# THE ATTEMPTED SYNTHESIS OF A DINAPHTH-1,6-BISDEHYDRO[10]ANNULENE\*

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Abstract—Attempts to prepare the dinaphth-1,6-bisdehydro[10]annulene 3 are described. 1-Ethynyl-8-(1'-iodo-8'-naphthylethynyl)naphthalene (13) was prepared in several steps from 1,8-diethynylnaphthalene (6), making use of the trimethylsilyl protecting group. The cuprous derivative of 13 on treatment with pyridine gave zethrene (9) and 7-iodozethrene (25), instead of 3. Zethrene (9) was also obtained from the attempted dehydrobromination of 1-(*trans*- $\beta$ -bromovinyl)-8-(1'-iodo-8'-naphthylethynyl)naphthalene (12) to 13 with strong base, and from the condensation of the di-cuprous derivative of 6 with 1,8-diiodonaphthalene (8). It appears that 3 is an unstable substance, which is readily converted to zethrene (9) and its derivatives.

RECENT work<sup>1, 2</sup> has shown that [10]annulene is an unstable non-aromatic substance, despite the fact that it contains (4n + 2)  $\pi$ -electrons. This is presumably due to steric interaction of the internal protons and/or bond angle strain. Such steric or bond angle strain may not be present in the related 1,6-bisdehydro[10]annulene (1),<sup>3</sup> which also contains (4n + 2) out-of-plane  $\pi$ -electrons, and it is possible that this substance will be aromatic. Indeed, 1,8-bisdehydro[14]annulene (2), a higher vinylogue of 1, has already been shown to be an aromatic substance.<sup>4</sup>



The possibility exists, of course, that there will be considerable interaction of the in-plane  $\pi$ -electrons of the acetylenes in 1,6-bisdehydro[10]annulene (indicated in formula 1), which might destabilize the molecule. The same effect is not expected in 1,8-bisdehydro[14]annulene (see formula 2), since the two acetylenic linkages in this substance are much further apart than in 1. In order to find out the importance of this

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type of interaction, it appeared worthwhile to prepare the dinaphth-1,6-bisdehydro-[10]annulene 3 as a suitable model. Like 1, 3 is presumably a planar 10-membered ring compound, containing two acetylenes on opposite sides of the ring, and the interaction of the in-plane  $\pi$ -electrons should be similar to that in 1. This interaction



might be reflected in the properties of 3, e.g. in its instability and transannular reactions. We have already shown that the related tetra-acetylene  $4,^5$  as well as the di-olefin  $5,^6$  are unstable substances.

In the present paper, we describe attempts to prepare 3. After completion of this work, related experiments designed to lead to 3 were reported in preliminary form by Staab *et al.*<sup>7</sup>

The cyclic diacetylene 3 could not be obtained from the di-olefin 5 by a simple halogenation-dehydrohalogenation sequence, since treatment of 5 with chlorine or bromine led to derivatives of zethrene (9).<sup>6</sup> We therefore decided to investigate a route starting from the recently synthesized 1,8-diethynylnaphthalene (6),<sup>5, 7</sup> making use of the fact that a disubstituted acetylene may be prepared by treating a cuprous acetylide with an aryl iodide in boiling pyridine.<sup>8</sup>

The diacetylene 6 was treated with cuprous iodide in ethanol and aqueous ammonia, or preferably in dimethylformamide and anhydrous ammonia (see below). The resulting unstable di-cuprous derivative 7 was then allowed to react with 1,8diiodonaphthalene  $(8)^9$  in boiling pyridine. The cyclic diacetylene 3 could not be



obtained from this reaction, but zethrene  $(9)^{6, 10}$  was isolated in low yield. We had already shown that the cyclic di-olefin 5 is readily converted to zethrene (via 7,14dihydrozethrene),<sup>6</sup> and it was considered probable at this stage of our work that 3 had in fact been formed from 7 and 8 as an unstable intermediate, which had undergone a transannular reaction to give zethrene (9). The possible conversion of 3 to 9, which of course involves the addition of two atoms of hydrogen, is discussed further below.

The attempted synthesis of 3 from 7 and 8 in boiling pyridine involves rather vigorous conditions, and it was desirable to investigate milder ones. Unfortunately, no reaction occurred at lower temperatures, probably due to the very low solubility of the di-cuprous derivative 7 in pyridine. Consequently, it was decided to investigate routes to 3 which utilized a mono-cuprous acetylide in the final cyclization step, since such a derivative is expected to be considerably more soluble in organic solvents than a di-cuprous derivative. To this end,  $1-(trans-\beta-bromovinyl)-8$ -ethynylnaph-thalene (10)<sup>5</sup> was converted to the cuprous derivative 11, which was heated in pyridine with 1,8-diiodonaphthalene (8). This reaction led to the bright orange bromo-iodo-



acetylene 12 (m.p. 169–170°) in rather poor yield, the best one (14%) being obtained when the condensation was carried out at 90° for 2 hr. The configuration of the double bond in 12 was shown to be *trans*, as in the precursor 10,<sup>5</sup> since the IR spectrum exhibited a relatively strong band at 967 cm<sup>-1</sup>. The NMR spectrum of 12 consisted of a 13 H multiplet at  $\tau$  2:0–3:2, as well as a 1 H doublet (J = 7 Hz) at  $\tau$  1:73; the coupling constant of this doublet does not correspond to that of a *trans*-olefinic bond, and the band is presumably due to a deshielded naphthalene proton.

Unexpectedly, we were unable to carry out the next step in the projected synthesis, the dehydrobromination of 12 to the ethynyl compound 13. Treatment of 12 with potassium t-butoxide in boiling t-butanol and dioxane or benzene led to recovered starting material, while sodamide in liquid ammonia resulted in insoluble polymeric material. Reaction of 12 with potassium t-butoxide in boiling tetrahydrofuran gave R. H. MITCHELL and F. SONDHEIMER

ca. 10% of a yellow-orange substance (m.p. 148–150°), assigned the isomeric cisolefinic structure 14. This formulation follows from the mass and NMR spectra, as well as the absence of the *trans* olefinic band at ca. 970 cm<sup>-1</sup> in the IR spectrum.

Treatment of 12 with potassium t-pentoxide in boiling t-pentyl alcohol gave a single red product in 17% yield,\* identified as zethrene (9). The formation of 9 from 12 under these conditions cannot involve the iodo-ethynyl compound 13 as an intermediate, since 13 (prepared by the method described below) gave no 9 under the same conditions. The mechanism of this reaction, which represents an unusual cyclization, is unknown.

Treatment of 12 under other basic conditions (see Experimental) also led to 9 and/or 14. Presumably, the inability of the bromovinyl group in 12 to undergo dehydrobromination is a reflection of the fact that  $H^{\alpha}$  (see formula 12a) is hindered



from attack of base by the neighbouring acetylene and/or naphthalene groupings. A similar case appears to be the acetylenic chlorovinyl compound 15, which also could not be dehydrohalogenated with base.<sup>11</sup>

In view of these results, it was decided to employ an acetylene protecting group which could be removed easily, and the trimethylsilyl group<sup>12</sup> appeared to be a suitable one. The first two steps of the projected synthesis involved the conversion of 1,8-diethynylnaphthalene (6) to the mono-trimethylsilyl compound 19, followed by



formation of the cuprous derivative 21. Unfortunately, the usual conditions for preparing cuprous acetylides are strongly basic (see Ref 8), and the protecting group in 19 might thereby be removed. In fact, we found that phenylethynyltrimethylsilane  $(16)^{13}$  was rapidly converted to cuprous phenylacetylide (17) by treatment with cuprous iodide and aqueous ammonia in ethanol. Other conditions for preparing cuprous acetylides were therefore investigated. After some experimentation, it was found that cuprous iodide in ethanol and dimethylformamide, through which gaseous ammonia had been passed briefly, was a suitable reagent. It converted phenylacetylene (18) to the cuprous derivative 17, but did not affect the trimethylsilyl derivative 16.

\* Both zethrene (9) and 7-iodozethrene (25) decompose in solution, and the quoted yields represent minimum values.

1,8-Diethynylnaphthalene (6) was now treated with 1 molar equivalent of butyllithium, and then with chlorotrimethylsilane. Chromatography on alumina furnished the monosilyl derivative 19 (liquid) and the disilyl derivative 20 (m.p. 40-42°), each in ca. 40% yield. Inferior yields of 19 and 20 were obtained when ethylmagnesium bromide was used instead of butyl-lithium in the first step. Substance 19 was then



converted to the cuprous derivative 21 in almost quantitative yield under the new conditions described above. Most conveniently, the mixture of 19 and 20 was used in this reaction, since only 19 was affected, and the resulting 21 separated directly from the reaction mixture. The cuprous derivative 21 proved to be considerably more stable in air than either 7 or 11.

The next step, the reaction between 21 and 1,8-diiodonaphthalene (8) in pyridine was investigated at different temperatures. The best results were achieved by heating at 100° for 90 min, conditions which gave rise to 26% of the desired iodo-silyl compound 22 (m.p. 91-92°) in addition to several other substances. The NMR spectrum of 22 showed a 9 H singlet at  $\tau$  10-06 due to the methyl protons. The methyl protons of 22 are therefore slightly shielded with respect to those of tetramethylsilane, in contrast to those of 19 ( $\tau$  9.63) and 20 ( $\tau$  9.68).

The protecting group in 22 was removed rapidly by means of sodium hydroxide in aqueous methanol at room temperature.<sup>12</sup> The resulting crude iodo-ethynyl compound 13 was obtained as an unstable oil, which was best converted directly to the relatively stable cuprous derivative 23 by treatment with cuprous iodide and aqueous ammonia in ethanol and dimethylformamide. A pure sample of the unstable 13 (m.p. 92–94° dec) could be obtained by hydrolysis of 23 in benzene with aqueous hydrochloric acid, but this resulted in much loss of material due to decomposition.

The cyclization of the cuprous derivative 23 to the cyclic diacetylene 3 was attempted under a variety of conditions. Boiling in pyridine for 90 min led to zethrene (9) in 22% yield.\* In addition, two other red products were obtained; the mass spectra of these showed them to be derived from the cyclic "dimer" and "trimer", respectively,



and they were not investigated further. When the cyclization of 23 in pyridine was carried out at 80° for 30 min,  $10\%^*$  of zethrene and  $11\%^*$  of another dark red substance (m.p. 126-128°) were isolated. The last mentioned substance proved to be 7-iodozethrene (25), as evidenced by the UV, NMR and mass spectra. In particular, the NMR spectrum consisted of a 1 H doublet (J = 7.5 Hz) at  $\tau 1.28$  (H<sup>1</sup>, H<sup>6</sup>, H<sup>8</sup> or H<sup>13</sup>), a 11 H multiplet at 2.0-2.9 (other naphthalene protons) and a 1 H singlet at 3.02 (H<sup>14</sup>). By comparison, the NMR spectrum of zethrene (9) showed a 2 H doublet (J = 7.5 Hz) at  $\tau 1.91$  (H<sup>1</sup> and H<sup>8</sup>, or H<sup>6</sup> and H<sup>13</sup>) and a 12 H multiplet at 2.2-2.8 (H<sup>7</sup>, H<sup>14</sup> and other naphthalene protons).

When the cyclization of 23 in pyridine was carried out at 35°, 7-iodozethrene (25) was obtained in 6% yield,\* as well as 6% of a yellow iodine-containing compound. We did not determine the structure of this substance, which appeared to be isomeric with 25 (mass spectrum) and did not contain acetylene groupings (IR spectrum). The cyclization of 23 in other solvents was also studied, and the same substances obtained in pyridine could be isolated in certain cases (e.g., 9 and 25 were obtained by heating 23 with hexamethylphosphorictriamide at 110°, or with dimethylformamide at 60°).

It is probable that the formation of both 9 and 25 from 23 involves the cyclic diacetylene 3 as an intermediate; transannular cyclization of 3 could give 24 (or an equivalent species), which by addition of the elements of hydrogen yields 9, and by addition of the elements of hydrogen iodide (e.g., by addition of CuI, followed by hydrolysis) yields 25. This indicates that there is severe interaction of the in-plane

\* See footnote on page 2144

 $\pi$ -electrons of the acetylenes in compounds of type 3, and that 1,6-bisdehydro[10]annulene (1) itself will probably not be a stable aromatic compound.

Our results are in agreement with those obtained by Staab *et al.*<sup>7</sup> These investigators obtained zethrene (9) in 50 % yield when an attempt was made to prepare 3 by heating the cuprous derivative 26 in pyridine at 115° for 8 hr, and zethrene was also formed in the reaction of 7 with 8.

## **EXPERIMENTAL**

General procedures. M.ps were taken on a Kofler block and are uncorrected. IR spectra: as KBr discs (for solids) on a Perkin-Elmer 257 spectrophotometer (only main bands are given). UV spectra: in 95% EtOH (unless otherwise stated) on a Cary model 14M spectrophotometer. NMR spectra: on a Perkin-Elmer R.10 or a Varian HA-100 instrument (TMS used as internal standard, unless indicated differently). Mass spectra: on an AEI MS9 mass spectrometer (70 eV, direct inlet system). Evaporations were carried out under reduced pressure. Al<sub>2</sub>O<sub>3</sub> for column chromatography was Woelm neutral, activity II-III. All operations involving the preparation and reactions of the acetylenic cuprous derivatives were conducted under N<sub>2</sub>.

#### Reaction of di-cuprous derivative 7 with 1,8-diiodonaphthalene (8)

A soln of 6 (176 mg, 1-0 mmole)<sup>5. 7</sup> in dry DMF (10 ml) was added to a stirred suspension of CuI (380 mg, 2-0 mmoles) in DMF (10 ml), and NH<sub>3</sub> gas was then bubbled into the mixture for ca. 10 sec. After being stirred for 15 min, the ppt was collected, washed successively with EtOH and ether, and was then briefly dried on the funnel in a stream of N<sub>2</sub>. The resulting dark yellow 7 was immediately transferred to a soln of 8 (380 mg, 1-0 mmole)<sup>9</sup> in dry pyridine (25 ml). The stirred mixture was boiled under reflux for 6 hr, and was then cooled. Ether and 2N HCl aq were added, the organic layer was dried, evaporated, and the residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (500 g). Pentane eluted 6 and then zethrene [ca. 6 mg (2%), determined from the UV spectrum], identical with the previously described sample<sup>6</sup> (UV, NMR and mass spectra).

## 1-(trans-β-Bromovinyl)-8-(1'-iodo-8'-naphthylethynyl)naphthalene (12)

A suspension of CuI (2·3 g, 11·4 mmole) in NH<sub>3</sub> aq (50 ml, ca. 17·5 % w/w) was added to a soln of 1-(*trans*β-bromovinyl)-8-ethynylnaphthalene (10, 2·92 g, 11·4 mmole)<sup>5</sup> in EtOH (100 ml) with vigorous stirring. After 15 min, the bright yellow 11 was collected, washed successively with H<sub>2</sub>O, EtOH and ether, and was then briefly dried on the funnel in a stream of N<sub>2</sub>. The resulting 11 was added to a soln of 8(4·3 g, 11·4 mmole) in dry pyridine (150 ml), and the mixture was stirred at 90° for 2 hr. Most of the pyridine was evaporated, and the residue was shaken with benzene and 2N HCl aq. The organic extract was filtered through Supercel, washed with 2N HCl aq and H<sub>2</sub>O, and dried. The solvent was evaporated and the residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (500 g). Pentane eluted unchanged 8 (2·05 g, 48 %), and then 12 (792 mg, 14 %), bright orange crystals from MeOH, m.p. 169–170°. (Found : C, 56·91; H, 2·84. C<sub>24</sub>H<sub>14</sub>BrI requires : C, 56·61; H, 2·77%);  $v_{max}$  967 (m), 905 (m), 837 (vs), 800 (m), 791 (m), 786 (s), 774 (vs), 753 (s), and 666 (m) cm<sup>-1</sup>;  $\lambda_{max}$  231 nm (log  $\varepsilon$  4·60), 256 inf (4·39), 293 inf (4·07), and 415 (4·24); NMR spectrum (CCl<sub>4</sub>), see Discussion; mass spectrum, peaks at *m/e* 510, 508 (M<sup>+</sup>; 35% each), 429 (M-Br; 7%), 428 (M-HBr; 8%), 383, 381 (M-I, 3% each), 382, 380 (M-HI; 2% each), and 302 (M-BrI; 100%).

#### Attempted dehydrobromination of 12

(a) With potassium t-butoxide in tetrahydrofuran. Dry KOBu<sup>4</sup> (1 g) was added to a soln of 12 (100 mg) in dry THF (25 ml). The mixture was boiled under reflux for 2 hr, cooled, and poured into benzene and 2N HCl aq. The benzene extract was washed with H<sub>2</sub>O, dried, and evaporated. Chromatography on Al<sub>2</sub>O<sub>3</sub> (200 g) and elution with pentane yielded 14 (10 mg, 10%), yellow-orange crystals from MeOH, m.p. 148–150° (with some previous softening);  $v_{max}$  832 (m), 813 (m), 770 (s), 758 (s), and 672 (m) cm<sup>-1</sup>;  $\lambda_{max}$  (cyclohexane) 230 nm (log e 4-52), 257 (4-45), 273 (4-39), 296 inf (4-25), 307 inf (4-14), 3-54 (3-90), 373 (4-18), and 393 (4-29); NMR spectrum (CCl<sub>4</sub>), multiplet at  $\tau$  1-6–3-3; mass spectrum, peaks at *m/e* 510, 508 (M<sup>+</sup>; 4% each), 428 (M-HBr; 61%), 382, 380 (M-HI; 4% each), and 302 (M-BrI; 100%).

(b) With potassium t-pentoxide in t-pentyl alcohol. K (1.6 g) was added to dry redistilled t-pentyl alcohol (50 ml), and the mixture was boiled under reflux for 3 hr. 12 (70 mg) was then added, and the mixture was boiled for a further 40 min. The deep red product, isolated as described under (a), was chromatographed

on  $Al_2O_3$  (100 g). Elution of the red band with benzene and crystallization from xylene gave 9 as deep purple crystals (7 mg, 17%), m.p. 260–262° (lit<sup>10</sup> m.p. 262°), identified with the previously described sample<sup>6</sup> by mixture m.p. determination and spectral comparison.

(c) With potassium hydroxide in ethanol. A soln of 12 (100 mg) and KOH (10 g) in EtOH (40 ml) and  $H_2O$  (2 ml) was boiled under reflux for 14 hr. Isolation as before and chromatography on  $Al_2O_3$  (100 g) yielded 14 (6%, determined by the UV spectrum) and then 9 (5%, determined from the UV spectrum).

(d) By fusion with potassium hydroxide. 12 (100 mg) was added to a mixture of KOH (1 g) and  $H_2O$  (0-15 ml) at ca. 230°. The mixture was maintained at this temp for 30 sec, and was then quenched with ice. The product was isolated as before. TLC analysis showed the presence of unchanged 12 admixed with some 14.

(c) With potassium t-butoxide in dimethyl sulphoxide. A mixture of 12 (50 mg), KOBu<sup>t</sup> (400 mg), Me<sub>2</sub>SO (7 ml) and Bu<sup>t</sup>OH (7 ml) was heated at 90° for 10 min. The product was isolated as before and chromatographed on Al<sub>2</sub>O<sub>3</sub> (50 g). Pentane eluted 9 (5%, determined by the UV spectrum), while later fractions contained unidentified sulphur-containing products.

#### Cuprous phenylacetylide (17)

A soln of 18 (1.0 g, 9.8 mmole) in EtOH (2 ml) was added to a vigorously stirred suspension of CuI (2.0 g, 10.5 mmole) in DMF (10 ml).  $NH_3$  gas was then bubbled into the mixture for ca. 15 sec, when a bright yellow ppt formed. The ppt was collected, washed successively with EtOH and ether, and was then dried. The resulting 17 weighed 1.50 g (92%). Similar treatment of 16 under identical conditions gave no 17.

#### 1-Ethynyl-8-(trimethylsilylethynyl)naphthalene (19) and 1,8-bis(trimethylsilylethynyl)naphthalene (20)

A soln of BuLi (Fluka, 57 mmoles) in hexane (31 ml) was added dropwise during 30 min to a stirred soln of 6 (100 g, 57 mmoles) in dry THF (200 ml) and ether (20 ml). The mixture was heated to reflux during the course of 30 min, and a soln of chlorotrimethylsilane (80 g, 73 mmole) in THF (10 ml) and ether (20 ml) was added in one portion. The mixture was boiled under reflux for 1 hr, cooled and poured into  $H_2O$ . The product was extracted with ether, and the organic extract was washed with  $H_2O$ , dried, and evaporated. The residue was pre-absorbed onto  $Al_2O_3$  (50 g) and then chromatographed on  $Al_2O_3$  (1 kg).

Pentane eluted firstly 20 (3-98 g, 22 %) as a colourless oil [b.p. 84–85° (0·2 mm)], which could be crystallized from cold pentane to give crystals, m.p. 40–42°. (Found : C, 75-02, H, 7·73.  $C_{20}H_{24}$ Si requires : C, 74-94; H, 7·55%);  $v_{max}$  2970 (s), 2155 (vs), 1378 (s), 1358 (s), 1260 (vs), 1254 (vs), 1241 (s), 1015 (vs), 855 (vs), 768 (vs), and 715 (s) cm<sup>-1</sup>;  $\lambda_{max}$  228 nm inf (log  $\epsilon$  4-63), 238 (4·87), 257 (3·94), 270 (4-00), 317 (4·14), 330 (4·25), 340 inf (4·14), and 345 (4·27); NMR spectrum (CCl<sub>4</sub>, relative to acetone at  $\tau$  7·95), 6 H five-line multiplet at  $\tau$  2·2-2·8 (aromatic protons) and 18 H singlet at 9·68 (methyl protons); mass spectrum, molecular ion *m/e* 320·142 (calcd for  ${}^{12}C_{20}{}^{11}H_{24}{}^{28}Si_2$ : 320·142), with peaks at *m/e* 320 (M<sup>+</sup>; 100%) and 305 (M-CH<sub>3</sub>; 30%).

Pentane next eluted a mixture of 19 and 20 (7.54 g; ratio ca. 3:2, estimated from the NMR spectrum) as a colourless oil which was used directly in the next reaction.

Pentane then eluted 19 (1·32 g, 9·4%) as a colourless liquid, b.p. 54–58° (0·2 mm). (Found : C, 82·34; H, 6·49.  $C_{17}H_{16}$ Si requires : C, 82·21; H, 6·49%);  $v_{max}$  (neat) 3290 (vs), 2956 (s), 2140 (s), 2100 (w), 1372 (vs), 1352 (s), 1261 (vs), 1251 (s), 850 (s), 828 (s), and 766 (s) cm<sup>-1</sup>;  $\lambda_{max}$  236 nm (log e 4·74), 255 sh (3·85), 263 (3·74), 270 (3·54), 321 (4·10), 325 (4·09), 333 (4·05), and 339 (4·03): NMR spectrum (CCl<sub>4</sub>, relative to acetone at  $\tau$  7·95), 6 H multiplet at  $\tau$  2·2–2·8 (aromatic protons), 1 H singlet at 6·56 (acetylenic proton), and 9 H singlet at 9·63 (methyl protons); mass spectrum, molecular ion m/e 248·101 (calcd for  ${}^{12}C_{17}{}^{14}H_{16}{}^{28}Si:$  248·102, with peaks at m/e 248 (M<sup>+</sup>; 48%), 247 (M-H; 10%), 233 (M-CH<sub>3</sub>; 100%), and 217 (M-C<sub>2</sub>H<sub>7</sub>; 38%).

Pentane finally eluted 6 (1.47 g, 15%). The yield of 19 was 41 % and of 20 38%.

When 6 was treated first with 1 molar equiv of EtMgBr in THF (boiling 1 hr) and then with chlorotrimethylsilane (essentially as above), chromatography of the product on  $Al_2O_3$  gave 15% of 19, 26% of 20, and 42% of 6.

## 1-(Trimethylsilylethynyl)-8-(1'-iodo-8'-naphthylethynyl)naphthalene (22)

A soln of the mixture of 19 and 20 from the above described chromatography (3.5 g; ca. 3:2; ca. 8.5 mmoles of 19) in EtOH (25 ml) was added to a vigorously stirred suspension of CuI (2.6 g, 13.7 mmoles) in dry DMF (25 ml). NH<sub>3</sub> gas was bubbled into the mixture for ca. 10 sec, which was stirred for a further 15 min. The yellow ppt was collected, washed successively with EtOH and ether, and was then briefly dried on the funnel in a stream of N<sub>2</sub>. The resulting bright yellow 21 was added under N<sub>2</sub> to a soln of 8 (4.6 g, 12.1 mmoles) in pyridine (80 ml, dried over CaH<sub>2</sub>). The mixture was stirred at 100° for 90 min under

 $N_2$ , and was then cooled and poured into ether and 2N HCl aq. The organic layer was washed with 2N HCl aq and  $H_2O_3$ , and was then dried and evaporated. The residue was pre-adsorbed on  $Al_2O_3$  (60 g), and chromatographed on  $Al_2O_3$  (500 g).

Pentane eluted firstly 8 (1.40 g, 30%). Next, pentane eluted two yellow and one red substance, having molecular weights > 650 (mass spectrometry). Pentane then eluted crude 22 (1.08 g, 26%) as an orange oil, which was hydrolyzed directly to 13 for preparative purposes. For characterization, the oil was purified by preparative layer chromatography [Kieselgel HF<sub>254 + 366</sub>; elution with pentane-ether (97:3)]; crystallization from methanol gave pure 22 as pale yellow crystals, m.p. 91–92°. (Found : I, 26.45. C<sub>27</sub>H<sub>21</sub>ISi requires : I, 26.36%);  $v_{max}$  2138 (m), 1376 (m), 1241 (s), 844 (s), 825 (s), 816 (s), 763 (s), and 753 (s) cm<sup>-1</sup>;  $\lambda_{max}$  (cyclohexane) 241 nm (log  $\epsilon$  4:80), 333 inf (4:21), 351 (4:31), and 375 inf (4:14); NMR spectrum (CCl<sub>4</sub>, relative to acetone at  $\tau$  7:95), 12 H multiplet at  $\tau$  1:5–3·1 (aromatic protons) and 9 H singlet at  $\tau$  10·06 (methyl protons); mass spectrum, molecular ion *m/e* 500-042 (calcd for  ${}^{12}C_{27}{}^{11}H_{21}{}^{127}I^{28}Si$ : 500-046), with peaks at *m/e* 500 (M<sup>+</sup>; 18%), 485 (M-CH<sub>3</sub>; 6%), 427 (M-C<sub>3</sub>H<sub>9</sub>Si; 51%), 374 (M-I + H or M-C<sub>10</sub>H<sub>6</sub>; 12%), 373 (M-I; 11%), 358 (M-CH<sub>3</sub>I; 100%), and 343 (M-C<sub>2</sub>H<sub>6</sub>I; 35%).

#### **Cuprous derivative 23**

Crude 22 (685 mg, 1-37 mmole) in ether (50 ml) was added to a soln of 10% NaOH aq (20 ml) in MeOH (50 ml), and shaken at room temp for 5 min. Ether and  $H_2O$  were added, and the organic layer was washed with 2N HCl aq and  $H_2O$ . Evaporation of the dried soln gave crude 13 (575 mg, 1-34 mmole) as an unstable dark oil, which was dissolved in EtOH (10 ml) and added to a vigorously stirred suspension of CuI (1 g, 5-25 mmole) in DMF (10 ml) and EtOH (10 ml). NH<sub>3</sub> aq (10 ml, ca. 17.5% w/w) was added, and the dark yellow ppt was collected, washed successively with  $H_2O$ , EtOH, and ether, and was then briefly dried on the funnel in a stream of N<sub>2</sub>. The resulting deep yellow 23 weighed 656 mg (98% based on 22). (Found : Cu, 12.4. C<sub>24</sub>H<sub>12</sub>CuI requires : Cu, 12.9%). The substance could be stored under N<sub>2</sub> for several weeks with little decomposition.

# 1-Ethynyl-8-(1'-iodo-8'-naphthylethynyl)naphthalene (13) by hydrolysis of 23

A mixture of 23 (350 mg, 0.71 mmole), benzene (50 ml) and 2N HCl aq (50 ml) was stirred vigorously at room temp for 12 hr. The benzene layer was washed with H<sub>2</sub>O, dried, and evaporated. Rapid filtration of the residue in pentane through Al<sub>2</sub>O<sub>3</sub> (20 g) gave 13 (155 mg, 51 %) as a yellow oil, homogeneous by TLC. Crystallization from petroleum ether (b.p. 80–100°) resulted in much decomposition (formation of black insoluble material), but gave pure 13 (15 mg), pale yellow crystals, m.p. 92–94° dec. (Found: I, 28.85. C<sub>24</sub>H<sub>13</sub>I requires: I, 29.64%); v<sub>max</sub> 3293 (m), 1382 (s), 831 (s), 820 (s), and 767 (s) cm<sup>-1</sup>;  $\lambda_{max}$  (ether) 238 nm (log  $\varepsilon$  4.84) and 353 (4.35); NMR spectrum (CDCl<sub>3</sub>), 12 H multiplet at  $\tau$  1.5–3.1 (aromatic protons) and 1 H singlet at 6.49 (acetylenic proton); mass spectrum, molecular ion *m/e* 428.005 (calcd for  ${}^{12}C_{24}{}^{11}H_{13}{}^{127}I$ : 428-006), with peaks at *m/e* 428 (M<sup>+</sup>; 38%), 305 (27%), 304 (55%), 303 (62%), 302 (M-I + H or M-C<sub>10</sub>H<sub>6</sub>; 100%), 301 (M-I; 36%), and 300 (M-HI; 53%). Substance 13 was unstable, and rapidly became dark yellow, brown, and then black, on standing in air.

#### Attempted cyclization of 23 to 3

(a) In boiling pyridine. A mixture of 23 (920 mg) and pyridine (50 ml, dried over CaH<sub>2</sub>) was stirred and boiled under reflux for 90 min under N<sub>2</sub>. The red mixture was cooled, poured into benzene and 2N HCl aq, and filtered through Supercel. The organic layer was washed with 2N HCl aq and H<sub>2</sub>O, and was then dried and evaporated. The residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (750 g). Pentane-benzene (4:1) eluted 9 (123 mg, 22%, determined from the UV spectrum) as a red band; evaporation and crystallization from xylene gave 9 (79 mg) as deep red-violet crystals, m.p. 261–262° (lit<sup>10</sup> m.p. 262°);  $\nu_{max}$  857 (m), 828 (s), 818 (m), and 759 (s) cm<sup>-1</sup>;  $\lambda_{max}$  (CHCl<sub>3</sub> flushed with N<sub>2</sub>, determined rapidly) 299 nm (log s 4:23), 307 (4:25), 366 (3:47), 386 (3:62), 408 (3:55), 476 (4:06), 510 (4:45), and 548 (4:59); NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>), 2 H doublet (J = 7:5 Hz) at  $\tau$  1:91 (H<sup>1</sup> and H<sup>8</sup>, or H<sup>6</sup> and H<sup>13</sup>) and 12 H multiplet at 2:2-2:9 (H<sup>7</sup>, H<sup>14</sup>, and other naphthalene protons); mass spectrum, molecular ion *m/e* 302:112 (calcd for <sup>12</sup>C<sub>24</sub><sup>1</sup>H<sub>14</sub>: 302:110), with peaks at *m/e* 302 (M<sup>+</sup>; 100%), 300 (M-H<sub>2</sub>; <10%) and 298 (M-H<sub>4</sub>; <10%). The substance was identified with the previously described sample<sup>6</sup> by mixture m.p. determination and spectral comparison.

Later chromatography fractions contained first a red "dimeric" product;  $\lambda_{mex}$  (CHCl<sub>3</sub>) 330 nm (rel int 1-00), 390 (0-30), 413 (0-26), 505 (0-33), and 534 (0-35); mass spectrum, peaks at m/e ca. 600 (100%) and 300 (58%). A red "trimeric" product was then obtained, which on crystallization from xylene-pentane gave

dark red crystals (9 mg), m.p. > 280°;  $\lambda_{max}$  (CHCl<sub>3</sub>) ca. 500 nm inf (rel int 0.73), 531 (1.00), and ca. 565 inf (0.71); mass spectrum, peaks at m/e ca. 900 (20%), 600 (100%), and 300 (100%).

(b) In pyridine at 80°. A stirred mixture of 23 (200 mg) and dry pyridine (25 ml) was heated at 80° for 30 min under N<sub>2</sub>. The product was isolated as described under (a), and chromatographed on Al<sub>2</sub>O<sub>3</sub> (250 g). Pentane-benzene (19:1) eluted 25 (19 mg, 11%, determined from the UV spectrum) as a red band; filtration through Al<sub>2</sub>O<sub>3</sub> (500 g) and immediate crystallization from MeOH (cooled to  $-40^{\circ}$ ) gave deep red crystals (7 mg) of 25, m.p. 126–128°;  $v_{max}$  854 (m), 828 (vs), 777 (vs), 770 (vs), 757 (s), and 750 (s);  $\lambda_{max}$  (CHCl<sub>3</sub>) 299 nm (log  $\varepsilon$  4·10), ca. 340–370 inf (3·36), 405 (3·45), 429 (3·74). 460 (4·03), 509 inf (4·32), and 530 (4·32): NMR spectrum (CCl<sub>4</sub>), 1 H doublet (J = 7.5 Hz) at  $\tau$  1·28 (H<sup>1</sup>, H<sup>6</sup>, H<sup>8</sup>, or H<sup>13</sup>), 11 H multiplet at 2·0–2·9 (other naphthalene protons), and 1 H singlet at 3·02 (H<sup>14</sup>); mass spectrum, molecular ion *m/e* 428·007 (calcd for <sup>12</sup>C<sub>24</sub><sup>1</sup>H<sub>13</sub><sup>127</sup>I:428·006), with peaks at *m/e* 428 (M<sup>+</sup>; 100%), 302 (M-I + H; 73%), 301 (M-I; 40%), and 300 (M-HI; 58%).

Later chromatography fractions, eluted with pentane-benzene (4:1), contained 9 (13 mg, 10.5%, determined from the UV spectrum).

(c) In pyridine at 35°. A mixture of 23 (150 mg) and dry pyridine (25 ml) was stirred at 35° for 4 hr under N<sub>2</sub>. The product was isolated as described under (a), and chromatographed on Al<sub>2</sub>O<sub>3</sub> (250 g). Benzene-pentane (19:1) eluted first 25 (7.6 mg, 6%, determined from the UV spectrum). This solvent mixture then eluted an unidentified yellow fluorescent compound, pale yellow crystals (8 mg, 6%) from benzene-pentane; the substance decomposed at ca. 140° on attempted m.p. determination, and was too insoluble in CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>, or C<sub>6</sub>D<sub>6</sub> for determination of the NMR spectrum;  $v_{max}$  832 (m), 825 (s), and 764 (s) cm<sup>-1</sup>;  $\lambda_{max}$  (CHCl<sub>3</sub>) 365 nm sh (log  $\varepsilon$  4.01), 376 inf (4.17), 384 sh (4.30), 395 (4.49), and 417 (4.75); mass spectrum, peaks at *m/e* 428 (M<sup>+</sup>; 5%), 302 (M-I + H; 37%), 301 (M-I; 28%) and 300 (M-HI; 100%).

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