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Preparation of 1,10-Dimethyl-benzo[*c*]cinnolines by Photochemical Cyclodehydrogenation of Azobenzenes

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Summary. Photocyclodehydrogenation of methylated azobenzene derivatives to the corresponding benzo[*c*]cinnolines was utilized for the synthesis of a number of compounds featuring sterically hindered methyl groups with different degrees of sterical hindrance including close mutual methyl-methyl interaction. Such compounds are of special theoretical interest in the context of intramolecular dynamics, spectroscopy, and quantum (tunneling) effects. Factors determining synthetic accessibility and product distribution are discussed.

Keywords. 1,10-Dimethyl benzo[*c*]cinnolines; Photochemical cyclization; Photocyclodehydrogenation; Buttressing effect; Methyl gearing.

Darstellung von 1,10-Dimethyl-benzo[*c*]cinnolinen durch photochemische Cyclodehydrogenierung von Azobenzolen

Zusammenfassung. Photocyclodehydrogenierung von methylsubstituierten Azobenzolderivatven zu den entsprechenden Benzo[*c*]cinnolinen wurde zur Synthese einer Reihe von Verbindungen benützt, die sich durch Methylgruppen unterschiedlicher sterischer Hinderung – einschließlich gegenseitiger Methyl-Methyl-Wechselwirkung – auszeichnen. Derartige Verbindungen sind aus theoretischer Sicht in Bezug auf intramolekular Dynamik, Spektroskopie und Quanten-(Tunnel-)Effekte von großem Interesse. Faktoren, die synthetische Zugänglichkeit und Produktverteilungen bestimmen, werden diskutiert.

Introduction

The 4,5-disubstituted phenanthrene skeleton is a very attractive structural motif for the investigation of sterical interactions of the substituents. The susceptibility of these aromatic hydrocarbon derivatives to migration of alkyl substituents makes them less suitable if high purity and stability over extended periods of time are required for thermodynamic or spectroscopic studies. We were therefore interested in the possibility of preparing aza analoga of 4,5-dimethyl-phenanthren, *i.e.* 1,10-

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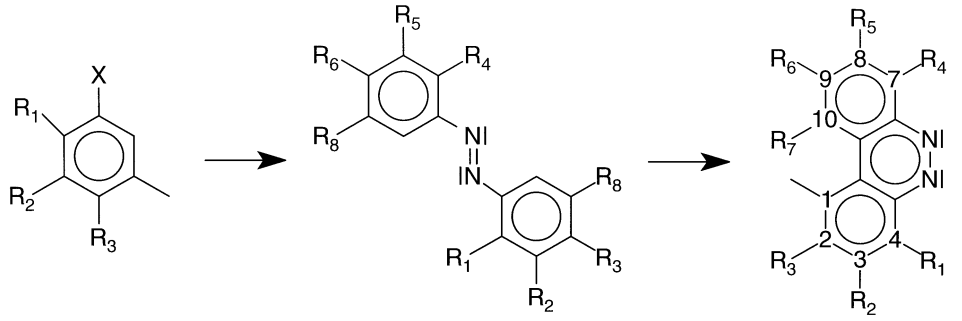

1,4,14 **2,5,7,9,10,15** **3,6,8,11,12,13**

Fig. 1. General transformation scheme and compound overview; the substituents are defined in Table 1

Table 1. Substituents of compounds **1–15** (cf. Fig. 1)

	X	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
1, **2**, **3**	$-NH_2$	–H	$-CH_3$	–H	–H	$-CH_3$	–H	$-CH_3$	$-CH_3$
4, **5**, **6**	$-NO_2$	$-CH_3$	–H	–H	$-CH_3$	–H	–H	$-CH_3$	$-CH_3$
7, **8**		$-CH_3$	–H	–H	–H	$-CH_3$	–H	$-CH_3$	$-CH_3$
9		Br	–H	–H	–H	–H	–H	–	$-CF_3$
10		$-CH_3$	–H	–H	–H	–H	–H	–	$-CF_3$
11		$-CH_3$	–H	–H	–H	$-CH_3$	–H	–H	–
12		–H	$-CH_3$	–H	–H	$-CH_3$	–H	–H	–
13, **14**, **15**	$-NH_2$	–H	$-CH_3$	–Br	–H	$-CH_3$	–Br	$-CH_3$	$-CH_3$

dimethyl-benzo[*c*]cinnolines. Compounds with this substitution pattern are of theoretical interest in many respects such as skeletal deformations resulting from methyl sterical interactions [1, 2], changes in electrophilic aromatic reactivity induced by skeletal deformations [3], reduced methyl rotational mobility [4], and the possibility of correlated methyl group rotation (methyl gearing) [5, 6]. We have therefore investigated scope and limitations of the photochemical cyclodehydrogenation of appropriately substituted azobenzenes to produce different benzo[*c*]-cinnoline derivatives (see Fig. 1 and Table 1).

The photochemical cyclodehydrogenation of azobenzenes to benzo[*c*]cinnolines has earlier been investigated by *Joshua* and *Pillai* [7, 8]. To our knowledge, no reports have been published so far concerning the formation of sterically hindered products *via* this synthetic pathway.

Results and Discussion

Using the symmetrical 3,3′,5,5′-tetramethyl-azobenzene (**2**) as a starting material, only 1,3,8,10-tetramethyl-benzo[*c*]cinnoline (**3**) is formed. Assuming the mechanism proposed by *Joshua* [7] in which three molecules azobenzene react to give 2 molecules benzo[*c*]cinnoline (one molecule of azobenzene is used for the oxidation

of the primary cyclization product), the theoretical yield is 2/3. The practical yield of 66% of **3** compares favorably to that reported for unsubstituted azobenzene (57%) [7]. We also found that the yield is essentially unaffected by a buttressing effect [1]: starting form 4,4′-dibromo-3,3′,5,5′-tetramethyl-azobenzene (**15**), a yield of 64% of benzo[*c*]cinnoline **13** was obtained.

A mechanism for the photocyclodehydrogenation has been proposed in Ref. [7]. In cases where an azobenzene derivative can react to give different products (*i.e.* if one benzene ring bears different substituents in the two *ortho* positions with respect to the azo group), one finds that the sterically less hindered product is favored, even if the reaction has to proceed *via* loss of a methyl group (Fig. 2).

However, the relative thermodynamic stability of the products cannot be responsible for the product distribution in this irreversible photochemical reaction. Assuming the mechanism proposed in Ref. [7], the symmetrical (*E*)-2,2′,5,5′-tetramethyl-azobenzene (**5**) could in principle react to three different benzo[*c*]cinnoline derivatives. Depending on the conformation of the (*Z*)-azobenzene intermediate ((*Z-anti*,*anti*)-**5**, (*Z-anti*,*syn*)-**5**, or (*Z-syn*,*syn*)-**5**), the photochemical

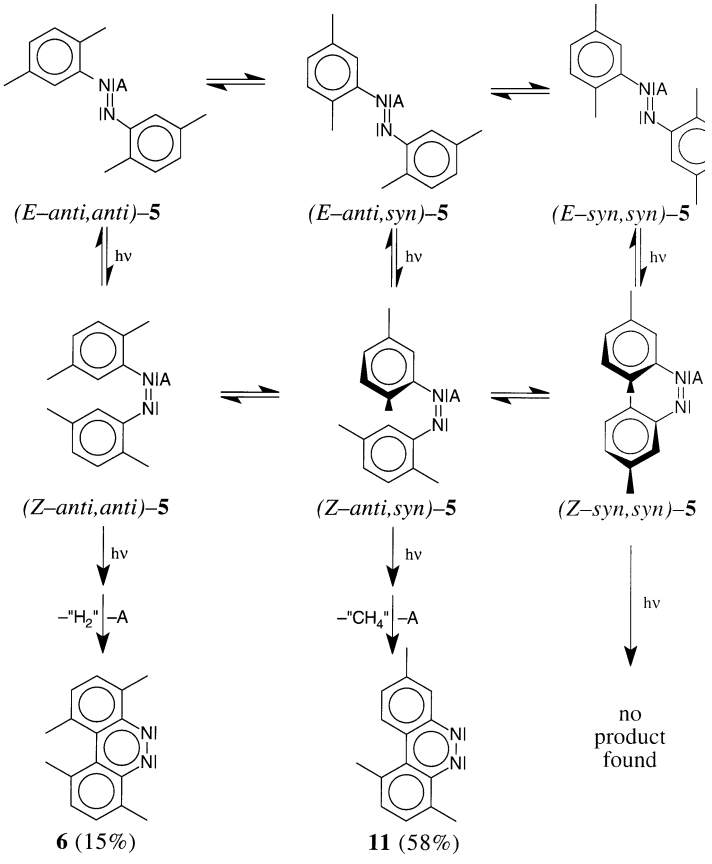

Fig. 2. Key steps in the acceptor *A* assisted photocyclization of azobenzenes; the formal loss of CH_4 or H_2 in the final multi-step transformation involves oxidation by another molecule of the respective azobenzene [7] which is not shown here for brevity

cyclization and subsequent oxidation would involve formal loss of H_2, CH_4, or C_2H_6.

Under the conditions given in the experimental part, 1,4,8-trimethyl-benzo[*c*]cinnoline (**11**) and 1,4,7,10-tetramethyl-benzo[*c*]cinnoline (**6**) were obtained in a ratio of about 4:1. We did not find any 3,8-dimethyl-benzo[*c*]cinnoline in the reaction mixture (considering the experimental setup, that means < 5% yield) which would arise from the (*syn*,*syn*) form *via* this pathway. Since this product ratio does not reflect the relative stabilities of the conformers of (*Z*)-2,2′,5,5′-tetramethyl-azobenzene ((*Z-anti*,*anti*) > (*Z-syn*,*anti*) ≫ (*Z-syn*,*syn*)) we conclude that the photochemical *Z*/*E*-isomerization of azobenzene is the rate determining step in the formation of **6** and **11**. The product distribution appears to correspond rather to the relative amounts of the (*anti*,*anti*) and (*syn*,*anti*) conformers of *E*-**5**. The statistical weight of 2 for the (*syn*,*anti*) conformer should largely determine the product ratio. Furthermore, with a sterically demanding acceptor *A* ($SnCl_4$ in our case) the (*E-syn*,*anti*) conformer is the least sterically hindered (*E*)-form, increasing its relative amount. A further excess of **11** over **6** can be attributed to the relative instability of the (*Z-anti*,*anti*)-**5** intermediate with respect to the other conformers due to the intermethyl interactions: (*Z-anti*,*anti*)-**5** (or corresponding photochemical intermediates in the reaction sequence) will most probably rapidly convert to the (*Z-syn*,*anti*) form which then can immediately undergo cyclization, ultimately yielding additional **11**. Cyclization of the (*Z-anti*,*anti*) form is very improbable or slow due to the unfavorable relative position of the two phenyl rings as schematically indicated in Fig. 2.

The non-symmetrical 2,3′,5,5′-tetramethyl-azobenzene (**7**), in which only one of the phenyl rings can undergo cyclization *via* two different pathways, yielded only a 10% excess of 1,3,8-trimethyl-benzo[*c*]cinnoline (**12**) over 1,3,7,10-tetramethyl-benzo[*c*]cinnoline (**8**). This reflects the fact that only one of two rings has a methyl group *ortho* to the azo group; hence, the probability for a methyl substituted carbon atom taking part in the formation of the new ring is reduced by approximately 50% with respect to the case of **5**. It should be noted that so far no experimental efforts have been undertaken to determine where the lost methyl groups end up in the reaction mixture. We also have to note that attempts to photocyclodehydrogenate two azobenzenes bearing CF_3 groups instead of methyl groups (**9** and **10**) to the corresponding trifluoromethyl-benzo[*c*]cinnolines were not successful. Neither any dominating products nor significant amounts of the starting material could be isolated from these reaction mixtures.

The photochemical cyclodehydrogenation procedure used is superior to thermal oxidative ring closure in an $AlCl_3$ melt as described by *Holt* and *Went* [9]. In an oxygen atmosphere, this reaction yielded a benzo[*c*]cinnoline only from 3,3′,5,5′-tetramethyl-azobenzene (**2**) as the educt in 12% yield (based on the total amount of azobenzene); no benzo[*c*]cinnolines could be found starting from any other azobenzenes used successfully in the cyclodehydrogenation reaction.

In conclusion, photochemical cyclodehydrogenation of methyl substituted azobenzenes in 1,2-dichloroethane solution in the presence of $SnCl_4$ was shown to provide a valuable and versatile synthetic route. It follows predictable reaction pathways and yields stable, easily purifiable methylated benzo[*c*]cinnolines. It also provides access to 1,10-dimethyl-benzo[*c*]cinnoline derivatives, a class of com-

pounds with the potential for methyl gearing interactions which serve as model compounds for spectroscopic studies [4–6] and generally are of high theoretical interest.

Experimental

All NMR spectra were acquired on Bruker Avance spectrometers (DPX 200 and a DRX 500 at the Johannes Kepler University Linz (Austria), DRX 500 and a DRX 600 at the MR Center of SINTEF UNIMED in Trondheim (Norway)). Mass and IR spectra were measured on HP 59987A and Bio-Rad FT-IR-45 instruments at the Johannes Kepler University Linz. Compounds **1** and **4** are commercially available (Aldrich) and were used without further purification. **2** was prepared from **1** following the procedure of *Goldstein* [11]. **14** was obtained by bromination of **1** as described in Ref. [10].

2,2′,5,5′-Tetramethyl-azobenzene (**5**; $C_{16}H_{18}N_2$)

5 was prepared from **4** following the procedure of *Terent'ev* [12] in 65% yield.

Orange crystals; m.p.: 115–118°C; ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.4 (s, 2H), 7.2 (d, 2H), 7.18 (d, 2H), 2.7 (s, 6H), 2.4 (s, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, δ): 150.93 (s), 135.95 (s), 134.88 (s), 131.41 (d), 131.03 (d), 116.17 (d), 21.08 (q), 17.24 (q) ppm; MS: (*m/z*) = 238 (M^+), 165, 133, 105, 79, 77, 57, 39; IR (KBr): ν = 3039, 3018, 2921, 2859, 2731, 1894, 1773, 1751, 1617, 1576, 1502, 1453, 1198, 1148, 1124, 1041, 810 cm^{-1}.

4,4′-Dibromo-3,3′,5,5′-tetramethyl-azobenzene (**15**, $C_{14}H_{16}N_2Br_2$)

15 was prepared from **14** analogously to **2** from **1**; yield: 19%. A preparation analogous to that of **5** was not successful.

Pale orange crystals; m.p.: 185–188°C; ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.62 (s, 4H), 2.50 (s, 12H) ppm.

2,3′,5,5′-Tetramethyl-azobenzene (**7**; $C_{16}H_{18}N_2$)

7 was prepared from **1** and **4** following the procedure given in Ref. [13] in 10% yield. The deeply orange crystals, although very pure (by NMR), showed a melting range from 25°C to 47°C. This could be due to *Z*/*E*-isomerism or to the existence of a liquid crystalline phase as is the case for other asymmetrically substituted azobenzenes.

^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.52 (s, 2H), 7.41 (s, 1H), 7.16 (d, 1H, J = 8.2 Hz, A of AB-system), 7.15 (d, 1H, J = 8.2 Hz, B of AB-system), 7.06 (s, 1H), 2.66 (s, 3H), 2.38 (s, 6H), 2.35 (s, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, δ): 153.2, 150.6, 138.5, 135.9, 134.9, 132.3, 131.5, 130.9, 120.6, 115.7, 21. 2 (q), 20.9 (q), 17.0 (q) ppm; MS: (*m/z*) = 238 (M^+), 179, 133, 105, 79, 77, 65, 39; IR (KBr): ν = 3042, 3014, 2919, 2861, 2360, 1609, 1503, 1457, 1420, 1375, 1284, 1275, 1150, 1128, 1104, 851, 804, 682, 668, 554, 531, 517 cm^{-1}.

2,2′-Dibromo-5,5′-bis(trifluoromethyl)-azobenzene (**9**; $C_{12}H_6N_2F_6Br_2$)

Preparation analogous to Ref. [14]: 0.1 g (0.4 mmol) commercial 2-bromo-5-trifluoromethyl-aniline were dissolved in benzene and refluxed with 1 g of freshly prepared and activated MnO_2 [15, 16] for 48 h. H_2O was constantly removed by passing the refluxing solvent through a short column of molecular sieves. The solution was filtered and washed with 10% HCl. Evaporation of the organic phase *in vacuo* yielded 80 mg (42.5%) of pure **9**.

Orange needles; m.p.: 163–166°C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.99 (d, 1H, $^4J = 1.7$ Hz), 7.93 (d, 1H, $^3J = 8.3$ Hz), 7.63 (dd, 1H, $^3J = 8.3$ Hz, $^4J = 1.7$ Hz) ppm; ^{19}F NMR (470 MHz, $CDCl_3$, δ, $CFCl_3$); −63.35 (s) ppm.

2,2′-Dimethyl-5,5′-bis(trifluoromethyl)-azobenzene (**10**; $C_{14}H_{12}N_2F_6$)

Prepared as described for **9**; 0.2 g (1.14 mmol) of commercial 2-methyl-5-trifluoromethyl-aniline yielded 0.166 g (42%) of **10**.

Orange needles; m.p.: 159–161°C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.87 (s, 1H), 7.63 (d, 1H, $J = 8$ Hz), 7.49 (d, 1H, $J = 8$ Hz), 2.81 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, δ): 150.45, 142.26, 132.05, 129.11 (q, ^2J(C–F) = 26 Hz), 127.29 (q, ^3J(C–F) = 3 Hz), 124.00 (q, ^1J(C–F) = 272 Hz), 113.03 (q, ^3J(C–F) = 4 Hz), 17.74 (q) ppm.

General procedure for the photocyclodehydrogenation of azobenzenes

500 mg of azobenzene were added to a mixture of 1.8 l of absolute 1,2-dichloroethane and 6 ml of $SnCl_4$ (Aldrich). The solution was refluxed for 3 h under anhydrous conditions and irradiated at ambient temperature (22–25°C) for 45 h with a high-pressure mercury UV lamp (125 W). Subsequently the reaction mixture was washed with saturated aqueous Na_2CO_3, dried, and evaporated to dryness *in vacuo*. Column chromatography (CH_2Cl_2/silica) was used to isolate the products. Except for **13**, the products were further purified by sublimation at 140°C/700 Pa. Note that the experimental yields given below for this reaction refer to a theoretical yield of 2/3, since according to the stoichiometry of the reaction [7] three molecules of azobenzene react to give two molecules of benzo[*c*]cinnoline.

1,3,8,10-Tetramethyl-benzo[c]cinnoline (**3**; $C_{16}H_{16}N_2$)

Prepared from **2** by the preceding photocyclodehydrogenation procedure; yield: 66%; yellow, prismatic crystals; m.p.: 196.5–197°C; ^{1}H NMR (C_6D_6, 200 MHz, δ): 8.45 (s, 2H), 7.04 (s, 2H), 2.208 (s, 3H), 2.199 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 146.8, 137.8, 135.1, 133.6, 127.3, 119.0, 22.4, 21.2 ppm.

1,4,7,10-Tetramethyl-benzo[c]cinnoline (**6**; $C_{16}H_{16}N_2$)

Photocyclodehydrogenation of 500 mg of **5** (2.1 mmol) yielded traces of unreacted **5**, 50 mg of **6** (15%) and 180 mg **11** (58%) which were separated by chromatography.

Yellow crystals; m.p.: 95–98°C; ^{1}H NMR (500 MHz, C_6D_6, δ): 7.26 (d, 2H, $J = 7.4$ Hz), 7.14 (d, 2H, $J = 7.4$ Hz), 3.16 (s, 6H), 2.18 (s, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, δ): 144.80, 135.36, 132.64, 131.71, 126.92, 120.87, 21.84 (q), 17.71 (q) ppm; MS: (m/z) = 236 (M^+), 193, 178, 149, 105, 77, 57, 39; IR (KBr): $\nu = 2956$, 2918, 2850, 1473, 1463, 1390, 1381, 1366, 1330, 1233, 814 cm^{-1}.

1,4,8-Trimethyl-benzo[c]cinnoline (**11**; $C_{15}H_{14}N_2$)

Photocyclodehydrogenation of 500 mg of **5** (2.1 mmol) yielded traces of unreacted **5**, 50 mg of **6** (15%) and 180 mg **11** (58%) which were separated by chromatography.

Yellow crystals; m.p.: 129–131°C: ^{1}H NMR (200 MHz, $CDCl_3$, δ): 8.28 (s, 1H), 8.22 (d, 1H), 7.25 (m, 3H), 2.94 (s, 3H), 2.68 (s, 3H), 2.48 (s, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, δ): 145.4, 144.1, 137.8, 137.3, 133.8, 131.7, 131.5, 130.1, 128.5, 124.6, 119.4, 119.3, 25.2 (q), 20.9 (q), 18.2 (q) ppm; MS: (m/z) = 222 (M^+), 179, 178, 152, 105, 89, 76, 54, 39; IR (KBr): $\nu = 3039$, 2952, 2920, 2867, 2362, 1623, 1589, 1559, 1551, 1511, 1468, 1446, 1359, 1172, 1133, 1086, 833, 819, 592 cm^{-1}.

2,9-Dibromo-1,3,8,10-tetramethyl-benzo[c]cinnoline (**13**; $C_{16}H_{14}N_2Br_2$)

By photocyclodehydrogenation of 320 mg (0.81 mmol) of **15**, 136 mg (64%) of **13** were obtained.

Yellow needles; m.p. (dec.): 235–238°C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.40 (s, 2H), 2.74 (d, 6H, $J = 0.51$ Hz), 2.60 (s, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, δ): 144.61, 139.19, 134.01, 133.94, 126.17, 119.06, 25.25 (q), 24.11 (q) ppm; MS: (*m/z*) = 394 (M^+), 287, 285, 206, 149, 113, 89, 44; IR (KBr): $\nu = 3013$, 2977, 2966, 2949, 2918, 1592, 1545, 1473, 1453, 1431, 1344, 1329, 1207, 1132, 1021, 997, 980, 956, 832, 717 cm^{-1}.

1,3,7,10-Tetramethyl-benzo[c]cinnoline (**8**; $C_{16}H_{16}N_2$)

Photocyclodehydrogenation of 500 mg of **7** (2.1 mmol) afforded 102 mg of **8** (31%) and 105 mg of **12** (34%).

Yellow crystals; m.p.: 139–142°C; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.28 (s, 1H), 7.55 (d, 1H, $J = 8.1$ Hz, A of AB-system), 7.54 (d, 1H, $J = 8.1$ Hz B of AB-system), 7.49 (d, 2H), 3.08 (s, 3H), 2.62 (s, 3H), 2.56 (s, 3H), 2.54 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, δ): 147.37 (s), 145.43 (s), 138.85 (s), 136.32 (s), 135.66 (d), 134.71 (s), 133.72 (d), 132.10 (s), 129.46 (d), 127.53 (d), 121.66 (s), 119.60 (s), 22.97 (q), 22.84 (q), 22.02 (q), 18.75 (q) ppm; MS: (*m/z*) = 236 (M^+), 193, 178, 152, 103, 89, 57, 43; IR (KBr): $\nu = 2992$, 2961, 2916, 2871, 1577, 1377, 1336, 1236, 1185, 1134, 1034, 865, 826, 812, 786, 724, 648, 601, 527 cm^{-1}.

1,3,8-Trimethyl-benzo[c]cinnoline (**12**; $C_{15}H_{14}N_2$)

Photocyclodehydrogenation of 500 mg of **7** (2.1 mmol) yielded 102 mg of **8** (31%) and 105 mg of **12** (34%).

Yellow crystals; m.p.: 171–173°C; ^{1}H NMR (200 MHz, $CDCl_3$, δ): 8.55 (d, 1H), 8.46 (s, 1H), 8.35 (s, 1H), 7.63 (d, 1H), 7.47 (s, 1H), 2.98 (s, 3H), 2.63 (s, 3H), 2.58 (s, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, δ): 146.76 (s), 146.12 (s), 136.17 (s), 136.11 (s), 136.47 (d), 134.21 (s), 132.69 (d), 130.89 (d), 129.47 (d), 124.85 (d), 119.96 (s), 117.94 (s), 25.61 (q), 21.30 (q), 21.22 (q) ppm; MS: (*m/z*) = 222 (M^+), 208, 179, 178, 165, 120, 89, 76, 42; IR (KBr): $\nu = 3014$, 2972, 2944, 2917, 2870, 1617, 1468, 1443, 1375, 1337, 1194, 1114, 1037, 1022, 1014 cm^{-1}.

1,3,8,10-Tetramethyl-benzo[c]cinnoline (**3**; $C_{16}H_{16}N_2$)

3 was obtained by non-photochemical oxidative cyclization (procedure similar to that of *Holt* and *Went* [9]). A mixture of 5 g $AlCl_3$, 0.62 g NaCl, and 0.077 g NaF was melted in an oxygen atmosphere at 120°C and cooled to 90°C under continuous stirring. To this mixture, **2** (464 mg, 1.95 mmol) was added within three minutes. The mixture was stirred for 90 min at 90°C. Then water was added cautiously until no more HCl vapor formed. The mixture was refluxed for 10 min, cooled to room temperature, and extracted with $CHCl_3$. The organic phase was washed with saturated sodium carbonate solution, dried, and evaporated to dryness. Repeated preparative TLC (Silicagel 60, eluent: CH_2Cl_2: ethylacetate = 10:3) afforded 55 mg (0.23 mmol) of **3** which was further purified by sublimation at 140°C/700 Pa. The substance was identical to that obtained above by photocyclodehydrogenation.

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