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Photochemical Study of Tris(benzotriazol-1-yl)methane

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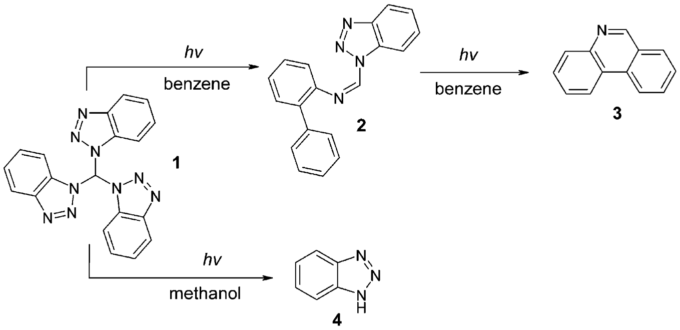

Photodecomposition of tris(benzotrizol-1-yl)methane (**1**) in benzene gives [1-benzotryazol-1-yl-methylidene]-biphenyl-2-ylamine (**2**) resulting from the loss of the benzotriazolyl radical and nitrogen followed by addition of benzene. Elimination of the second benzotriazolyl radical from **2** provides the biphenyl-2-ylmethyleneamine radical, which affords phenantridine (**3**) after ring closure. In contrast, the photolysis of **1** in methanol gives a high yield of benzotriazole (**4**).

Introduction

The benzotriazole ring is highly stable to acids and bases, oxidation and reduction, and heat. Ring opening by pyrolysis requires forcing conditions (200 °C) and 1-alkylbenzotriazoles afford complex rearranged products in low yields after elimination of nitrogen.[1] Flash-vacuum pyrolysis (500−700 °C) of *N*-vinylbenzotriazoles yields *N*-phenylketene imines with loss of nitrogen.[2] Photolysis of 1-aryl-substituted benzotriazoles extrudes nitrogen to form diradicals,[3] which then cyclize: thus 1-phenylbenzotriazole on irradiation gave carbazole in nearly quantative yield.[4] Prolonged irradiation of benzotriazole and its derivatives gives poor yields of isolable products formed by nitrogen elimination.[5−7] Nevertheless, some derivatives of benzotriazole have been propagated as a new family of light-activated DNA cleaving agents (triazole photonucleases).[8] Two nitrogen molecules are lost during the photolysis of 1-aminobenzotriazole. One nitrogen molecule is lost on photolysis, and another nitrogen is lost thermally.[9] Photochemical reaction of 1-aminobenzotriazole in polymer film was used for modulation of various properties such as its solubility, absorption, and refractive index.[10]

We studied tris(benzotriazo-1-yl)methane (**1**) as a potential component that can extrude nitrogen molecules. Such a system could find application as a molecular part of novel polymer compositions, which can be used for read-only holographic memories, waveguide lithography, microlenses, and other optical elements.[11−15] In this report we present the mechanisms of

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[†] Contribution No. 614.

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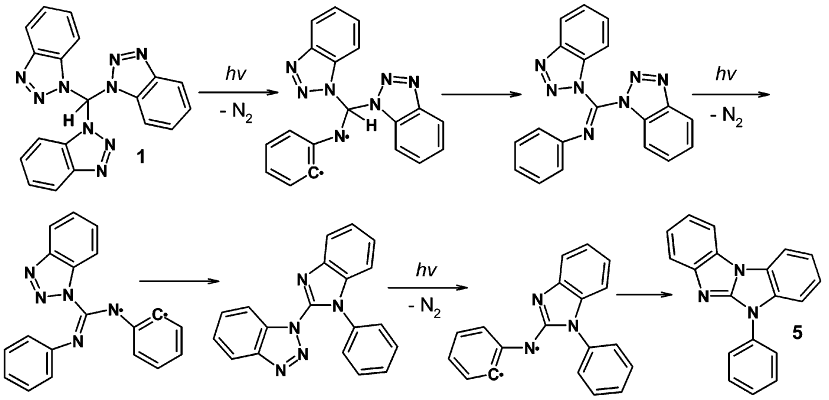
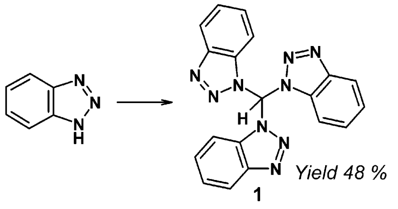
SCHEME 1

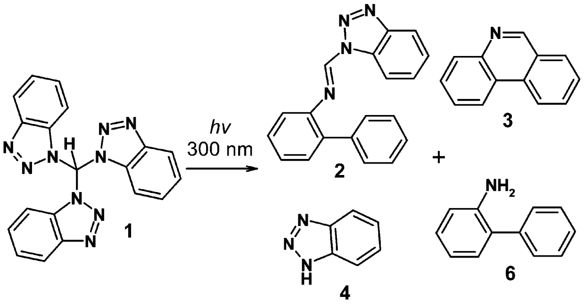


SCHEME 2



Conditions: $CHCl_3/NaOH_{(aq.\ conc.)}/Bu_4\overset{+}{N}\overset{-}{Br}$
reflux 48 h.

SCHEME 3



photochemical dissociation of **1**. The effect of the nature of the solvents used and wavelengths employed is discussed.

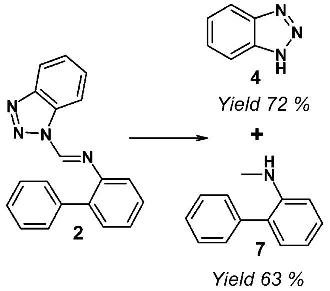
Results and Discussion

Our attention was initially focused on the presumption that **1** with three benzotriazole rings can liberate nitrogen in a stepwise fashion. A possible product of the reaction might be 9-phenyl-9*H*-4,*b*,9,10-triazaindeno[1,2-*a*]indene (**5**). This product is a planar cyclic system containing four conjugated rings (Scheme 1).

Compound **1** was prepared from benzotriazole and chloroform according to a literature procedure (Scheme 2).[16]

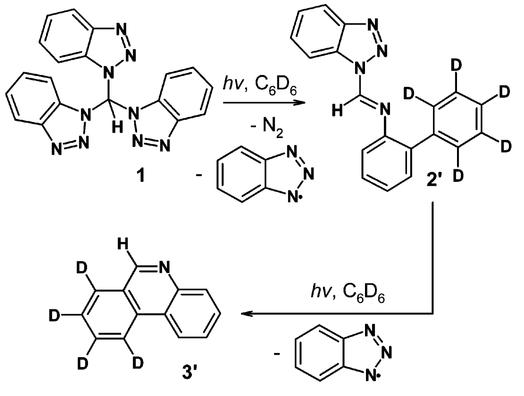
When diluted benzene solutions of **1** were subjected to prolonged irradiation with 300 nm light, only phenantridine (**3**) and 2-aminobiphenyl (**6**) were observed, in nearly quantative yield. Other intermediates of the photodecomposition of **1** to [1-benzotryazol-1-ylmethylidene]biphenyl-2-ylamine (**2**) and benzotriazole (**4**) could be isolated by using more concentrated solutions of **1** and a moderate time of irradiation (1−2 h) (Scheme 3).

SCHEME 4



Conditions: (1) $LiAlH_4$ (5 eq.) THF (30 ml), 0 °C, 10 min; (2) MeOH - several drops; (3) AcOH several drops (pH ~ 7); (4) Solvent evaporation and chromatography.

SCHEME 5



Compounds **2** and **3** could be isolated from column chromatography. The structure of **2** was established by reducing it with $LiAlH_4$ in THF. The problem in the spectroscopic identification of **2** results from negligible intensity of its molecular ion (*m*/*z* 298) in GS/MS and MALDI experiments. Moreover, *m*/*z* 269 attributed to $[M - N_2 - H]$ is detected by GC/MS and *m*/*z* 271 corresponding to $[M - N_2 + H]$ is detected by MALDI. In contrast, the products of reduction of **2** (2-methylaminobiphenyl, **7** and **4**) are easily identifiable (Scheme 4).

We also irradiated **1** in deuterated benzene. This produced the products **2′** and **3′** (Scheme 5). The evidence for this was

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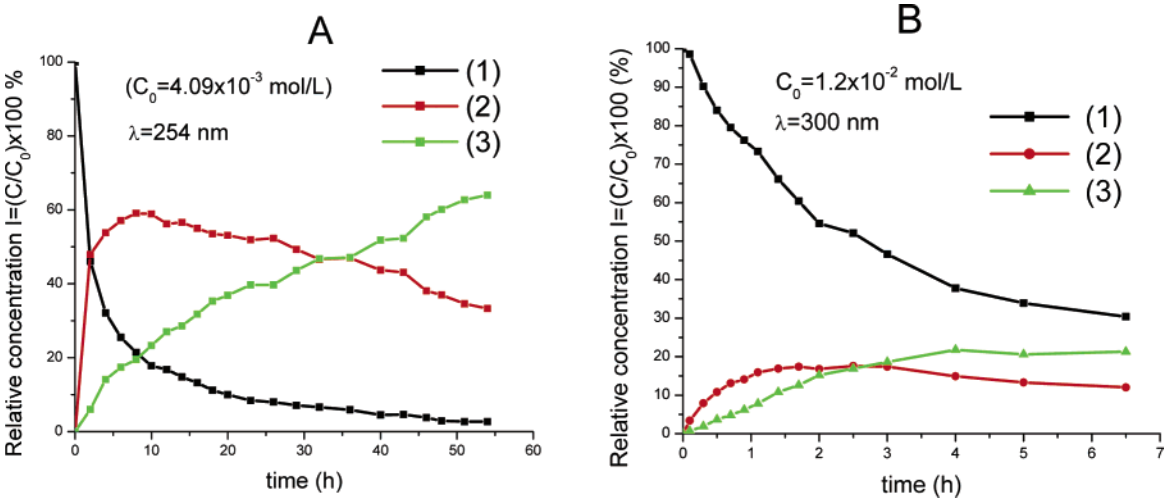
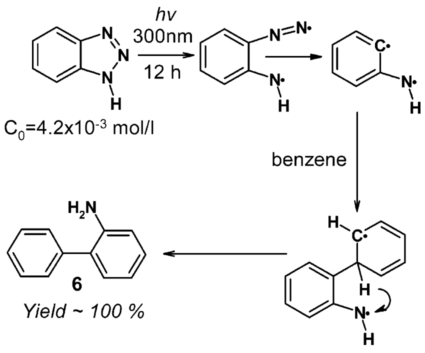
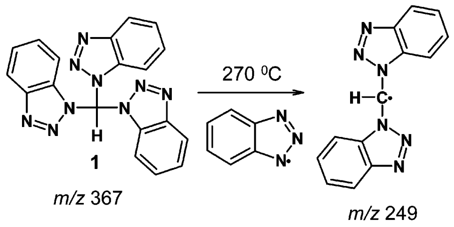


FIGURE 1. Photodecomposition of **1** in C_6D_6 at $\lambda = 254$ nm ($C_0 = 4.09 \times 10^{-3}$ mol/L) (A) and at $\lambda = 300$ nm ($C_0 = 1.201 \times 0^{-2}$ mol/L) (B) and relative formation of products **2** and **3**.

SCHEME 6



SCHEME 7



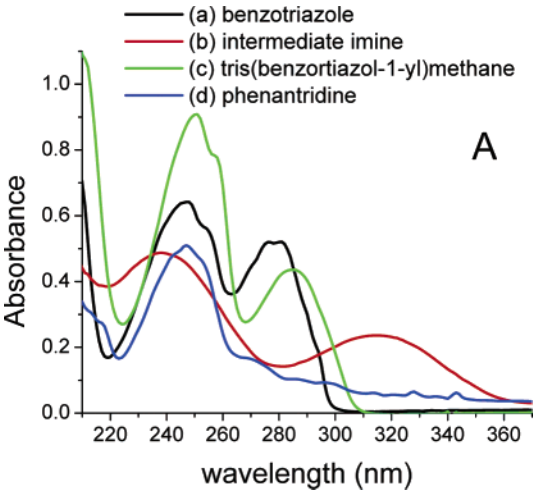


FIGURE 2. UV spectra of **1** (c) and its photoproducts, recorded in cyclohexane.

the resonance of C*H*═N moiety protons at 8.70 ppm in semideuterted **2′** and at 9.13 ppm in **3′**. This indicates that the H-atom of the CH moiety of **1** keeps its position through the reaction. The GC/MS confirmed the incorporation of a single deuterobenzene molecule resulting in the formation of **2′** (*m*/*z* 303) and **3′** (*m*/*z* 183).

The analysis of the reaction mixture at differing degrees of conversion of **1** indicates whether elimination of the benzotriazolyl radical or loss of the nitrogen molecule is the initial step (Scheme 6). Monitoring of the reaction at short times shows that **4** prevails in the reaction mixture, but in the process the amount of semideuterated analogue of 2-aminobiphenyl (**6**) gradually increases.

The benzotriazolyl radical should be rather stable. Though it should abstract H-atom from the substrate or solvent, the absence of biphenyl in the reaction mixture ruled out this abstraction from benzene.

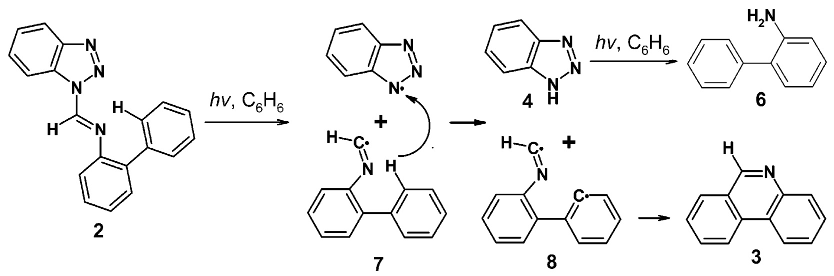
An independent experiment showed that **4** converts into **6** in benzene ($C_0 = 4.2 \times 10^{-3}$ mol/L) after 12 h of irradiation at 300 nm (Scheme 6).

Compelling evidence that suggests elimination of the benzotriazolyl radical being the initial step is obtained during characteristic thermal decomposition of **1**. Only the benzotriazolyl radical elimination was observed under the conditions of the GC/MS experiments. The thermal decomposition of **1** in the GC column at 270 °C affords bis(benzotriazol-1-yl)methane detected as a broad peak giving the intensive molecular ion *m*/*z* 249 (Scheme 7).

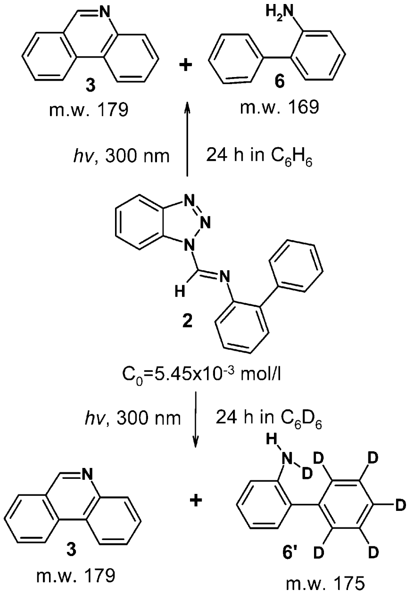
Additional evidence for primary benzotriazolyl radical elimination is provided by the DIP-MS of **1**. Only an intense peak corresponding to benzotriazolyl radical elimination was observed (*m*/*z* 249) and no peak corresponding to nitrogen extrusion was detected.

Profiles of **1** photodecomposition in C_6D_6 at $\lambda = 254$ nm ($C_0 = 4.091 \times 0^{-3}$ mol/L) and at $\lambda = 300$ nm ($C_0 = 1.20 \times 10^{-2}$ mol/L) were obtained by using ^{1}H NMR (Figure 1).

SCHEME 8



SCHEME 9



When irradiated at 254 nm, a larger amount of **2** was formed in comparison with 300 nm light being used as the irradiation source (Figure 1). This can be explained by the strong absorbance of benzene (solvent) in the 254 nm region. In contrast, benzene does not absorb at 300 nm while the intermediate imine **2** absorbs intensively at this wavelength. So, **2** does not accumulate in reasonable amounts during 300 nm irradiation. The UV−vis absorption spectra of **1** and its photoproducts are presented in Figure 2.

The main route of photodecomposition of **2** also involves the initial step of elimination of the benzotriazole ring. The transfer of H-atom from **7** to the benzotriazolyl radical followed by cyclization of **8** results in the formation of **3**. GC monitoring of the reaction at short times of irradiation shows that **4** prevails in the reaction mixture but in the process the amount of **6** gradually increases (Scheme 8).

Replacement of benzene by deuterated benzene does not influence the nature of **3**, but leads to the formation of semideuterated 2-aminobiphenyl (**6′**). GC/MS analyses of solutions of **2** in C_6H_6 and C_6D_6 ($C_0 = 5.45 \times 10^{-3}$ mol/L) after 24 h of irradiation at 300 nm show only **3** and **6** or **3** and **6′**, respectively (Scheme 9). Formation of **3**, **6**, and **6′** was also confirmed by NMR spectroscopy.

In summary, photodecomposition of **1** proceeds by elimination of the benzotriazolyl radical giving bis(benzotriazol-1-yl)methyl radical (**9**), which converts to an intermediate radical (**10**) after extrusion of nitrogen. Benzene adds to **10** forming **11**, which converts to intermediate **2** via abstraction of H-atom. Compound **2** loses **4** resulting in the formation of **3** via the radical **8**. In turn, **4** loses nitrogen upon irradiation and forms **6** (Scheme 10).

Sensitized Experiments. No photodecomposition was observed after irradiation of **1** in benzene ($C_0 = 1.36 \times 10^{-3}$ mol/L) at 350 nm for 25 h. Using 1 equiv of triplet sensitizer such as benzophenone or triphenylamine in the presence of air gave only traces of photodecomposition under the same conditions. Irradiation of an argon purged 1:1 mixture of **1** and triphenylamine ($E_T = 291$ kJ/mol[17]) afforded a mixture of starting material and **3** in the ratio of 1:1 after 50 h of irradiation. The same mixture of **1** and **3** in the ratio 1.86:1 was observed after 21 h of irradiation (350 nm) when benzophenone ($E_T = 287$ kJ/mol[17]) was used as the sensitizer. Only traces of **2** were detected in both cases. The considerable absorbance of **2** in the 350 nm region may be the reason for the higher rate of photodecomposition than the rate of its formation at this wavelength.

The similarity (absence of new products and pathways of the reaction) between photodecomposition of **1** in the presence and absence of triplet sensitizers suggests the reaction passes through the exited triplet state.

In a proton donating solvent such as methanol, photodecomposition of **1** results in **4** (yield 47%). Some amount of resinous products was also observed. However, no anticipated intermediate products were detected after 48 h of irradiation at 254 nm as shown Scheme 11. Thus, the only way **1** photodecomposes in methanol is by extrusion of the benzotriazolyl radical. No loss of nitrogen takes place.

Formation of a yellow intermediate was observed following irradiation of **1** in dilute MeOH ($C_0 = 4.09 \times 10^{-5}$ mol/L). At the end of photodecomposition the yellow color disappears resulting in a clear solution that does not contain **4** (see the Supporting Information). These results correlate with the observation of Wirz[18] et al., who showed that irradiation of **4** in acidic water gave only a low yield of 2-aminophenol. In neutral and basic water solutions only resinous products of 2-aminophenol photooxidation were formed.

Conclusions

In conclusion, it was established that photodecomposition of **1** involves benzotriazol ring elimination affording the bis(benzotriazol-1-yl) radical (**9**). The fate of the radical **9** depends on the solvent. In benzene, **9** liberates nitrogen molecule and combines with a molecule of solvent. This leads to the formation

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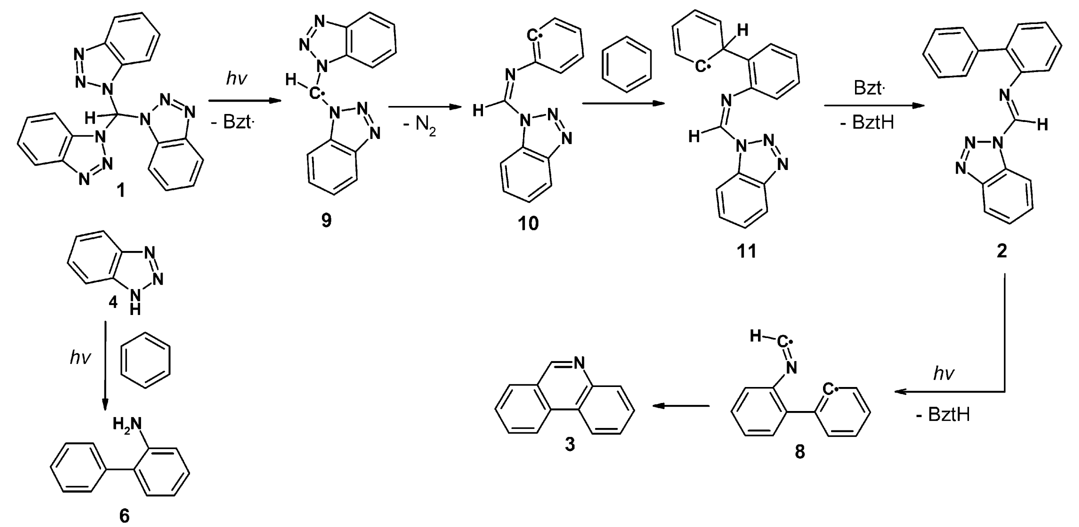
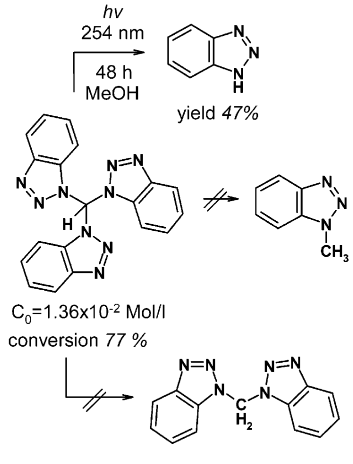
SCHEME 10



SCHEME 11



of **3**. Methanol as a proton donating solvent promotes transformation of **9** into **4**.

Experimental Section

Tris(benzotriazol-1-yl)methane (1). A mixture of benzotriazole (2.0 g; 0.5 mol), aq NaOH (40%, 50 mL), and Bu_4NBr (1.6 g) in $CHCl_3$ (50 mL) is heated under reflux for 48 h. The reaction mixture is cooled and the organic material extracted with $CHCl_3$ (2 × 100 mL). The organic layer is washed with H_2O (5 × 50 mL) and concentrated at reduced pressure to give a brown solid. The pure product (29 g; yield 46.8%) was obtained after crystallization from $CHCl_3$−MeOH, with the addition of charcoal. White needles, mp 197−198 °C (lit.[16] mp 194−196 °C). ^{1}H NMR (C_6D_6) δ 6.75−6.78 (m, 6H), 6.98−7.01 (m, 3H), 7.75−7.79 (m, 3H), 9.59 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 78.1, 110.0, 120.7, 125.4, 129.5, 132.0, 146.4. *m*/*z* (EI$^+$ mode) 367 (M$^+$, 25%), 249 (100), 221 (58), 192 (85), 166 (35), 140 (17).

[1-Benzotryazol-1-yl-methylidene]biphenyl-2-ylamine (2). A solution of tris(benzotriazol-1-yl)methane **1** (0.3 g; 0.82 mmol) in 200 mL of benzene was irradiated for 24 h with 254 nm UV light in a Rayonet photoreactor. Solvent was evaporated under reduced pressure. The residue was chromatographed (ethyl acetate/hexanes 1/8) to give the first fraction (R_f 0.55) [1-benzotryazol-1-ylmethylidene]biphenyl-2-ylamine **2 (**0.092 g; 0.31 mmol), after crystallization from dichloromethane/hexanes [colorless needless; mp 120 °C; ^{1}H NMR (DMSO-d_6) δ 7.33−7.59 (m, 11H), 7.92−7.98 (m, 1H), 8.16−8.22 (m, 1H), 9.59 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 114.2, 119.8, 119.9, 126.4, 127.0, 127.2, 128.0, 128.9, 129.8, 130.0, 130.1, 130.4, 136.5, 139.4, 144.5, 145.9, 146.0; *m*/*z* (EI$^+$ mode) 298 (M$^+$, 4%), 269 (100), 180 (55), 152 (80); HRMS (EI$^+$ mode) calcd for M$^+$ 298.1218, found 298.1223], and the second fraction (R_f 0.20) phenantridine **3** (0.04 g; 0.22 mmol) [white solid; mp 100 °C (CAS Registry No. 229-87-8); ^{1}H NMR ($CDCl_3$) δ 6.63−6.77 (m, 3H), 7.81−7.87 (m, 1H), 8.02 (dd, 1H), 8.53−8.60 (m, 2H), 9.27(s, 1H); ^{13}C NMR ($CDCl_3$) δ 121.8, 122.2, 124.1, 126.3, 127.0, 127.4, 128.6, 128.7, 130.1, 130.9, 132.5, 144.5, 153.5; *m*/*z* (EI$^+$ mode) 179 (M$^+$, 100)].

Reduction of [1-Benzotryazol-1-yl-methylidene]biphenyl-2-ylamine (2). To the well-stirred mixture of **2 (**52 mg; 0.17 mmol) in 30 mL of dry THF was added $LiAlH_4$ (39 mg; 1 mmol). The mixture was stirred for 10 min. Several drops of methanol and several drops of acetic acid were added to neutralize the solution. Solvent was evaporated under reduced pressure. The residue was chromatographed (ethyl acetate/hexanes 1/8) to give 2-methylaminobiphenyl **7** (CAS Registry No. 14925-09-8) (20 mg; yield 63%) as the first fraction [R_f 0.85; ^{1}H NMR ($CDCl_3$) δ 2.79 (s, 3H), 3.95 (br s, 1H), 6.69 (d, 1H), 7.09 (dd, 1H), 7.23−7.47 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 30.7, 109.8, 116.8, 127.1, 127.6, 128.7, 128.8, 129.4, 130.0, 139.5, 146.2; *m*/*z* (EI$^+$ mode) 183 (M$^+$, 100), 167 (38)] and benzotriazole **4** (CAS Registry No. 95-14-7**)** **(**15 mg; yield 72%**)** as the second fraction [R_f 0.20; ^{1}H NMR (C_6D_6) δ 6.96−7.02 (m, 2H), 7.68 (br s, 2H), 14.35 (br s, 1H); *m*/*z* (EI$^+$ mode) 119 (M$^+$, 64), 91 (64), 83 (43), 64 (100)].

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Supporting Information Available: General information, materials and methods, characterization data, and copies of MS, UV−vis, and ^{1}H and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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