Dibenzo[*b*,*h*][1,4,7]thiadiazonines: Examples of a Novel Ring System

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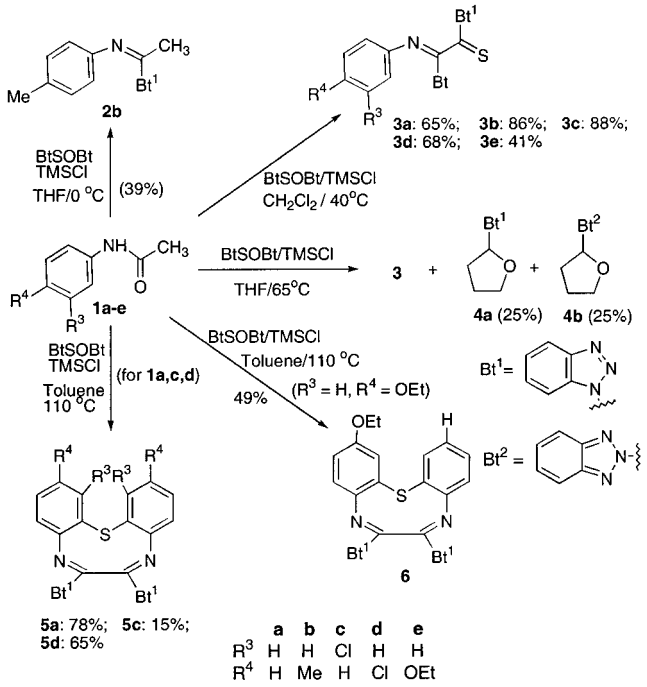
Acetanilides **1a**−**e** react with 1,1′-sulfinylbis(benzotriazole)/trimethylchlorosilane at 45−65 °C to form 1,2-di(benzotriazol-1-yl)-2-arylimino-1-ethanethiones **3a**−**e**, while heating the same reagents at 110 °C results in dibenzo[*b*,*h*][1,4,7]thiadiazonines **5a**,**c**,**d**, and **6**. X-ray crystal structures are reported for three representative examples.

Introduction

Short routes for the efficient construction of medium-ring heterocycles are currently a major challenge in synthetic organic chemistry. Until now, few representatives of 1-thia-4,7-diazacyclononanes have been reported, and those are almost exclusively simple derivatives of the parent saturated heterocycle[1] or peptide-like analogues.[2] To the best of our knowledge, no 1,4,7-thiadiazonines, formally representing a 10π Hückel aromatic ring, have previously been synthesized. We now disclose that acetanilides **1a**−**e** and the 1,1′-sulfinylbis(benzotriazole)/chlorotrimethylsilane reagent, heated over 50 °C, form 1,2-di(benzotriazol-1-yl)-2-arylimino-1-ethanethiones **3a**−**e** and dibenzo[*b*,*h*][1,4,7]thiadiazonines **5a**,**c**,**d** and **6**, the first representatives of fully unsaturated 1-thia-4,7-diazacyclononanes, along with the corresponding imidoylbenzotriazoles **2**.

Secondary amides have previously been converted into imidoylbenzotriazoles by treatment with (1) 1,1′-sulfinylbis(benzotriazole), prepared in situ from benzotriazole and thionyl chloride,[3] or (2) benzotriazole and phosphorus oxychloride under basic conditions.[4] Imidoylbenzotriazoles, stable analogues of imidoyl chlorides, were demonstrated to be important precursors for the preparation of imidates and thioimidates[3a] and guanidines,[5] as well as ketones[4] and various heteroaromatics.[3b,6]

Scheme 1



Results and Discussion

Preparation of Iminothiones 3. The 1,1′-sulfinylbis(benzotriazole)/trimethylchlorosilane (BtSOBt/TMSCl) reagent was prepared in situ by treatment of 1-trimethylsilylbenzotriazole with thionyl chloride as described previously,[3a] except that, considering the high sensitivity of the BtSOBt/TMSCl reagent to atmospheric moisture, this reaction was carried out in a solvent (THF, CH_2Cl_2, or toluene) appropriate for the further transformations.

We found that heating acetanilides **1a**−**e** with a 3-fold excess of the BtSOBt/TMSCl reagent in methylene chloride under reflux for 6−12 h gave iminothiones **3a**−**e** in 41−88% yields (Scheme 1). The intermediacy of the

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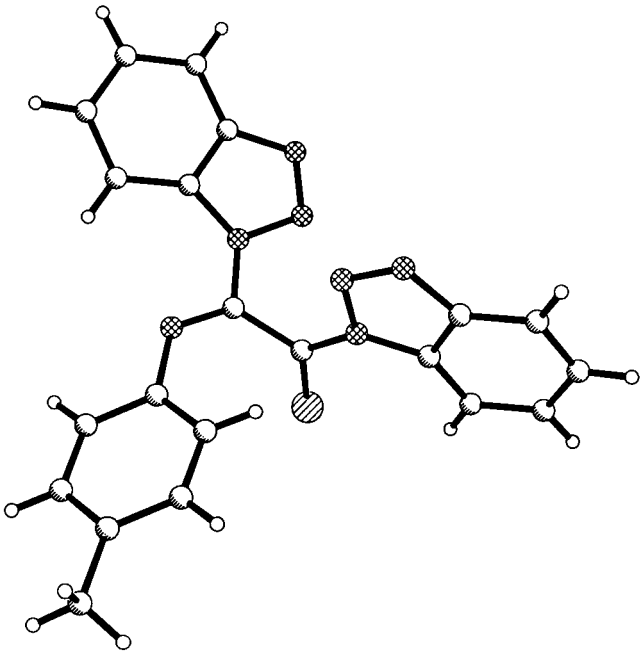
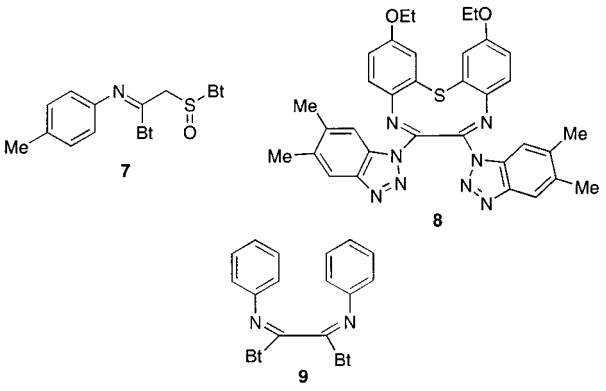


Figure 1. Perspective view of one of the two independent molecules in the crystal structure of **3b**.

corresponding imidoylbenzotriazoles was supported by (1) independent preparation of imidoylbenzotriazole **2b** from *N*-(4-methylphenyl)acetamide **1b** at 0 °C (all the other conditions being the same) and (2) the presence of traces of compounds **2** in the NMR spectra of the reaction mixtures even after a prolonged reaction time (up to 3 days). The formation of **3a**−**e** from acetamides **1a**−**e** may involve intermediates of type **7**.



Structure **3b**, suggested by ^{1}H and ^{13}C NMR spectra, was confirmed by X-ray crystallography. This compound crystallizes with two independent molecules in the asymmetric unit, which adopt very similar conformations. As shown in Figure 1, the planes of the imine and thiocarbonyl functionalities are approximately orthogonal [N−C−C−S torsional angles = 69.5 and 74.2° for the two independent molecules]. In contrast, each of the benzotriazole groups is approximately coplanar with the adjacent functional group. The structures of compounds **3a**,**c**−**e** were assigned by analogy and by spectroscopic data comparisons. In the ^{1}H NMR spectra of compounds **3a**−**e**, the 4- and 7-benzotriazole aromatic protons signals are significantly shifted downfield, probably because of deshielding by the adjacent functional groups. Methylene chloride was an advantageous solvent for the preparation

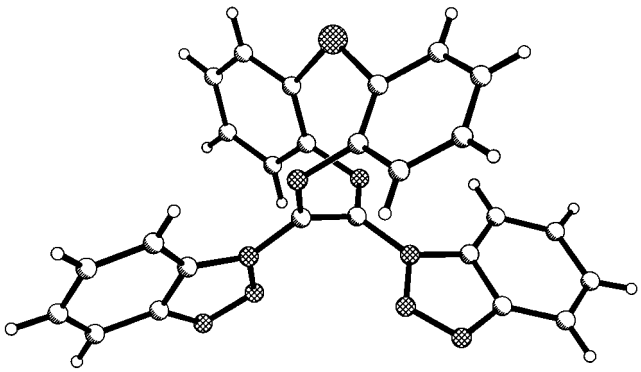


Figure 2. Perspective view of the crystal structure of **5a**. The solvate molecule is not shown.

of **3a**−**e**: in THF, concurrent benzotriazolation of tetrahydrofuran led to 2-(benzotriazol-1-yl)- (**4a**) and 2-(benzotriazol-2-yl)tetrahydrofuran (**4b**) (Scheme 1). Analogous benzotriazolation of tetrahydrofuran was previously observed with *N*-chlorobenzotriazole under Lewis acid catalysis.[7]

Preparation of Thiadiazonines 5. Heating acetanilides **1a**,**c**,**d** with excess BtSOBt/TMSCl reagent under reflux in toluene for 6−12 h formed dibenzo[*b*,*h*][1,4,7]-thiadiazonines **5a**,**c**,**d** as shown in Scheme 1. The nature and the position of the substituent R in the starting acetanilide influence the reaction significantly: a chlorine at the meta position decreases the yield of the desired product to 15% (compare with 65% for the *p*-chloro derivative), while *p*-nitroacetanilide gave no thiadiazonine **5**.

Surprisingly, reaction of ethoxy-substituted acetanilide **1e** (R^3 = H, R^4 = EtO) with the BtSOBt/TMSCl reagent under the aforementioned conditions occurred with an unexpected ethoxy group cleavage to afford the unsymmetrically substituted thiadiazonine **6** in 49% yield. However, when 4,5-dimethylbenzotriazole was used in place of benzotriazole, this cleavage did not occur and thiadiazonine **8** resulted.

The structures of compounds **5a**,**c**,**d** and **6** were initially assigned on the basis of their ^{1}H and ^{13}C NMR spectra and confirmed by X-ray structure determinations for **5a** and **6**. Perspective views of the crystal structures of **5a** and **6** are displayed in Figures 2 and 3, respectively.

Compounds **5** structurally possess C_2 symmetry, which explains the simplified sets of signals in both ^{1}H and ^{13}C NMR spectra. The absence of C_2 or C_s symmetry in **6** leads to a more complicated pattern. As shown by X-ray analysis, the [1,4,7]thiadiazonine ring of both **5a** and **6** is twisted and therefore not aromatic. Kinetic as well as thermodynamic factors appear to enhance the stability of **5a**,**c**,**d**, **6**, and **8**. The two bulky benzotriazolyl groups and two benzo substituents shield the internal imidoyl groups from nucleophilic attack. Further, as is apparent from Figures 2 and 3, the molecules of **5a** and **6** adopt very similar conformations, which have the two imine components in approximately orthogonal orientations (N−C−C−N torsional angles = 85.7−88.4°) within each molecule. In all cases, the plane of the benzotriazole ring is almost exactly coplanar with the plane of its attached imine functionality.

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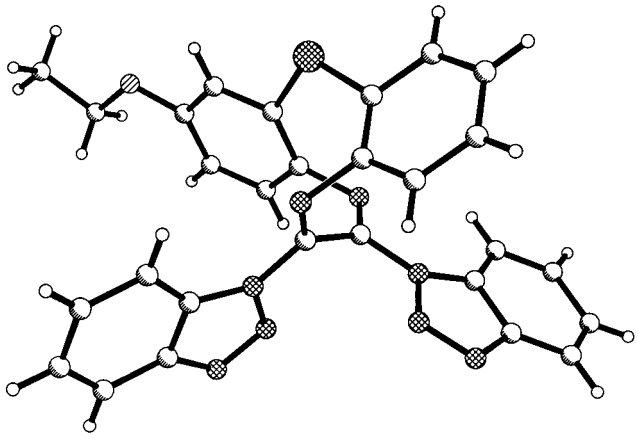
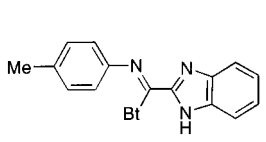


Figure 3. Perspective view of one of the two independent molecules in the crystal structure of **6**.

The mechanism of formation of [1,4,7]thiadiazonines **5a**,**c**,**d**, **6**, and **8** may involve intermediates of type **9**. Indeed, bis(imidoylbenzotriazole) **9**, prepared by reaction of oxalic dianilide with BtSOBt/TMSCl in 86% yield, on further treatment with an additional 2 equiv of the BtSOBt/TMSCl reagent gave [1,4,7]thiadiazonine **5a** in 71% yield.

1,2-Di(*1H*-1,2,3-benzotriazol-1-yl)-2-arylimino-1-ethanethione **3b** reacted with *o*-benzenediamine to give **10** (11%). Reactions of 6,7-di(1,2,3-benzotriazol-1-yl)dibenzo-



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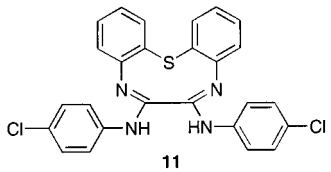

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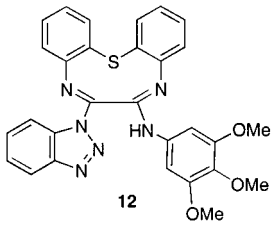

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[*b*,*h*][1,4,7]thiadiazonine (**5a**) with 2 equiv of 4-chloroaniline in benzene in the presence of a catalytic amount of DBU afforded 6,7-di(4-chlorophenylamino)dibenzo[*b*,*h*]-[1,4,7]thiadiazonine (**11**) in excellent yield. The readiness of this benzotriazolyl group substitution with a strong nucleophile could provide a plausible explanation for the formation of unsymmetrical thiadiazonine **12** as a major product on treatment of *N*-(3,4,5-trimethoxyphenyl)-acetamide (**1f**) with the BtSOBt/TMSCl reagent.

In summary, we have developed preparatively useful procedures for the synthesis of novel 1,2-di(benzotriazol-1-yl)-2-arylimino-1-ethanethiones (**3a**−**e**) and dibenzo-[*b*,*h*]-[1,4,7]thiadiazonines (**5a**,**c**,**d**, **6**, and **8**) stemming from one-pot reactions of acetanilides with the 1,1′-sulfinylbis(benzotriazole)/trimethylchlorosilane reagent under different conditions.

Experimental Section

General Methods. Melting points were determined on a capillary melting point apparatus equipped with a digital thermometer and are uncorrected. NMR spectra were recorded in $CDCl_3$ (if not stated otherwise) with tetramethylsilane as the internal standard for ^1H (300 MHz) or a solvent as the internal standard for ^{13}C (75 MHz). Tetrahydrofuran, benzene, and toluene were distilled from sodium/benzophenone (THF) or from sodium under nitrogen immediately prior to use. All reactions with air-sensitive compounds were carried out under argon atmosphere. Column chromatography was conducted with silica gel 230−400 mesh.

1,1′-Sulfinylbis(benzotriazole)/trimethylchlorosilane reagent (BtSOBt/TMSCl) was prepared by treatment of 1-trimethylsilyl benzotriazole (BtTMS) with thionyl chloride in dichloromethane, THF, or toluene at 20 °C following the reported procedure.[3a]

***N*-(4-Tolyl)acetoimidoyl-1-benzotriazole (2b).** A solution of *N*-(4-methylphenyl)acetamide **1b** (0.3 g, 2 mmol) and of 1,1′-sulfinylbis(benzotriazole) (3 mmol), prepared *in situ* as described above, in dry dichloromethane was stirred at 0 °C for 4 h. Then the solvent was removed under reduced pressure and the residue obtained was subjected to column chromatography using hexane/ethyl acetate (15:1) as eluent to afford *N*-(4-tolyl)acetoimidoyl-1-benzotriazole (**2**) in 39% yield as orange needles. Analytically pure product was obtained as yellow crystals by recrystallization from methylene chloride−ethanol: mp 111−112 °C (lit.[3a] mp 108 °C); ^1H NMR δ 2.39 (s, 3H), 2.75 (s, 3H), 6.85 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 16.5, 21.1, 116.0, 120.0, 120.4, 125.6, 129.4, 130.0, 134.1, 145.0, 146.8, 154.2.

General Procedure for the Preparation of Compounds 3. A solution of an acetanilide (2 mmol) and BtSOBt/TMSCl reagent (6−7 mmol) in dry dichloromethane (25 mL) was heated under reflux for 6−12 h. Then the solvent was removed under reduced pressure and the residue was subjected to purification by column chromatography using hexane/ethyl acetate (15:1) as an eluent to afford the corresponding 1,2-di-(benzotriazol-1-yl)-2-arylimino-1-ethanethione (**3**). Analytically pure product was obtained by recrystallization from methylene chloride−ethanol.

When THF was used as a solvent, the similar reactions gave compounds **3** in 11−35% yields (compared to 41−69% in dichloromethane) as well as **4a** and **4b** in 25% yield each.

1,2-Di(benzotriazol-1-yl)-2-[(phenyl)imino]-1-ethanethione (3a): orange prisms (from dichloromethane−ethanol); yield 65%; mp 167−168 °C; ^1H NMR δ 6.97 (d, J = 7.5 Hz, 2H), 7.04 (t, J = 7.5 Hz, 1H), 7.18−7.25 (m, 1H), 7.51−7.62 (m, 2H), 7.67−7.73 (m, 2H), 8.12 (d, J = 8.2 Hz, 1H), 8.14 (d, J = 8.1 Hz, 1H), 8.58 (d, J = 8.2 Hz, 1H), 8.62 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 115.3, 115.4, 120.3, 120.4, 121.2, 125.3, 126.4, 128.2, 129.2, 130.1, 130.8, 131.5, 132.2, 145.9, 146.3, 147.0, 147.6, 187.0. Anal. Calcd for $C_{20}H_{13}N_7S$: C, 62.65; H, 3.42; N, 25.57. Found: C, 62.36; H, 3.34; N, 25.41.

1,2-Di(benzotriazol-1-yl)-2-[(4-methylphenyl)imino]-1-ethanethione (3b): orange hexagons (from dichloromethane−ethanol); yield 86%; mp 155−156 °C; ^1H NMR δ 2.21 (s, 3H), 6.87 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 7.47−7.58 (m, 2H), 7.63−7.70 (m, 2H), 8.10 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.63 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 20.8, 115.1, 115.2, 119.9, 120.1, 120.9, 126.0, 128.0, 129.6, 129.8, 130.5, 131.2, 131.9, 134.8, 143.0, 145.9, 146.7, 147.1, 187.2. Anal. Calcd for $C_{21}H_{15}N_7S$: C, 63.46; H, 3.80; N, 24.67. Found: C, 63.41; H, 3.63; N, 24.74.

Crystal data for 3b: $C_{21}H_{15}N_7S$, MW 379.46, monoclinic, space group $P2_1/c$, a = 14.466(5) Å, b = 9.489(4) Å, c = 28.115-(10) Å, β = 95.708(5)°, V = 3846(2) Å^3, F(000) = 1648, Z = 8, T = −110 °C, μ(Mo Kα) = 0.191 mm^{-1}, D_{calcd} = 1.373 g·cm^{-3}, $2\theta_{max}$ 53° (CCD area detector, Mo Kα radiation, 47 627 reflections collected, R(int) = 0.028, 99.2% completeness), GOF = 1.04, wR(F^2) = 0.1028 (all 7860 data), R = 0.0374 (6592 data with $I > 2\sigma I$).

1,2-Di(benzotriazol-1-yl)-2-[(3-chlorophenyl)imino]-1-ethanethione (3c): yellow prisms (from dichloromethane−ethanol); yield 88%; mp 111−112 °C; ^1H NMR δ 6.83 (d, J = 7.9 Hz, 1H), 6.97−7.10 (m, 3H), 7.47 (d, J = 7.9 Hz, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.63 (t, J = 7.3 Hz, 1H), 7.64 (t, J = 7.7

Hz, 1H), 8.08 (d, J = 8.2 Hz, 2H), 8.49 (d, J = 8.2 Hz, 1H), 8.55 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 115.0, 115.2, 118.3, 120.2, 120.8, 121.1, 125.2, 126.4, 128.3, 130.2, 130.5, 131.2, 132.2, 134.8, 146.1, 146.8, 146.9, 148.1, 186.0. Anal. Calcd for $C_{20}H_{12}ClN_7S$: C, 57.49; H, 2.89; N, 23.46. Found: C, 57.23; H, 2.72; N 23.40.

1,2-Di(benzotriazol-1-yl)-2-[(4-chlorophenyl)imino]-1-ethanethione (3d): red prisms (from dichloromethane−ethanol); yield 68%; mp 180−181 °C; ^{1}H NMR δ 6.92 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.8 Hz, 2H), 7.53−7.78 (m, 4H), 8.15 (t, J = 8.1 Hz, 2H), 8.55 (d, J = 8.3 Hz, 1H), 8.67 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 115.3, 115.5, 120.4, 121.3, 121.8, 126.5, 128.5, 129.4, 130.3, 130.8, 131.4, 132.4, 144.5, 146.3, 147.1, 148.1, 186.6. Anal. Calcd for $C_{20}H_{12}ClN_7S$: C, 57.49; H, 2.89; N, 23.46. Found: C, 57.84; H, 2.91; N, 23.61.

1,2-Di(benzotriazol-1-yl)-2-[(4-ethoxyphenyl)imino]-1-ethanethione (3e): orange prisms (from dichloromethane−ethanol); yield 41%; mp 128−129 °C; ^{1}H NMR δ 1.34 (t, J = 7.0 Hz, 3H), 3.92 (q, J = 7.0 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 9.1 Hz, 2H), 7.51−7.78 (m, 4H), 8.12 (d, J = 8.3 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 8.60 (d, J = 8.3 Hz, 1H), 8.71 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 15.0, 63.8, 110.3, 115.1, 115.5, 115.6, 120.3, 121.3, 122.1, 126.3, 128.3, 130.0, 130.9, 131.6, 132.3, 138.7, 146.3, 147.1, 156.9, 188.1. Anal. Calcd for $C_{22}H_{17}N_7OS$: C, 61.81; H, 4.01; N, 22.94. Found: C, 61.77; H, 3.90; N, 22.64.

1-(2-Tetrahydrofuryl)benzotriazole (4a):[8] colorless oil; yield 25%; ^{1}H NMR δ 2.15−2.23 (m, 1H), 2.35−2.59 (m, 2H), 3.12−3.21 (m, 1H), 4.00−4.14 (m, 2H), 6.51 (dd, J = 6.7, 2.3 Hz, 1H), 7.37 (dt, J = 7.7, 1.0 Hz, 1H), 7.50 (dt, J = 7.7, 1.2 Hz, 1H), 7.71 (d, J = 8.3 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 24.6, 31.0, 69.5, 88.1, 110.6, 120.1, 124.3, 127.7, 133.0, 146.6.

2-(2-Tetrahydrofuryl)benzotriazole (4b):[8] colorless oil; yield 25%; ^{1}H NMR δ 2.11−2.18 (m, 1H), 2.45−2.57 (m, 2H), 2.72−2.77 (m, 1H), 4.14 (dd, J = 14.1, 8.1 Hz, 1H), 4.34 (dd, J = 13.9, 8.1 Hz, 1H), 6.60 (dd, J = 6.3, 2.4 Hz, 1H), 7.36−7.42 (m, 2H), 7.85−7.91 (m, 2H); ^{13}C NMR δ 24.5, 32.6, 70.5, 94.4, 118.7, 126.8, 144.5.

General Procedure for the Preparation of Compounds 5 and 6. A solution of an acetanilide (2 mmol) and BtSOBt/TMSCl reagent (6−7 mmol) in dry toluene (25 mL) was heated under reflux for 12 h. The solvent was removed under reduced pressure, and the residue was subjected to purification by column chromatography using hexane/ethyl acetate (6:1) as an eluent to afford the corresponding dibenzo[*b,h*][1,4,7]-thiadiazonine (**5** or **6**). Analytically pure product was obtained by recrystallization from dichloromethane−ethanol.

6,7-Di(benzotriazol-1-yl)dibenzo[*b,h*][1,4,7]thiadiazonine (5a): pale yellow prisms (from dichloromethane−ethanol); yield 78%; mp 232−233 °C; ^{1}H NMR δ 6.71−6.78 (m, 2H), 6.81−6.83 (m, 4H), 7.28 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.57 (t, J = 7.5 Hz, 2H), 8.02 (d, J = 8.2 Hz, 2H), 8.27 (d, J = 8.2 Hz, 2H); ^{13}C NMR δ 114.5, 120.2, 122.5, 122.8, 125.7, 126.5, 126.9, 130.0, 130.2, 130.4, 145.0, 146.3, 147.4. Anal. Calcd for $C_{26}H_{16}N_8S.0.5C_2H_6O$ (ethanol solvate): N, 22.61. Found: N, 22.86.

Crystal data for 5a: $C_{26}H_{16}N_8S.0.5C_2H_6O$, FW 495.56, monoclinic, space group $C2/c$, a = 14.557(11) Å, b = 11.785(9) Å, c = 28.21(2) Å, V = 4740(6) Å^3, F(000) = 2056, Z = 8, T = −105 °C, μ(Mo Kα) = 0.173 mm^{-1}, D_{calcd} = 1.389 g·cm^{-3}, $2\theta_{max}$ 53° (CCD area detector, Mo Kα radiation, 29 914 reflections collected, R(int) = 0.025, 98.4% completeness), GOF = 1.04, wR(F^2) = 0.1289 (all 4807 data), R = 0.0471 (3867 data with $I > 2\sigma I$).

1,12-Dichloro-6,7-di(benzotriazol-1-yl)dibenzo[*b,h*]-[1,4,7]thiadiazonine (5c): red needles (from dichloromethane−ethanol); yield 15%; mp 155−156 °C; ^{1}H NMR δ 7.38 (dd, J = 8.0, 1.6 Hz, 2H), 7.60−7.72 (m, 6H), 7.79 (dd, J = 7.6, 1.7 Hz, 2H), 8.16 (d, J = 8.1 Hz, 2H), 8.23 (dd, J = 7.5, 1.8 Hz, 2H); ^{13}C NMR δ 120.1, 122.2, 123.7, 124.1, 124.6, 127.2, 128.1, 129.9, 134.1, 138.2, 139.3, 154.4, 158.2. Anal. Calcd for $C_{26}H_{14}Cl_2N_8S$: C, 57.68; H, 2.61. Found: C, 57.94; H, 2.95.

2,11-Dichloro-6,7-di(benzotriazol-1-yl)dibenzo[*b,h*]-[1,4,7]thiadiazonine (5d): red needles (from dichloromethane−ethanol); yield 65%; mp 159−160 °C; ^{1}H NMR δ 7.51 (t, J = 7.6 Hz, 2H), 7.65 (t, J = 7.6 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 8.2 Hz, 2H), 8.26 (s, 4H), 8.40 (s, 2H); ^{13}C NMR δ 110.5, 112.9, 120.9, 123.3, 125.2, 125.7, 129.2, 132.2, 138.2, 147.0, 154.0, 154.6. Anal. Calcd for $C_{26}H_{14}Cl_2N_8S$: C, 57.68; H, 2.61. Found: C, 57.38; H, 2.73.

2-Ethoxy-6,7-di(benzotriazol-1-yl)dibenzo[*b,h*][1,4,7]-thiadiazonine (6): yellow plates (from dichloromethane−ethanol); yield 49%; mp 213−214 °C; ^{1}H NMR (DMSO-d_6) δ 1.10 (t, J = 6.9 Hz, 3H), 3.75−3.80 (m, 2H), 6.50 (dd, J = 8.8, 2.7 Hz, 1H), 6.71 (d, J = 8.8 Hz, 1H), 6.78 (dd, J = 7.5, 1.6 Hz, 1H), 6.85−6.94 (m, 3H), 7.40 (dd, J = 7.6, 1.4 Hz, 1H), 7.60−7.68 (m, 2H), 7.74−7.84 (m, 2H), 8.16−8.28 (m, 4H); ^{13}C NMR δ 14.2, 63.4, 113.7, 113.8, 114.1, 120.3, 120.4, 121.4, 122.1, 122.7, 123.7, 126.2, 127.1, 127.2, 127.4, 129.3, 129.4, 130.1, 131.1, 131.2, 136.7, 144.7, 145.4, 145.5, 147.0, 147.7, 155.8. Anal. Calcd for $C_{28}H_{20}N_8OS$: C, 65.10; H, 3.90; N, 21.69. Found: C, 64.56; H, 3.98; N, 21.35.

Crystal data for 6: $C_{28}H_{20}N_8OS$, MW 516.58, monoclinic, space group $P2_1/c$, a = 21.005(7) Å, b = 18.076(6) Å, c = 13.811-(5) Å, β = 106.960(5)°, V = 5016(3) Å^3, F(000) = 2144, Z = 8, T = −105 °C, μ(Mo Kα) = 0.168 mm^{-1}, D_{calcd} = 1.368 g·cm^{-3}, $2\theta_{max}$ 45° (CCD area detector, Mo Kα radiation, 47 338 reflections collected, R(int) = 0.1017, 99.9% completeness), GOF = 1.09, wR(F^2) = 0.1166 (all 6564 data), R = 0.0537 (4680 data with $I > 2\sigma I$).

2,11-Diethoxy-6,7-di(5,6-dimethylbenzotriazol-1-yl)-dibenzo[*b,h*][1,4,7]thiadiazonine 8. A solution of *N*-(4-ethoxyphenyl)acetamide (0.36 g, 2 mmol) and DMBt-SO-DMBt/TMSCl reagent (7 mmol) in dry toluene (25 mL) was heated at 100 °C for 12 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography using hexane/ethyl acetate (9:1) as an eluent to afford dibenzo[*b,h*][1,4,7]thiadiazonine **8** in 59% yield. The analytically pure product was obtained by recrystallization from dichloromethane−ethanol: purple needles; mp 193−194 °C; ^{1}H NMR δ 1.48 (t, J = 7.0 Hz, 6H), 2.43 (s, 12H), 4.17 (q, J = 7.0 Hz, 4H), 7.19 (dd, J = 8.4, 2.6 Hz, 2H), 7.49 (s, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 2.3 Hz, 2H), 7.95 (s, 2H); ^{13}C NMR δ 15.2, 19.8, 20.3, 64.5, 108.0, 119.6, 119.9, 120.5, 127.3, 134.0, 136.2, 137.0, 139.9, 151.1, 151.6, 152.5, 156.5; HRMS (FAB) calcd for $C_{34}H_{33}N_8O_2S$ (M + 1) 617.2447, found 617.2444.

Bis(phenylimidoyl-1-benzotriazole) (9). A mixture of oxalic anilide (0.24 g, 1 mmol) and BtSOBt/TMSCl reagent (3 mmol) in benzene (10 mL) was heated under reflux for 4 h. Then the solvent was removed under reduced pressure, and the residue was subjected to column chromatography using hexane/ethyl acetate (5:1) as an eluent to afford the product **9** in 86% yield as orange needles. Analytically pure product was obtained as yellow crystals by recrystallization from dichloromethane−ethanol: mp 85−86 °C; ^{1}H NMR δ 7.05 (dd, J = 8.5, 1.2 Hz, 4H), 7.17−7.22 (m, 2H), 7.33−7.41 (m, 6H), 7.50−7.55 (m, 2H), 7.91 (d, J = 8.3 Hz, 2H), 8.14 (d, J = 8.3 Hz, 2H); ^{13}C NMR δ 114.7, 119.9, 120.7, 125.9, 126.1, 129.3, 129.9, 131.3, 142.0, 146.0, 146.4; HRMS (FAB) calcd for $C_{13}H_9N_4$ ($^1/_2$ M) 221.0827, found 221.0835.

Procedure for the Preparation of Imidoyl Benzotriazole 10. A solution of 1,2-di(benzotriazol-1-yl)-2-[(4-methylphenyl)imino]-1-ethanethione (**3b**) (0.40 g, 1 mmol) and *o*-phenylenediamine (0.11 g, 1 mmol) in dry benzene (10 mL) was heated under reflux for 2 h. The solvent was removed under reduced pressure, and the residue was subjected to purification by column chromatography using hexane/ethyl acetate (9:1) as an eluent to afford product **10** in 11% yield. When THF was used as a solvent, the reaction gave compounds **4a** and **4b** in 30−40% yields; only traces of **10** were observed by NMR spectra.

***N*-[Benzimidazol-2-yl(1,2,3-benzotriazol-1-yl)methylidene]-4-methylaniline (10):** orange needles; yield 11%; mp 154−155 °C; ^{1}H NMR (CD_2Cl_2) δ 2.39 (s, 3H), 7.23 (m, 2H),

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7.51−7.78 (m, 5H), 7.87 (m, 3H), 7.99 (d, J = 8.1 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 8.86 (d, J = 8.4 Hz, 1H), 10.52 (s, 1H); ^{13}C NMR δ 21.2, 30.2, 116.5, 120.7, 121.6, 126.5, 126.6, 126.7, 128.4, 129.9, 130.4, 130.8, 134.0, 135.1, 136.1, 137.1, 140.4, 143.0, 146.0. HRMS (FAB) Calcd for $C_{21}H_{17}N_6$ (M + 1) 353.1515; found 353.1514.

Preparation of 6,7-Di(4-chlorophenylamino)dibenzo-[*b*,*h*][1,4,7]thiadiazonine 11. A solution of a mixture of 6,7-di(benzotriazol-1-yl)dibenzo[*b*,*h*][1,4,7]thiadiazonine (**5a**) (0.24 g, 0.5 mmol), DBU (a catalytic amount), and 4-chloroaniline (0.14 g, 1.10 mmol) in dry benzene (10 mL) was stirred at 20 °C for 6 h. Then the solvent was removed under reduced pressure, and the residue was subjected to column chromatography using hexane/ethyl acetate (5:1) as an eluent to afford the thiadiazonine **11** as red needles. The analytically pure product was obtained as yellow crystals by recrystallization from methylene chloride−ethanol: yield 97%; mp 96−97 °C; ^{1}H NMR δ 7.27 (d, J = 8.7 Hz, 4H), 7.53 (t, J = 7.7 Hz, 2H), 7.65−7.70 (m, 6H), 8.15 (d, J = 8.2 Hz, 2H)), 8.48 (d, J = 8.2 Hz, 2H), 9.85 (s, 2H); ^{13}C NMR δ 114.0, 119.3, 120.4, 126.4, 127.7, 129.2, 130.3, 132.0, 138.3, 145.2, 147.0. Anal. Calcd for $C_{26}H_{18}Cl_2N_8S$: C, 63.81; H, 3.71; N, 11.45. Found: C, 63.35; H, 4.37; N, 11.33.

Preparation of 6-(4,5,6-Trimethoxanilino)-7-(benzotriazol-1-yl)dibenzo[*b*,*h*][1,4,7]thiadiazonine (12). A solution of *N*-(3,4,5-trimethoxyphenyl)acetamide **1f** (0.45 g, 2 mmol) and DMBt-SO-DMBt/TMSCl reagent (7 mmol) in dry toluene (25 mL) was heated under reflux for 12 h. The solvent was removed under reduced pressure, and the residue was subjected to purification by column chromatography using hexane/ethyl acetate (9:1) as an eluent to afford dibenzo[*b*,*h*]-[1,4,7]thiadiazonine **12** in 27% yield. The analytically pure product was obtained by recrystallization from methylene chloride-ethanol: yellow needles; yield 39%; mp 77−78 °C; ^{1}H NMR δ 3.86 (s, 3H), 3.88 (s, 3H), 3.93 (s, 3H), 6.89 (s, 1H), 7.06 (t, J = 7.3 Hz, 1H), 7.30−7.39 (m, 5H), 7.44 (dt, J = 7.8, 1.4 Hz, 1H), 7.61 (dt, J = 7.8, 1.2 Hz, 1H), 7.76 (d, J = 7.7 Hz, 2H), 7.83−7.88 (m, 2H), 8.09 (dd, J = 8.1, 1.2 Hz, 1H), 8.87 (s, 1H); ^{13}C NMR δ 56.4, 61.2, 61.4, 105.2, 107.4, 107.5, 118.6, 120.2, 120.8, 123.2, 126.1, 126.7, 127.0, 127.2, 129.0, 130.8, 134.4, 139.4, 142.2, 143.8, 145.1, 153.0, 154.2; HRMS (FAB) calcd for $C_{29}H_{25}N_6O_3S$ (M + 1) 537.1660, found 537.1769.

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Supporting Information Available: Crystal data collection and refinement parameters, full tables of atom coordinates, bond lengths and angles, and thermal displacement parameters (Tables S1−S15) for X-ray crystal structures of **3b**, **5a**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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