

## Notes

## Synthesis of Siloles Condensed with Benzothiophene and Indole Rings

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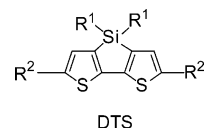
**Summary:** Compounds having a silole ring condensed with benzothiophene and *N*-methylindole units (BBTS and BMIS) were prepared. The electronic states of BBTS and BMIS were examined with respect to their UV and emission spectra and CV measurements, in comparison with those of bibenzothiophene and bi-*N*-methylindole, indicating that the existence of the silole ring in BBTS and BMIS affects the electronic states to decrease the HOMO–LUMO energy gaps. The results of MO calculations on model compounds agree well with the experimental observations.

## Introduction

Current interest has been focused on the silole (silacyclopentadiene) ring system. Orbital interactions between the silicon  $\sigma^*$  orbital and  $\pi^*$  orbital of the butadiene unit lowers the LUMO energy level, making it possible to utilize silole-containing compounds as novel functional materials.<sup>1</sup> Since Tamao et al. reported that 2,5-dipyridylsilole is applicable to electron transport in electroluminescent (EL) devices,<sup>2</sup> many papers concerning the functionalities of silole-containing compounds have been published.<sup>3</sup> In addition, it has been demonstrated that silole may be used also as a component of polymers with small band gap energies.<sup>4</sup>

To develop a new conjugated skeleton based on silole, we synthesized dithienosilole (DTS) that has a silole ring condensed with two thiophene units (Chart 1).<sup>5</sup> On the basis of both experimental and theoretical studies, we concluded that a  $\sigma^*-\pi^*$  type interaction takes place efficiently in this system to lower the LUMO energy levels, which enhances the electron affinity of DTS.

Chart 1



R<sup>1</sup> = Ph, Tol  
R<sup>2</sup> = SiMe<sub>3</sub>, aryl, H

Indeed, vapor-deposited films of DTSs are useful as effective electron-transporting materials in multilayer EL device systems. However, the DTS films are thermally unstable, and applying a high voltage to the devices having a DTS layer resulted in a rapid decrease in the current and luminance, probably due to crystallization or melting of the DTS film. To improve the thermal stability and electron affinity, we recently synthesized DTSs bearing conjugated substituents on the thiophene ring and found that a vapor-deposited film of bis(trimethylsilylpyridyl)-substituted DTS (R<sup>1</sup> = Ph, R<sup>2</sup> = 6-(trimethylsilyl)pyrid-2-yl in Chart 1) exhibits better electron-transporting properties and thermal stability than simple DTSs.<sup>6</sup>

In the hope of obtaining DTS-based materials with even better electron-transporting properties and thermal stability, we synthesized bis(benzothieno)silole (BBTS), which has a more condensed conjugated system. Bis(*N*-methylindolo)silole (BMIS) was also synthesized as the first example of a silole condensed with N-based heterocyclic units, to know how the nature of the heteroatom affects the electronic state of the silole.

## Results and Discussion

Siloles BBTS and BMIS were prepared as outlined in Scheme 1. Thus, the reaction of dilithiated bibenzothiophene (BBT) with difluorodiphenylsilane gave

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(1) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693.

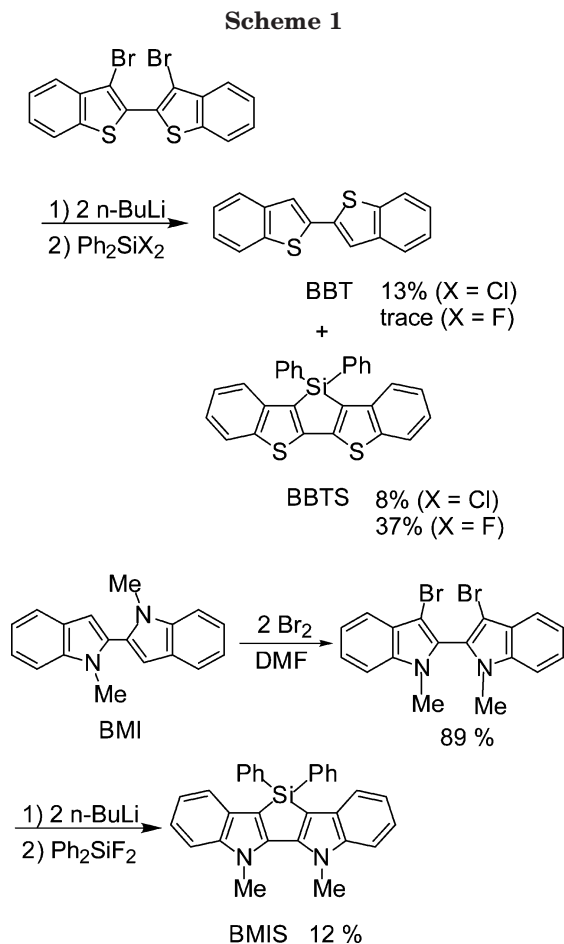
(2) Tamao, K.; Uchida, M.; Izumikawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *116*, 11974.

(3) For recent work, see: (a) Uchida, M.; Izumikawa, T.; Nakano, T.; Yamaguchi, S.; Tamao, K. *Chem. Mater.* **2001**, *13*, 2680. (b) Luo, J.; Xie, Z.; Lam, W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740. (c) Tamao, K.; Yamaguchi, S. *J. Organomet. Chem.* **2000**, *611*, 5. (d) Adachi, A.; Yasuda, H.; Sanji, T.; Sakurai, H.; Okita, K. *J. Lumin.* **2000**, *87–9*, 1174. (e) Chen, J.; Law, C. C. W.; Lam, J. W. Y.; Dong, Y.; Lo, S. M. F.; Williams, I. D.; Zhu, D.; Tang, B. Z. *Chem. Mater.* **2003**, *15*, 1535.

(4) For recent works, see: (a) Liu, M. S.; Luo, J.; Jen, A. K.-Y. *Chem. Mater.* **2003**, *15*, 3496. (b) Sohn, H.; Sailor, M. J.; Magde, D.; Trogler, W. C. *J. Am. Chem. Soc.* **2003**, *125*, 3821. (c) Zhang, G.; Ma, J.; Jiang, Y. *Macromolecules* **2003**, *36*, 2130.

(5) (a) Ohshita, J.; Nodono, M.; Watanabe, T.; Ueno, Y.; Kunai, A.; Harima, Y.; Yamashita, K.; Ishikawa, M. *J. Organomet. Chem.* **1998**, *553*, 487. (b) Ohshita, J.; Nodono, M.; Kai, H.; Watanabe, T.; Kunai, A.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Okita, K.; Harima, Y.; Yamashita, K.; Ishikawa, M. *Organometallics* **1999**, *18*, 1453. (c) Ohshita, J.; Kai, H.; Sumida, T.; Kunai, A.; Adachi, A.; Sakamaki, K.; Okita, K. *J. Organomet. Chem.* **2002**, *642*, 137. (d) Ohshita, J.; Lee, K.-H.; Hamamoto, D.; Kunugi, Y.; Ikada, J.; Kwak, Y.-W.; Kunai, A. *Chem. Lett.* **2004**, *33*, 892.

(6) Ohshita, J.; Kai, H.; Takata, A.; Iida, T.; Kunai, A.; Ohta, N.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Sakamaki, K.; Okita, K. *Organometallics* **2001**, *20*, 4800.



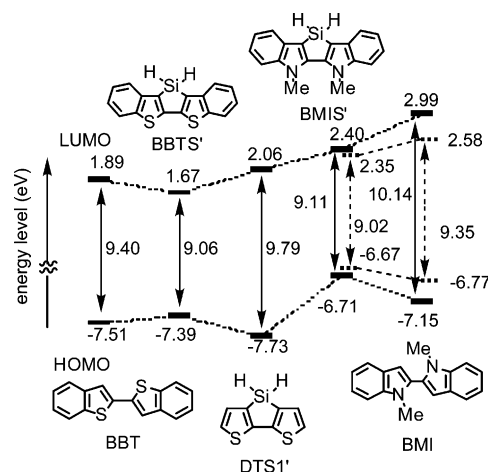
**Table 1. Properties of Silole Derivatives and Related Compounds**

compd	UV abs $\lambda_{\text{max}}/\text{nm}^a$	emissn $\lambda_{\text{max}}/\text{nm}^a$	CV <sup>b</sup> $E_{\text{p,a}}/\text{V}$	mp/ <sup>c</sup> °C
BBTS	382	454	0.99	219–220
BBT	320, 336, 352	412	1.10	194–196
BMIS	392	468	0.65	283–285
BMI	300	374	0.70	172–174
DTS1	345	420	1.05	140–143

<sup>a</sup> In THF, with [substrate] =  $2.0 \times 10^{-5}$  M. <sup>b</sup> In benzonitrile containing LiClO<sub>4</sub> as a supporting electrolyte using Pt wires as working and counter electrodes at a scan rate of 100 mV/s. <sup>c</sup> Anodic peak potential vs Ag/Ag<sup>+</sup>.

BBTS, together with BBT as the major byproduct. Using dichlorodiphenylsilane as the silicon source resulted in a lower yield of BBTS. Similarly, bis(*N*-methylindolo)silole (BMIS) was obtained from treatment of dilithiated bi-*N*-methylindole (BMI) with difluorodiphenylsilane. Since the TLC analysis of the reaction mixture from dilithiobiindole and difluorodiphenylsilane showed a clean spot of BMIS without any other major spots, the relatively low yield of BMIS may be due to its decomposition during the workup process, including alumina column chromatography and recrystallization from hexane/THF. In fact, warming a mixture including BMIS in hexane/THF led to the formation of oligomeric oily substances to an extent. BBTS and BBIS are yellow solids and melt at higher temperature than simple DTS derivatives, as expected.

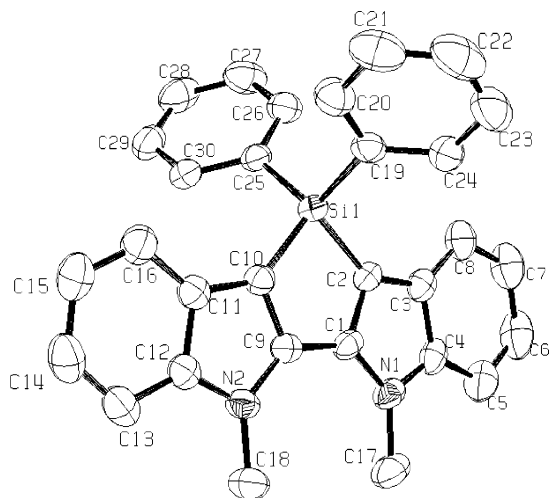
Table 1 summarizes optical and cyclic voltammometric (CV) properties of the present silole derivatives BBTS and BMIS, in comparison with those of BBT and



**Figure 1.** Relative HOMO and LUMO energy levels for silole derivatives and related energy levels derived from MO calculations at the level of RHF/6-31G\*. Solid lines show the levels of the compounds with an optimized geometry, while broken lines indicate those with a planar conformation.

BMI, which have no silole ring, and the simple dithienosilole DTS1 ( $R^1 = \text{Ph}$ ,  $R^2 = \text{H}$  in Chart 1). As shown in Table 1, BBTS and BMIS exhibited UV absorption and emission maxima at longer wavelengths than for DTS1. They were red-shifted also from the absorption and emission maxima of BBT and BMI by about 40 and 90 nm, respectively. This would indicate a higher degree of electronic effects of the silicon bridge on the biindole system as compared to those on the bibenzothiothene unit, leading to absorption and emission of BMIS red-shifted by about 10 nm compared to those of BBTS, despite the fact that the parent BMI exhibited maxima at much shorter wavelength than BBT. The emission quantum yields were determined to be 0.74 and 0.67 for BBTS and BMIS solutions in THF, respectively, relative to a standard solution of 9,10-diphenylanthracene ( $1 \times 10^{-5}$  M in THF,  $\Phi = 0.90$ ). These values are comparable to that of DTS with  $R^1 = \text{Ph}$  and  $R^2 = \text{SiMe}_3$  (see Chart 1) under the same conditions ( $\Phi = 0.69$ ). The CVs of BBTS and BMIS were measured in benzonitrile, which revealed an irreversible anodic peak and no cathodic counterpart. Similar irreversible CV profiles are generally observed for DTS derivatives that undergo anodic oxidation, producing polythiophene-like polymeric materials.<sup>5</sup> BBTS and BMIS showed no reductive peaks down to  $-2.0$  V vs Ag/Ag<sup>+</sup>. This is again similar to the case for simple DTSs, reported previously. BBTS and BMIS were oxidized at slightly lower potentials than those of BBT and BMI, indicating that the existence of the silicon bridge elevates the HOMO energy level in both cases. The oxidation peaks of silole derivatives moved to higher voltages in the order BMIS < BBTS < DTS, presumably reflecting the characteristics of the corresponding parent  $\pi$ -conjugated systems: i.e., BBT, BMI, and bithiophene.

To know more about the electronic states of the present silole derivatives, we carried out ab initio molecular orbital (MO) calculations on model compounds at the level of RHF/6-31G\*. Relative HOMO and LUMO energy levels derived from the MO calculations are given in Figure 1. For thiophene derivatives, HOMOs are elevated in the order DTS1' < BBT < BBTS',



**Figure 2.** ORTEP drawing of BMIS showing thermal ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity.

while LUMOs are lowered in the same order, giving rise to the smallest energy gap for BBTS' among them, in accordance with the experimental observations. The difference between LUMO energy levels of BBTS' and BBT was calculated to be larger (0.22 eV) than that of HOMO levels (0.11 eV), this being more responsible for the smaller HOMO–LUMO gap of BBTS' as compared to that of BBT. For indole derivatives, the silicon bridge exerts a considerable effect on both the HOMO and LUMO energy levels, narrowing the energy gap by more than 1 eV. In this case, fixation of the biindole unit by the silicon bridge, which forces the unit to retain higher planarity, plays an important role. In fact, the N–C–C'–N' dihedral angles of the optimized geometries of BMI and BMIS' are 127.0 and 17.6°, respectively. Moreover, when the calculations were performed for planar molecules of BMI and BMIS', the differences in HOMO and LUMO energy levels between BMI and BMIS' were reduced, as shown in Figure 1. However, there still can be seen an evident influence of the silicon bridge on the electronic states of the planar biindole system. Similar to bibenzothiophene derivatives, the silicon bridge in the biindole system affects primarily the LUMO energy level to decrease the HOMO–LUMO energy gap. The planar structures were predicted to be more thermally unstable than the optimized twisted forms by 7.64 and 1.57 kcal/mol for BMI and BMIS', respectively. The solid-state structure of BMIS was determined by an X-ray crystallographic analysis, as shown in Figure 2.<sup>7</sup> It was found that the tricyclic ring system of BMIS was highly planar but slightly twisted, as indicated by the dihedral angle of N1–C1–C9–N2 = –5.5°. This is similar to the optimized geometry of BMIS' obtained by the MO calculations, although the actual twisting in the crystal structure is slightly smaller.

(7) Crystal data for BMIS: C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>Si, MW = 440.62, space group P2<sub>1</sub>/n (No. 14), *a* = 9.6901(3) Å, *b* = 15.6311(5) Å, *c* = 16.1127(5) Å, β = 102.4017(9)°, *V* = 2382.6(1) Å<sup>3</sup>, *Z* = 4, calcd density 1.228 g/cm<sup>3</sup>, *F*(000) = 928.00, μ(Mo Kα) = 1.19 cm<sup>-1</sup>. A total of 21 956 intensity data were collected at –120 °C on a Rigaku RAXIS-RAPID imaging plate diffractometer using a 0.30 × 0.20 × 0.15 mm<sup>3</sup> crystal. There were 10 984 unique reflections with *I* > 3σ(*I*) (reflections/parameters = 34.11) in refinement; *R* = 7.0, *R<sub>w</sub>* = 7.8%.

The low-lying LUMO energy level of BBTS estimated by the optical and electrochemical analyses of this compound, as well as by the MO calculations on the model system, encouraged us to evaluate its vapor-deposited film as the electron transport in an EL device system. However, a device with the structure of ITO (indium tin oxide)/TPD (40 nm)/Alq<sub>3</sub> (50 nm)/BBTS (20 nm)/Mg–Ag, where TPD (*N,N'*-diphenyl-*N,N'*-dimethylbiphenyl-4,4'-diamine), Alq<sub>3</sub> (tris(8-quinolinolato)-aluminum(III)), and BBTS were the hole transport, emitter, and electron transport, respectively, emitted no EL. We also attempted to use BMIS, which would have high-lying HOMO and LUMO, as the hole transport. Although the device composed of ITO/BMIS (40 nm)/Alq<sub>3</sub> (60 nm)/Mg–Ag emitted a green light arising from Alq<sub>3</sub> emission, the maximum luminance was only 89 cd/cm<sup>2</sup> at the applied voltage of 20 V, indicating the poor hole-transporting properties of the vapor-deposited film of BMIS.

In conclusion, we prepared the first silole derivatives condensed with benzothiophene and indole units. Although the performance of EL devices based on these compounds was poor, in contrast to our expectation, it is true that the existence of the silole ring system affects the electronic states, leading to narrow HOMO–LUMO energy gaps. The highly conjugated systems may be useful as the core fragments of functionality materials.

## Experimental Section

**General Considerations.** All reactions were carried out under an atmosphere of dry nitrogen. The usual workup mentioned below involves separation of the organic layer, extraction of the aqueous layer, drying of the combined organic layer and the extracts, and evaporation of the solvents, in that order.

**Materials.** Ether and THF were dried over sodium–potassium alloy and distilled just before use. *N,N*-Dimethylformamide was dried over calcium hydride and distilled just before use. 3,3'-Dibromo-2,2'-bibenzo[*b*]thiophene,<sup>8</sup> *N*-methylindole,<sup>9</sup> 2,2'-bi-*N*-methylindole,<sup>10</sup> and 3,3'-dibromo-2,2'-bi-*N*-methylindole<sup>10</sup> were prepared as reported in the literature.

**Preparation of BBTS.** To a solution of 0.50 g (1.18 mmol) of 3,3'-dibromo-2,2'-bibenzo[*b*]thiophene in 30 mL of ether and 15 mL of THF was added 1.50 mL (2.36 mmol) of 1.56 M *n*-butyllithium/hexane solution at –80 °C. After the mixture was stirred for 30 min at the same temperature, 0.25 g (1.18 mmol) of difluorodiphenylsilane was added. After it was refluxed overnight, the resulting mixture was hydrolyzed with water. After the usual workup, the residue was chromatographed on a silica gel column with hexane/chloroform (15/1) as an eluent to afford 0.19 g (37%) of BBTS as yellow solids: mp 219–220 °C; MS *m/z* 446 (M<sup>+</sup>); <sup>1</sup>H NMR (δ in CDCl<sub>3</sub>) 7.29–7.46 (m, 10H, *m*- and *p*-Ph and benzothiophene), 7.77 (d, 4H, *J* = 6.8 Hz, *o*-Ph), 7.84 (d, 2H, *J* = 7.7 Hz, benzothiophene), 7.91 (d, 2H, *J* = 8.0 Hz, benzothiophene); <sup>13</sup>C NMR (δ in CDCl<sub>3</sub>) 123.29, 124.07, 124.17, 125.40, 128.44, 130.59, 131.09, 135.56, 136.65, 141.48, 143.69, 150.61; <sup>29</sup>Si NMR (δ in CDCl<sub>3</sub>) –18.76. Anal. Calcd for C<sub>28</sub>H<sub>18</sub>SiS<sub>2</sub>: C, 75.29; H, 4.06. Found: C, 75.05; H, 4.16.

**Preparation of BMIS.** To a solution of 1.20 g (2.87 mmol) of 3,3'-dibromo-2,2'-bi-*N*-methylindole in 80 mL of ether was added 3.63 mL (5.74 mmol) of 1.56 M *n*-butyllithium/hexane solution at –80 °C. After the mixture was stirred for 30 min

(8) Dahlmann, U.; Neidlein, R. *Helv. Chim. Acta* **1997**, *80*, 111.

(9) Ottoni, O.; Cruz, R.; Alves, R. *Tetrahedron* **1998**, *54*, 13915.

(10) Pindur, U.; Kim, Y.-S. *J. Heterocycl. Chem.* **1994**, *31*, 377.

at the same temperature, 0.79 g (2.87 mmol) of difluorodiphenylsilane and 20 mL of THF were added. After it was stirred overnight at room temperature, the resulting mixture was hydrolyzed with water. After the usual workup, the residue was chromatographed on a alumina column with hexane/ethyl acetate (30/1) as an eluent to give crude solids, which were recrystallized from THF/hexane to afford 0.15 g (12% yield) of BMIS as yellow crystals: mp 283–285 °C; MS  $m/z$  440 ( $M^+$ );  $^1\text{H}$  NMR ( $\delta$  in THF- $d_8$ ) 4.22 (s, 6H, NMe), 7.04–7.15 (m, 4H, indole), 7.25–7.32 (m, 6H, *m*- and *p*-Ph), 7.43 (d, 2H,  $J = 8.2$  Hz, indole), 7.60 (d, 2H,  $J = 6.9$  Hz, indole), 7.78 (dd, 4H,  $J = 7.4$  and 1.8 Hz, *o*-Ph);  $^{13}\text{C}$  NMR ( $\delta$  in THF- $d_8$ ) 34.97 (NMe<sub>3</sub>), 111.18, 114.09, 121.61, 121.70, 122.10, 128.63, 130.27, 132.19, 135.65, 136.19, 143.68, 148.71;  $^{29}\text{Si}$  NMR ( $\delta$  in THF- $d_8$ ) –23.24. Anal. Calcd for C<sub>30</sub>H<sub>24</sub>SiN<sub>2</sub>: C, 81.78; H, 5.49; N, 6.36. Found: C, 81.57; H, 5.47; N, 6.32.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

**CV Measurements.** CV measurements were carried out using a three-electrode system in benzonitrile solutions containing 100 mM of lithium perchlorate as the supporting electrolyte and 4 mM of the substrate. Pt wires were used as the working and counter electrodes, and Ag/Ag<sup>+</sup> was the reference electrode. The current–voltage curves were recorded at room temperature.

**MO Calculations.** MO calculations were carried out using the restricted Hartree–Fock (RHF) method at the 6-31G\* level within the Gaussian 98 suite of programs.<sup>11</sup> In the calculations of planar molecules of BMI and BMIS', all dihedral angles concerning the biindole and bis(indolo)silole rings were fixed to be 0 or 180°, and bond distances and angles were optimized. The positions of hydrogens on the silicon atom and those of methyl carbons and hydrogens in BMIS' were also optimized, giving rise to a Me–N–N–Me dihedral angle of 36.7°.

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**Supporting Information Available:** Crystallographic data as a CIF file for BMIS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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