **11**. This compound was irradiated for 90 hrs (100W high-pressure Hg-lump, Pyrex filter) in trimethylphosphite to give [2](2,6)biphenyleno[2]-(2,6)naphthalenophane (**2**) as yellow crystals (m.p. 193-195°C) in 24.7% yield, and 2-thia[3](2,6)biphenyleno[2](2,6)naphthalenophane (**12**) in 33.8% yield. The ^{1}H-NMR spectrum of **12** supported the assigned structure. In the ^{1}H-NMR spectrum ($CDCl_3$) of **2**, one of the α-protons of the biphenylene moiety and one of the α-protons of napthalene moiety appeared at δ 5.33 and 6.80, respectively. Such an upfield shift of the α-protons indicates that **2** has the crossed form similar to **1**. An upfield shift in the α-protons was considerably large in the biphenylene moiety as compared with the naphthalene moiety. This seems to be due to the shortened distance between the naphthalene and biphenylene planes which causes a bend distortion more in the biphenylene moiety than in the naphthalene one, increasing the olefinic character of ring protons, especially the α-proton, of the biphenylene nucleus. The electronic spectrum of **2** was considerably complicated because of interaction between two different, distorted chromophores, but the disappearance of the β-band due to a biphenylene chromophore may reflect a bend distortion of the biphenylene plane of **2**, as indicated by the ^{1}H-NMR spectrum of **2**. Compound **2** showed a broad and strong fluorescence peak at 400 nm in cyclohexane at room temperature.

Further investigation of the cyclophanes **1** and **2** is in progress.



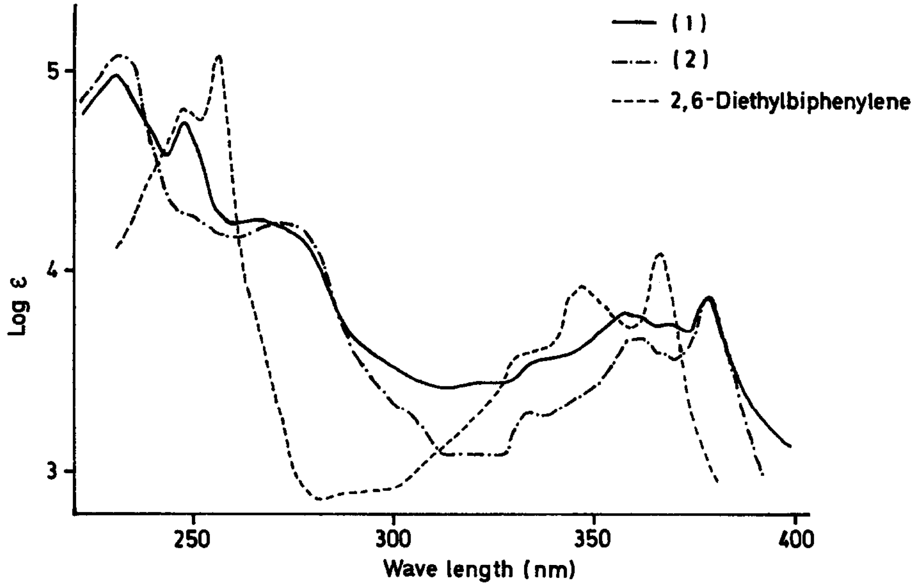


Figure. Electronic spectra of 1, 2, and related compounds (in cyclohexane)

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