Cyclodehydrogenation of *N*-Benzylidene-*o*-phenylenediamines to 2,2′-Diaryl-1,1′-bibenzimidazoles with Dioxygen Catalyzed by Copper(I) Chloride in Pyridine. A Structural Study of 2,2′-Bis(3,4,5-trimethoxyphenyl)-1,1′-bibenzimidazole[1]

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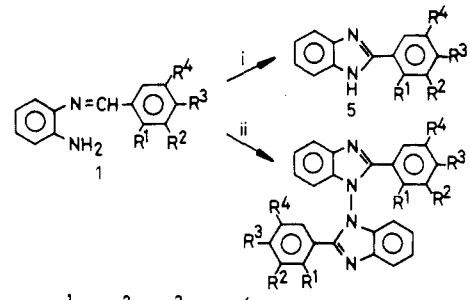
2,2′-Diaryl-1,1′-bibenzimidazoles (**10**) were prepared in 32–66% yields from *N*-benzylidene-*o*-phenylenediamines (**1**) through oxidation with dioxygen catalyzed by copper(I) chloride in pyridine. Substitution on the benzene ring in the benzylidene group seems to determine the reactions. Ortho substitution causes cyclization to 2-arylbenzimidazoles (**5**). With the *p*-methoxy derivative **1d** only oxidative coupling of the amino groups to the diazo compound **9d** was found. In unsubstituted and para- and/or meta-substituted cases of **1** cyclodehydrogenation with coupling to 1,1′-bibenzimidazoles (**10**) was established. A mechanism is proposed involving intermediate radicals. The stabilities of these radicals—depending upon the substitution—govern partitions in parallel reactions leading to the diverse products **5**, **10**, and **9d**. The X-ray structure determination of **10i** reveals an N–N bond distance of 1.380 (1) Å and a 71.9° angle of twist between the two benzimidazole rings.

Many C,C-linked and C,N-linked dimers of benzimidazole are easily obtainable by trivial procedures.[2,3] No similar situation holds, however, for the preparation of N,N′-linked dimers. The treatment of silver benzimidazole with iodine yielded 2,2′-bibenzimidazole and 1-iodobenzimidazole and the starting material.[4] The same experiment carried out by de Mendoza et al.[5] either with 2-substituted or unsubstituted benzimidazoles yielded only an equimolar mixture of 1-iodobenzimidazole and the starting material. Refluxing in ethane-1,2-diol or *m*-xylene gave reduction to benzimidazole and 1-(*m*-methyltolyl)-benzimidazole, respectively. Attempts to prepare N,N′-linked dimers through the intermediacy of 1,1′-azobisbenzimidazole have also failed since its preparation from benzimidazol-1-ylamine by oxidation with mercury(II) oxide was unsuccessful.[5] The monoacetyl derivative of 2,2′-azoaniline could be transformed in two steps into 2,2′-dimethyl-1,1′-bibenzimidazole involving condensation with acetaldehyde and subsequent cyclization by polyphosphoric acid.[5]

Aliphatic amines are generally unreactive toward copper(II). In contrast to the aliphatic case, primary aromatic amines are readily oxidized to azobenzenes by cuprous chloride and dioxygen when pyridine is used as the solvent.[6] Under analogous conditions *o*-phenylenediamines give *cis,cis*-muconitrile.[7] Secondary aromatic amines are coupled to the hydrazine derivatives by the same reagent.[8] The presence of an ortho imino group changes the copper(II) oxidation of primary aromatic amines from an intermolecular dimerization to an intramolecular cyclization. Thus, acetaldehyde *o*-aminoanil is cyclized to 2-methylbenzimidazole by cupric acetate.[9] *N*-Benzylidene-*o*-phenylenediamine gives in a copper(I) chloride catalyzed oxygenation 2,2′-diphenyl-1,1′-bibenzimidazole in relatively good yield.[10] In this paper we present an extension of our earlier work with respect to generalization of the copper-catalyzed coupling of *N*-benzylidine-*o*-phenylenediamines to N,N′-linked bibenzimidazoles and attempts to elucidate and understand the mechanism of the reaction.

Scheme I



	R^1	R^2	R^3	R^4
a)	H	H	H	H
b)	H	H	CH_3	H
c)	H	H	$N(CH_3)_2$	H
d)	H	H	OCH_3	H
e)	CH_3	H	H	H
f)	OCH_3	H	H	H
g)	H	H	OCH_3	OCH_3
h)	OCH_3	H	H	CH_3
i)	H	OCH_3	OCH_3	OCH_3

Results and Discussion

In an earlier study the copper(I) chloride mediated oxidation of N-substituted and N,N′-disubstituted *o*-phenylenediamines was investigated.[10] In these studies it has been found that the oxidation of *N*-benzylidene-*o*-phenylenediamine gives 2,2′-diphenyl-1,1′-bibenzimidazole

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Table I. Products and Yields in the Oxidation of *N*-Benzylidene-*o*-phenylenediamines (1) by the Dioxygen–CuCl–Pyridine System

substrate	product	isolated yield, %	substrate	product	isolated yield, %
1a	10a	42	1f	5f	63
1b	10b	37	1g	10g	66
1c	10c	42	1h	5h	17
1d	9d	9	1i	10i	32
1e	5e	58			

(**10a**) instead of 2-phenylbenzimidazole (**5a**) as expected from literature data using copper(II) as the oxidant.[9] This unique result prompted us to clarify the possible mechanism of the reaction and the possibility of extending the scope of the reaction to different substituted 2-aryl derivatives of the 1,1′-bibenzimidazoles (**10**). With that in mind a series of *N*-benzylidene-*o*-phenylenediamines (**1a–i**) were prepared and oxidized with dioxygen in the presence of copper(I) chloride in pyridine (Scheme I).

In the case of **1d** no ring closure was achieved and the coupled *N,N′*-bis(4-methoxybenzylidene)-2,2′-diaminoazobenzene (**9d**) was obtained as the single product in only 9% yield. In the other cases oxidative ring closure took place and resulted in two types of products. 2-Arylbenzimidazoles (**5**) were obtained in the case of ortho substitution of the benzylidene group in the Schiff bases, e.g., **1e**, **1f**, and **1h**. Mass spectral data revealed that in the oxidation products of them either no or only negligible amounts of N,N′-coupled compounds (**10**) were formed. In all other cases, except of **1d**, ring closure and N,N′-coupling took place to give 2,2′-diaryl-1,1′-bibenzimidazoles (**10**) in 32–66% yields. These data seem to suggest that steric reasons may govern the reaction on the two paths leading to (i) benzimidazole (**5**), when $R^1 \neq H$, or (ii) 1,1′-bibenzimidazoles (**10**), when $R^1 = H$. The lack of ring formation in the case of **1d** ($R^3 = OMe$; $R^1 = H$) indicates, however, that probably even small electronic effects of remote substitutents may influence certain intermediates (possible radicals) to prefer one or the other of parallel reactions. Products and yields are compiled in Table I.

In order to learn more about the possible mechanism of the copper-assisted ring formation and N,N′-coupling reactions shown in Scheme I, we oxidized some of the supposed intermediates of these reactions proposed in Scheme II. The *N*-benzylidene-*o*-phenylenediamines (**1**) do not tend to form imidazolines (**2**), and the equilibrium between them is largely shifted to the left.[11] 2-Phenylbenzimidazole (**5a**) behaved inert toward oxidation with the CuCl–O_2–py system; no N,N′-coupling occurred. The very similar N,N′-coupling of diphenylamine to tetraphenylhydrazine, however, is easily feasible with the same reagent.[8] For that reason the oxidative coupling of the radical **4** to N,N-coupled **7** cannot be excluded but could not be proved. Therefore, we assume that the N,N′-coupling has to precede the ring closure in these reactions. This supposition is also supported by the success of others to synthesize 2,2′-dimethyl-1,1′-bibenzimidazole, starting from a precursor having already the N,N′-linkage.[5]

The course of these reactions may be as proposed in Scheme II. We believe that the CuCl–O_2–py system abstracts a hydrogen atom from the Schiff base (**1**), forming first chlorohydroxocopper(II) complexes, then water and copper(I) chloride and the radical (**3**). This radical is expected to undergo intramolecular attack of the adjacent double bond (path a) to give the radical **4** and then 2-arylbenzimidazole (**5**) after a second hydrogen atom abstraction and aromatization. Alternatively, intermolecular dimerization of **3** (path b) leads to the N,N′-coupled intermediate **6**. It can be concluded that the partition between paths a and b are influenced by the substituents, and ortho substitution prefers path a for steric reasons. **6** may be in equilibrium with **7**, but the concentration of **7** may be low (cf. the situation in the cases of **2** and **1**). The next step is again a hydrogen abstraction, giving the radical intermediate **8**. At this point the reaction path may branch again. Path c, which is again a hydrogen abstraction, leads to the azobenzene derivative **9**. In the case of **1d** in fact, **9d** was the only isolated product. The azobenzene derivatives **9** are not intermediates in the title reaction. This statement is based on the observation that **9i**, prepared from 2,2′-diaminoazobenzene and 3,4,5-trimethoxybenzaldehyde, could not be transformed into the N,N′-coupled product **10i** by the CuCl–O_2–py system. Reaction path d running over cyclization steps and hydrogen abstractions leads then to 1,1′-bibenzimidazoles (**10**). Unfortunately, the intermediate **6** could not be prepared in an independent way. Hydrogenations of 2,2′-diaminoazobenzene did not give 2,2′-diaminohydrazobenzene but *o*-phenylenediamine.[5] Efforts to selectively hydrogenate the N,N double bond in **9i** to give **6i** failed too; therefore, the intermediacy of **6** in the proposed mechanism could not be proved directly.

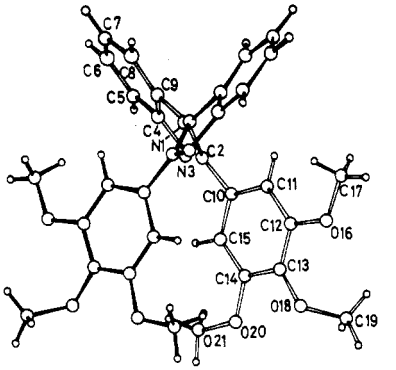
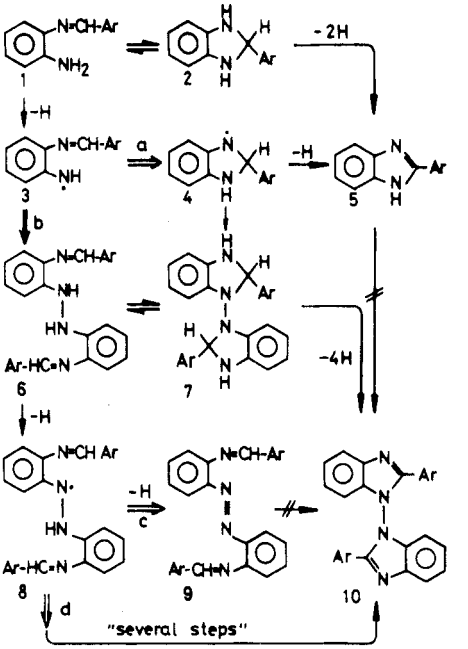


Figure 1. Molecular diagram of **10i** with the labeling of atoms used in the crystal structure analysis.

Scheme II



A perspective diagram of **10i** is depicted in Figure 1. The molecule has a twofold axis intersecting the N(1)–N-

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(1)′ [2 − x, y, 1.5 − z] bond. The dihedral angle between the weighted least-squares planes of the benzimidazole rings is 71.90 (4)°. The preference for a perpendicular or quasi-perpendicular conformation of N,N-linked biazoles was established by theoretical calculations.[12] The deviation by 18° from the perfect perpendicular conformation in **10i** is presumably due to the presence of the trimethoxyphenyl groups (the weighted least-squares planes of the benzimidazole and the phenyl groups form a dihedral angle of 41.96 (5)°). While the O(16)–C(17) and O(20)–C(21) methoxy substituents are close to the plane of the phenyl ring (the normal distances (*d*) of the C(17) and C(21) atoms from this plane are 0.06 and 0.10 Å), the O(18)–C(19) methoxy group is nearly perpendicular ($d_{C(19)}$ = 1.05 Å) in order to minimize repulsive nonbonded interactions.

The N(1)–N(1)′ bond length is 1.380 (1) Å, close to the value reported[13] for 4-triazolyl-4*H*-1,2,4-triazole, showing that there is practically no delocalization between the benzimidazole moieties. The distribution of the endocyclic bond angles at the imidazole ring atoms [N(1), 107.4 (2)°; C(2), 111.9 (2)°; N(3), 105.5 (2)°; C(4), 110.9 (2)°; C(9), 104.1 (2)°] is in accord with the VSEPR theorem, i.e. the bond angle at the substituted nitrogen atom is always greater than at the other one bearing only a lone pair. Other internal bond angles are also deformed, while the planarity of the five-membered ring is maintained.[14]

Experimental Section

General Procedures. Melting points were determined on a Buchi apparatus and are uncorrected. Elemental analyses were performed at this university. IR spectra were obtained on a Specord IR 75 instrument. UV–vis spectra were run on Specord M 40 spectrometer. ^{1}H NMR spectra were determined in solvents indicated with internal tetramethylsilane or hexamethyldisiloxane as the standard on one of the following spectrometers: Varian T-60, Varian CFT 20. MS spectra were obtained on a JEOL MS O1 SG 2 mass spectrometer.

Materials. Pyridine was dried over potassium hydroxide and then distilled over calcium hydride and stored under argon. Copper(I) chloride (Reanal) was used as supplied. Benzylidene-*o*-aminoaniline (mp 61 °C, lit.[15] mp 60–61 °C) was synthesized by the method described in the literature and recrystallized from ligroin.[15] The other Schiff bases from *o*-phenylenediamine and the aldehydes [4-methylbenzaldehyde, 4-(dimethylamino)benzaldehyde, 3,4-dimethoxybenzaldehyde, 3,4,5-trimethoxybenzaldehyde, 2-methylbenzaldehyde, 2-methoxy-5-methylbenzaldehyde, 2-methoxybenzaldehyde, 4-methoxybenzaldehyde] were prepared in analogous manner and their structures determined by elemental analyses and IR, ^{1}H NMR, and mass spectra. 2,2′-Diaminoazobenzene was prepared according to literature method.[16]

X-ray Structure Analysis. The determination of the unit cell parameters and the collection of the intensity data of **10i** were performed on an Enraf-Nonius CAD4 four-circle computer-controlled diffractometer. The approximate size of the crystal used was 0.20 × 0.20 × 0.40 mm.

Crystal Data: $C_{32}H_{30}N_4O_6$; fw 566.62; a = 17.911 (1), b = 10.717 (1), c = 15.219 (1) Å; β = 96.33 (1)°; V = 2903.5 (7) Å^3; space group $C2/c$ (from structure refinement); Z = 4; $F(000)$ = 1192; d_{obsd} = 1.296 g cm^{-3}; μ(Cu K$_\alpha$) (λ = 1.5418 Å) = 7.07 cm^{-1}. A total of 2795 nonzero unique intensities were collected by using graphite-monochromated Cu K$_\alpha$ radiation in the range of $1.5 \leq \theta \leq 75.0°$.

Structure Solution and Refinement. The structure was solved by direct methods (MULTAN program[17]). A total of 2537 reflections ($I \leq 3\sigma(I)$) were used in least-squares refinement. At the end of isotopic refinement (R = 0.123) an empirical absorption correction[18] was applied that dropped R to 0.102 (the maximum and minimum absorption corrections were 0.817 and 1.375, respectively). Full-matrix anisotropic least-squares refinement of the non-hydrogen atoms resulted in final R values of R_{obsd} = 0.048, R_w = 0.090, and R_{tot} = 0.052. All hydrogen atomic positions were generated from assumed geometries and were included in structure factor calculations with individual isotopic thermal parameters. The highest peak of in the final difference map was 0.35 e/Å^3. The final values of positional and thermal parameters are given in the supplementary mateiral.[19]

2,2′-Diphenyl-1,1′-bibenzimidazole (10a). Copper(I) chloride (1.98 g, 20 mmol) was dissolved in dry pyridine (10 mL) and stirred under dioxygen until dioxygen uptake ceased (ca. 5 mmol during 1 h). To this stirred solution was added *N*-benzylidene-*o*-phenylenediamine (1.96 g, 10 mmol) dissolved in pyridine (10 mL) slowly. When the dioxygen consumption stopped, the solvent was evaporated under vacuum and the dry residue extracted with ether (100 mL). The ether was stripped under diminished pressure and the residue recrystallized from ethanol to give **10a** (0.81 g) as colorless prisms: mp 196 °C; ^{1}H NMR (CCl_4) δ 7.15 (m, 16 H), 7.85 (dd, J = 7.5 Hz, J = 2.0 Hz, 2 H); UV–vis (EtOH) 204, 240, 294 nm; IR (KBr) 3065, 1615, 1535, 1483, 1450, 1340, 1314, 1287, 1272 cm^{-1}; mass spectrum (75 eV) m/e 386, 193. Anal. Calcd for $C_{26}H_{18}N_4$: C, 80.80; H, 4.70; N, 14.50. Found: C, 80.40; H, 4.60; N, 14.20.

Standard Procedure for the Oxygenation of Substituted *N*-Benzylidene-*o*-phenylenediamines (1a–i) Catalzyed by Copper(I) Chloride. Copper(I) chloride (7.92 g, 80 mmol) was dissolved in dry pyridine (50 mL) and stirred under dioxygen until dioxygen uptake ceased (ca. 20 mmol during 1 h). To this stirred solution was added *N*-benzylidene-*o*-phenylenediamines **1a–i** (20 mmol) dissolved in pyridine (20 mL) slowly. When the dioxygen consumption stopped, the solvent was evaporated under vacuum and the dry residue treated with ammonium hydroxide solution (10 mL) three times by stirring for 2–3 h. After filtration the residue was dried and extracted with ether or tetrahydrofuran (100 mL) in a Soxhlet extraction apparatus. Evaporation of the solvent yielded the desired products. They were then recrystallized.

2,2′-Bis(4-methylphenyl)-1,1′-bibenzimidazole (10b). Compound **1b** (5.97 g, 20 mmol) was oxygenated with the copper(I) catalyst using the general procedure to the bibenzimidazole **10b** (1.5 g). The crystalline product exhibited the following characteristics: mp 182 °C (from EtOH using decolorizing carbon); ^{1}H NMR ($CDCl_3$–Me_2SO-d_6) δ 2.25 (s, 6 H), 6.91–7.43 (m, 14 H), 7.89 (d, J = 6.9 Hz, 2 H); UV–vis (EtOH) 216, 243, 294 nm; IR (KBr) 3045, 1610, 1484, 1447, 1432, 1326, 1267, 1184, 820, 759, 740, 718, 504 cm^{-1}; mass spectrum (75 eV) m/e 414, 207, 192, 90. Anal. Calcd for $C_{28}H_{22}N_4$: C, 81.13; H, 5.35; N, 13.52. Found: C, 81.31; H, 5.35; N, 13.48.

2,2′-Bis(3,4-dimethoxyphenyl)-1,1′-bibenzimidazole (10g). Compound **1g** (5.12 g, 20 mmol) was oxygenated according to the general procedure. The residue was dissolved in tetrahydrofuran (10 mL), and on addition of diethyl ether (50 mL) crystals of **10g** separated, which were filtered off and dried under vacuum (3.35 g): mp 185–186 °C (from EtOH using decolorizing carbon); ^{1}H NMR ($CDCl_3$) δ 3.41 (s, 6 H), 3.79 (s, 6 H), 6.55–6.88 (m, 4 H), 7.16–7.46 (m, 8 H), 7.87–7.97 (m, 2 H); UV–vis (EtOH) 220, 310 nm; IR (KBr) 2998, 2958, 2838, 1600, 1526, 1485, 1463, 1449, 1434, 1280, 1255, 1244, 1147, 1118, 1123, 1003, 763, 734 cm^{-1}; mass spectrum (75 eV) m/e 506, 253. Anal. Calcd for $C_{30}H_{26}N_4O_4$: C, 71.23; H, 5.17; N, 11.06. Found C, 71.15; H, 5.20; N, 10.85.

***N*,*N*′-Bis(4-methoxybenzylidene)-2,2′-diaminoazobenzene (9d).** Compound **1d** (18.1 g, 80 mmol) was oxygenated as described earlier. On stripping the solvent fine orange needles of **9d** de-

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(19) See paragraph at the end of paper regarding supplementary material.

posited (1.6 g): mp 166–168 °C; ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3 H), 3.87 (s, 3 H), 6.98–8.13 (m, 16 H), 8.24 (s, 1 H), 8.62 (s, 1 H); IR (KBr) 3059, 3010, 2967, 2933, 2903, 2838, 1622, 1605, 1587, 1510, 1465, 1306, 1159, 1026, 821, 746, 529 cm^{-1}; UV–vis (CH_2Cl_2) 228, 286, 299, 366 nm; mass spectrum (75 eV) *m/e* 448, 224, 209, 181. Anal. Calcd for $C_{28}H_{24}N_4O_2$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.87; H, 5.66; N, 12.50.

2,2′-Bis[4-(dimethylamino)phenyl]-1,1′-bibenzimidazole (10c). Compound **1c** was oxygenated according to the general procedure. After stripping of the solvent, **10c** was obtained as the dry residue (2.0 g): mp 305–307 °C (from Me_2SO); ^{1}H NMR ($CDCl_3$–Me_2SO-d_6) δ 2.91 (s, 12 H), 6.49 (d, *J* = 8.7 Hz, 4 H), 7.36 (d, *J* = 8.7 Hz, 4 H), 6.55–7.92 (m, 8 H); UV–vis (EtOH) 218, 340 nm; IR (KBr) 3049, 2892, 2852, 2805, 1607, 1585, 1532, 1485, 1452, 1432, 1366, 1201, 1072, 820, 793 cm^{-1}; mass spectrum (75 eV) *m/e* 472, 236. Anal. Calcd for $C_{30}H_{28}N_6$: C, 76.24; H, 5.97; N, 17.79. Found: C, 76.13; H, 5.94; N, 17.85.

2,2′-Bis(3,4,5-trimethoxyphenyl)-1,1′-bibenzimidazole (10i). Compound **1i** (5.72 g, 20 mmol) was oxygenated as described in the general procedure to give **10i** (1.8 g): mp 198–201 °C (from Me_2SO); ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 12 H), 3.77 (s, 6 H), 6.23 (s, 4 H), 7.23–7.48 (m, 6 H), 7.86 (d, *J* = 7 Hz, 2 H); UV–vis (EtOH) 219, 300 nm; IR (KBr) 3005, 2958, 2936, 2834, 1586, 1492, 1452, 1425, 1345, 1269, 1242, 1128, 1005, 836, 765, 752 cm^{-1}; mass spectrum (75 eV) *m/e* 566, 283, 195. Anal. Calcd for $C_{32}H_{30}N_4O_6$: C, 67.83; H, 5.34; N, 9.89. Found: C, 67.84; H, 5.46; N, 9.74.

Preparation of *N,N′*-Bis(3,4,5-trimethoxybenzylidene)-2,2′-diaminoazobenzene (9i). 2,2′-Diaminoazobenzene (2.12 g, 10 mmol), 3,4,5-trimethoxybenzaldehyde (4.00 g, 20 mmol), and ethanol (25 mL) were refluxed for 3 h. The solution was kept overnight, while fine flesh-colored needles separated. It was filtered and dried under vacuum to give **9i** (2.0 g, 35%) (From the filtrate, after stripping the solvent and treating with ether (25 mL), a further 1.5 g of **9i** could be obtained.): mp 264–266 °C; ^{1}H NMR ($CDCl_3$–Me_2SO-d_6) δ 3.80 (s, 6 H), 3.93 (s, 12 H), 7.05–7.28 (m, 4 H), 7.53 (s br, 4 H), 12.45 (s, 2 H); UV–vis (EtOH) 401, 613,715 nm; IR (KBr) 3053, 2927, 2840, 1587, 1497, 1480, 1464, 1429, 1274, 1240, 1132, 1006, 744 cm^{-1}; mass spectrum (75 eV) *m/e* 568, 464, 284, 269. Anal. Calcd for $C_{32}H_{32}N_4O_6$: C, 67.56; H, 5.67; N, 9.85. Found: C, 67.80; H, 5.50; N, 9.82.

Attempted Oxidation of *N,N′*-Bis(3,4,5-trimethoxybenzylidene)-2,2′-diaminoazobenzene (9i). Copper(I) chloride (0.79 g, 8 mmol) in pyridine (10 mL) were oxygenated (O_2 uptake ca. 50 mL, 2 mmol) for 3 h. Then, *N,N′*-bis(3,4,5-trimethoxybenzylidene)-2,2′-diaminoazobenzene (568 mg, 1 mmol) was added in crystalline form from a connected side-arm. During 12 h no dioxygen consumption was observed. The pyridine solvent was then evaporated under reduced pressure, and the dry residue was shaken with a mixture of chloroform (20 mL) and a solution (25 mL) containing ethylenediaminetetraacetic acid disodium salt (3.36 g, 10 mmol), with pH 7.5–8.0 adjusted with sodium hydrocarbonate. The blue precipitate formed was filtered. From the filtrate the organic layer was separated and washed twice with water (10 mL) and dried over calcium chloride, and the chloroform was then stripped to give a dry residue (105 mg). On the basis of ^{1}H NMR, IR and mass spectral data, it was identified as the starting material.

In a separate experiment, which was worked up according to the general procedure, no 2,2′-bis(3,4,5-trimethoxyphenyl)-1,1′-bibenzimidazole (**10i**) could be traced by MS.

2-(2′-Methylphenyl)benzimidazole (5e). Compound **1e** (4.2 g, 20 mmol) was oxygenated as described in the general procedure but extracted with ether (100 mL). The ether was then stripped under diminished pressure to give **5e** as pale yellow residue (1.2 g): mp 198–200 °C (from EtOH); ^{1}H NMR ($CDCl_3$–Me_2SO-d_6) δ 1.6 (s, 3 H), 6.43–7.84 (m, 8 H); IR(KBr) 3063, 2960, 2926, 1610, 1484, 1450, 1427, 1322, 1267, 1247, 765, 747, 728, 640 cm^{-1}; mass spectrum (75 eV) *m/e* 208. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.73; H, 5.81; N, 13.45. Found: C, 80,48; H, 5.25; N, 13.50.

2-(2′-Methoxyphenyl)benzimidazole (5f). Compound **1f** was oxygenated according to the general procedure. After the solvent was stripped, a pulp was obtained, from which on adding ether fine yellowish microcrystals of **5f** could be separated (1.4 g): mp 155–158 °C; ^{1}H NMR ($CDCl_3$–Me_2SO-d_6) δ 4.06 (s, 3 H), 7.01–7.69 (m, 7 H), 8.44 (d, *J* = 6 Hz, 1 H), 11.44 (br, 1 H); IR (KBr) 3437, 3157, 1607, 1587, 1473, 1427, 1390, 1310, 1286, 1247, 1090, 1026, 740 cm^{-1}; mass spectrum (75 eV) *m/e* 224, 194, 119. Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.70; H, 5.11; N, 12.25.

2-(2′-Methoxy-5′-methylphenyl)benzimidazole (5h). Compound **1h** (4.8 g, 20 mmol) was oxygenated according to the general procedure to give **5h** (0.80 g): mp 222–223 °C (from EtOH); ^{1}H NMR ($CDCl_3$–Me_2SO-d_6) δ 2.25 (s, 3 H), 3.94 (s, 3 H), 5.82 (dd, *J* = 7 Hz, *J* = 2 Hz, 2 H); IR (KBr) 3050 (br), 2963, 1613, 1587, 1490, 1440, 1380, 1281, 1247, 1180, 1150, 1090, 1023, 821, 806, 753, 575 cm^{-1}; mass spectrum (75 eV) *m/e* 238, 208, 119. Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.50; H, 5.85; N, 11.50.

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Registry No. **1a**, 717-57-7; **1b**, 99618-04-9; **1c**, 61022-73-9; **1d**, 85972-04-9; **1e**, 7192-12-3; **1f**, 7191-91-5; **1g**, 99618-05-0; **1h**, 99618-06-1; **1i**, 99618-07-2; **5e**, 2963-64-6; **5f**, 6528-85-4; **5h**, 99618-12-9; **9d**, 99618-10-7; **9i**, 99618-14-1; **10a**, 80785-71-3; **10b**, 99618-08-3; **10c**, 99618-09-4; **10g**, 99618-11-8; **10i**, 99618-13-0; 2,2′-diaminoazobenzene, 554-55-2; 3,4,5-trimethoxybenzaldehyde, 86-81-7.

Supplementary Material Available: Listings of final fractional coordinates and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.