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SYNTHESES OF THREE [2.2]PYRENOPHANES AS AN EXCIMER MODEL[1]

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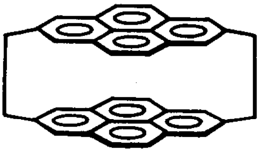
Previously we reported the synthesis of [2.2](2,7)pyrenophane **1** as a suitable pyrene excimer model and observed a characteristic excimer fluorescence band in its emission spectrum, the maximum (540 nm) of which showed rather red shift compared with that (470 nm) of the pyrene excimer.[2,3] In order to correlate the structure of the pyrene excimer to the excimer fluorescence, we designed to synthesize [2.2]pyrenophanes with different stacking modes. In this communication, we wish to report on the syntheses of three [2.2]pyrenophanes, **2**, **3**, and **4**, and discuss the orientation dependence of excimer emission.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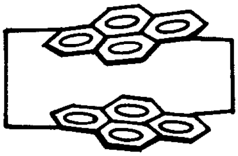
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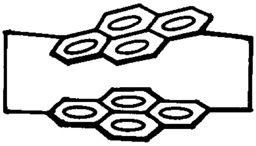
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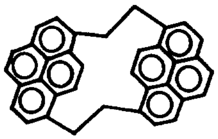
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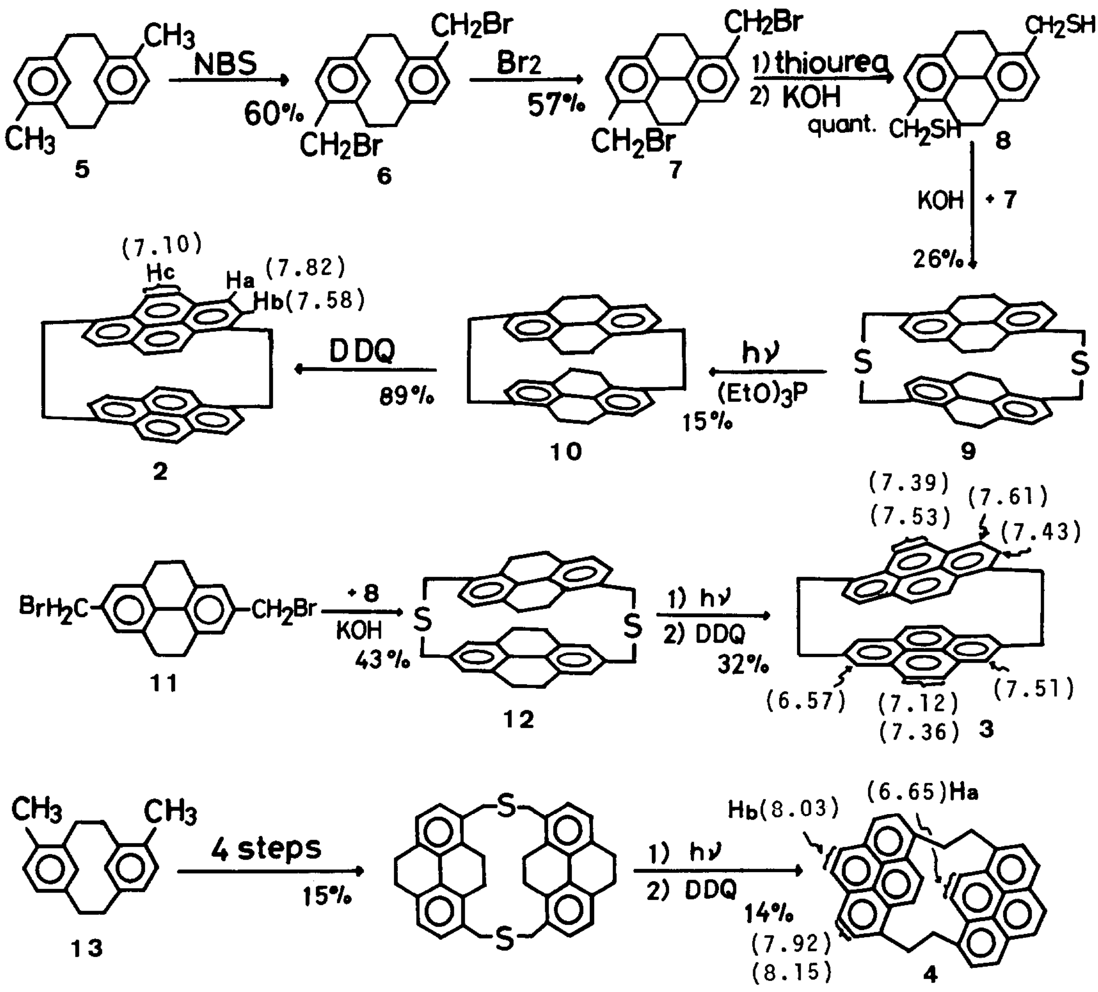
All the three pyrenophanes, **2-4**, were prepared by a synthetic route using a unique transannular reaction of [2.2]metacyclophane[4] as shown in the scheme. Reaction of 4,12-dimethyl[2.2]metacyclophane **5**[5] with NBS led to dibromide **6** [**6**: colorless prisms from CCl_4, mp 209.5-210°C]. When treated with bromine in CH_2Cl_2, **6** underwent the transannular reaction to produce tetrahydropyrene derivative **7** [**7**:colorless plates from benzene, mp 243-244°C (decomp)]. Dibromide **7** was converted in the usual way to dimercaptan **8** [**8**: colorless scales from benzene, mp 196-197°C]. Coupling of **8** with **7** under high dilution gave cyclic disulfide **9** in 26% yield [**9**: colorless prisms from benzene, mp 249-251°C (decomp)]. Irradiation of **9** in triethylphosphite with a high pressure mercury lamp under nitrogen bubbling for 16 h gave tetrahydropyrenophane **10** [**10**: colorless plates from benzene-hexane, mp 307-309°C (decomp)]. Dehydrogenation of **10** with DDQ in toluene under reflux for 7 h afforded [2.2](1,6)pyrenophane **2** [**2**: yellow plates from benzene-ethanol, mp 324-325°C (decomp)].

[2.2](1,6)(2,7)Pyrenophane **3** was similarly synthesized via cyclic disulfide **12** which was obtained by coupling of **8** and **11** [**3**:yellow plates from benzene, mp 319-320°C (decomp)]. [2.2](1,8)Pyrenophane **4** was also prepared from 4,14-

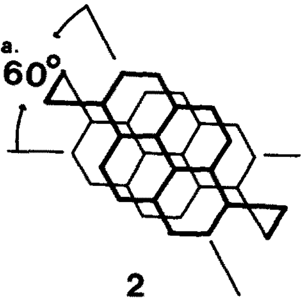


[The values in parentheses are NMR chemical shifts (δ ppm, 100 MHz) in $CDCl_3$.]

dimethyl[2.2]metacyclophane **13**$^{5)}$ in a similar way [**4**: yellow fine crystals from benzene, mp 309-310°C (decomp)].

The structure of the three pyrenophanes were characterized by NMR and MS spectra and elemental analysis. The NMR data given in the reaction scheme indicate that the structure of **2** is assigned to D_2-symmetric isomer but not to C_{2h}-symmetric one because of marked upfield shift of Hc relative to both Ha and Hb. Similarly, the marked upfield shift of Ha of **4** indicates anti-form to be preferred to syn-form for the structure of **4**.

The X-ray crystallographic analysis of **1** showed that the two pyrene rings were fully stacked face to face.$^{3b,6)}$ A consideration of **2** and **3** with molecular model suggests that the two molecular axes through C_2 and C_7 of the pyrene



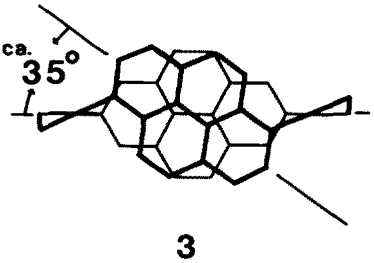


Fig. 1. Possible conformations of **2** and **3**.

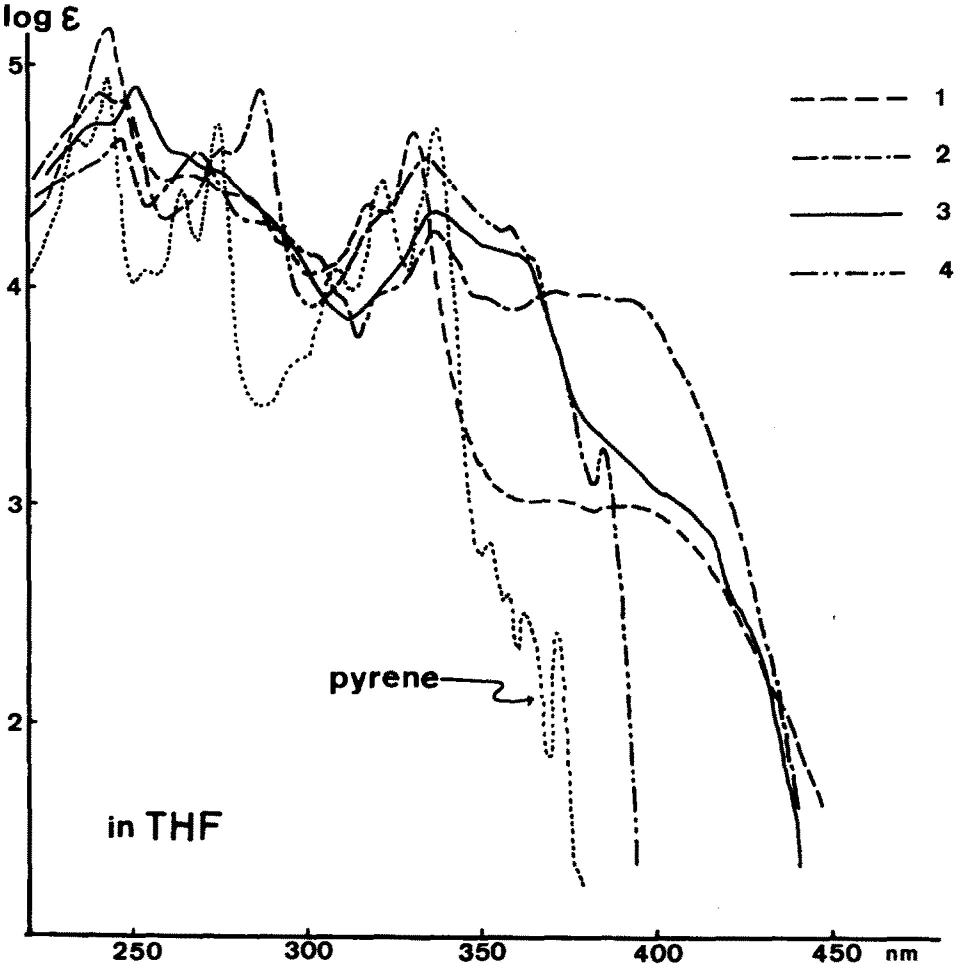


Fig. 2. Electronic sprctra of **1 - 4** and pyrene.

moieties intersect at an angle of ca. 60° in **2** and of ca. 35° in **3**, respectively, as shown in Fig. 1.

As seen in Fig. 2, the electronic spectra of **1**-**3** show large bathochromic shifts of the longest wavelength bands as compared with that of pyrene itself, indicating remarkable transannular electronic interactions between two pyrene chromophores. On the other hand, relatively small change in the curve of **4** suggests a weak interaction owing to partial stacking of the two pyrene rings.

These pyrenophanes show interesting fluorescence spectra. Thus, relatively intensive fluorescence band of **2** appears in the region of 440-450 nm, with broadening at room temperature and fine structure at 77 K. Compound **4** shows an intensive band at 410 nm (at R.T.). On the other hand, **3** exhibits a weak and broad structureless band in a longer wavelength region (λ_{max} 500 nm at R.T. and 480-505 nm at 77 K). The spectral feature above stated clearly demonstrates that the emissions of **2** and **4** are of pyrene monomer type, whereas the emission of **3** is of pyrene excimer type and similar to that of **1**.

On the basis of the structures and the emission spectra of the four pyrenophanes, it is concluded that the pyrene excimer may have a considerably limited structure comparable to those of **1** and **3**.

References

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