

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231441524>

# Antiaromatic Bis(1,2,3-dithiazoles) with Zwitterionic Ground States

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JULY 2000

Impact Factor: 12.11 · DOI: 10.1021/ja0016497

---

CITATIONS

24

---

READS

18

5 AUTHORS, INCLUDING:



Kathryn E Preuss

University of Guelph

53 PUBLICATIONS 854 CITATIONS

SEE PROFILE

# Antiaromatic Bis(1,2,3-dithiazoles) with Zwitterionic Ground States

Leanne Beer, Richard T. Oakley,\* James R. Mingie,  
Kathryn E. Preuss, and Nicholas J. Taylor

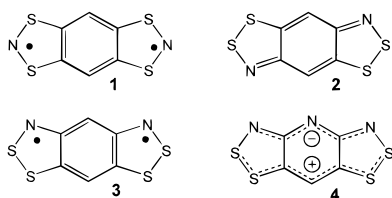
Department of Chemistry, University of Waterloo  
Waterloo, Ontario N2L 3G1 Canada

A. Wallace Cordes

Department of Chemistry and Biochemistry  
University of Arkansas, Fayetteville, Arkansas 72701

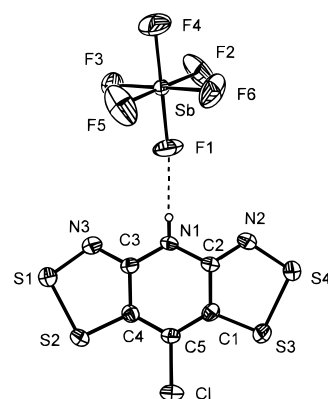
Received May 16, 2000

Interest in the use of 1,3,2- and 1,2,3-dithiazolyl radicals in the design of conductive<sup>1</sup> and magnetic<sup>2</sup> materials is rapidly growing.<sup>3</sup> For bifunctional variants, different spin and orbital arrangements are possible.<sup>4</sup> Thus, while the benzo-bis(1,3,2-dithiazole) **1** is biradical,<sup>5,6</sup> the isomeric bis-1,2,3-dithiazole **2** exhibits a quinoidal<sup>7</sup> rather than biradical ground state. In light of these results and the recent finding that hexa-azaanthracenes are zwitterionic,<sup>8</sup> we have pursued the isolation of a zwitterionic 16 $\pi$ -electron bis-1,2,3-dithiazole. Theoretical calculations (B3LYP/6-31G\*\*) on potential targets indicated that the triplet state of the benzene bridged system **3** lies 5.1 kcal/mol below the zwitterionic singlet. However, the order is reversed (by 2.1 kcal/mol) for the pyridine-bridged compound **4**.



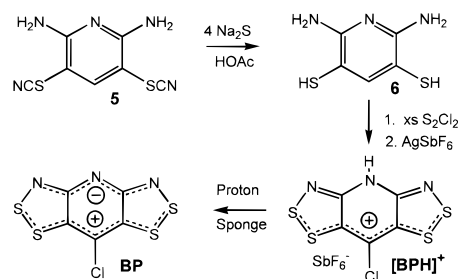
Our synthetic sequence to a derivative of **4** is outlined in Scheme 1. Oxidative thiocyanation<sup>10</sup> of 2,6-pyridinediamine

- (1) Barclay, T. M.; Cordes, A. W.; Haddon, R. C.; Itkis, M. E.; Oakley, R. T.; Reed, R. W.; Zhang, H. *J. Am. Chem. Soc.* **1999**, *121*, 969.
- (2) (a) Barclay, T. M.; Cordes, A. W.; George, N. A.; Haddon, R. C.; Itkis, M. E.; Mashuta, M. S.; Oakley, R. T.; Patenaude, G. W.; Reed, R. W.; Richardson, J. F.; Zhang, H. *J. Am. Chem. Soc.* **1998**, *120*, 352. (b) Fujita, W.; Awaga, K. *Science* **1999**, *286*, 261.
- (3) (a) Rawson, J. M.; McManus, G. D. *Coord. Chem. Rev.*, **1999**, *189*, 135. (b) Torroba, T. *J. Prakt. Chem.* **1999**, *341*, 99.
- (4) (a) Genin, H.; Hoffmann, R. *Macromolecules* **1998**, *31*, 444. (b) Barclay, T. M.; Cordes, A. W.; Haddon, R. C.; Itkis, M. I.; Oakley, R. T.; Preuss, K. E.; Reed, R. W. *J. Am. Chem. Soc.* **1999**, *121*, 6657.
- (5) Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, R. O., Jr.; Wudl, F. *J. Am. Chem. Soc.* **1987**, *109*, 2594.
- (6) Barclay, T. M.; Cordes, A. W.; de Laat, R. H.; Goddard, J. D.; Haddon, R. C.; Jetter, D. Y.; Mawhinney, R. C.; Oakley, R. T.; Palstra, T. T. M.; Patenaude, G. W.; Reed, R. W.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1997**, *119*, 2633.
- (7) Barclay, T. M.; Cordes, A. W.; Goddard, J. D.; Mawhinney, R. C.; Oakley, R. T.; Preuss, K. E.; Reed, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 12136.
- (8) Hutchison, K.; Srdanov, G.; Hicks, R.; Yu, H.; Wudl, F.; Strassner, T.; Nendel, M.; Houk, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 2989.
- (9) Geometry optimizations within  $C_{2v}$  constraints performed with Gaussian 98: 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.6; Gaussian, Inc.: Pittsburgh, PA, 1998.



**Figure 1.** ORTEP drawing of a [BPH][SbF<sub>6</sub>] cation/anion pair. Mean distances: S–C, 1.697(5); S–S, 2.070(5); S–N, 1.635(5); (S)N–C, 1.302(6); (C)N–C, 1.367(6) Å. Numbers in parentheses are the larger of the range and the ESD.

## Scheme 1



afforded the bis(thiocyanate) **5**, which was converted to the corresponding diaminodithiol **6**.<sup>11</sup> The latter was condensed with excess S<sub>2</sub>Cl<sub>2</sub> at reflux (16 h) in chlorobenzene. The product of this cyclization was not, by analogy with the preparation of **2**,<sup>7</sup> the radical cation of the chlorinated bis-dithiazole [BP]<sup>•+</sup>, but rather the protonated, closed shell (ESR silent) cation [BPH]<sup>+</sup>, isolated as its chloride salt (75% yield from **6**). At first this result surprised us, as normally such harsh oxidizing conditions are more than sufficient to remove all the protons from a dithiazole. The structural identity of the [BPH]<sup>+</sup> cation was established by metathesis of the insoluble, black chloride salt with AgSbF<sub>6</sub> in SO<sub>2</sub>(l). The deep turquoise solutions ( $\lambda_{\text{max}} = 661 \text{ nm}$ ,  $\log \epsilon = 4.5$ ) so formed afforded, upon evaporation of the solvent, golden crystals of the hexafluoroantimonate salt [BPH][SbF<sub>6</sub>] (70% yield, based on crude [BPH][Cl]).

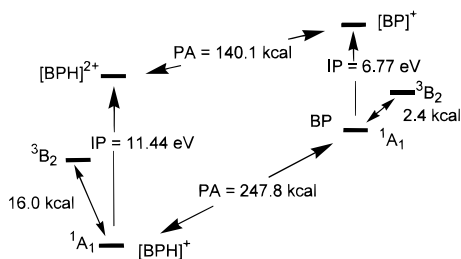
The crystal structure<sup>12</sup> of this salt consists of [BPH]<sup>+</sup> cations (Figure 1) weakly hydrogen bonded to partially disordered SbF<sub>6</sub><sup>−</sup> anions (N–H = 0.927(4), H...F = 1.906(4) Å, N–H–F = 171.4(3)°); there are no close intermolecular S...S contacts. The heterocyclic molecule is planar to within 0.072(2) Å.

The computed ion energetics of BP are summarized in Figure 2. As in the case of the parent compound **4** the zwitterionic form is predicted to be slightly preferred over the triplet state. However, protonation of BP to [BPH]<sup>+</sup> leads to a marked stabilization of the singlet. Perhaps more notable than the singlet/triplet splittings

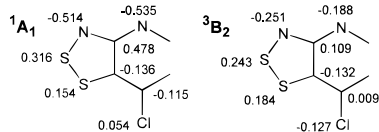
(10) The procedure was that used for the corresponding benzene derivative. See (a) Lochon, P.; Méheux, P.; Néel, J. *Bull. Soc. Chim. Fr.* **1967**, *11*, 4387. (b) Okada M., Marvel, C. S. *J. Polym. Sci., Part A: Polym. Chem.* **1968**, *6*, 1259.

(11) The procedure was that used for the corresponding benzene derivative. See Huestis, L. D.; Walsh, M. L.; Hahn, N. *J. Org. Chem.* **1965**, *30*, 3.

(12) Crystal data for [BPH][SbF<sub>6</sub>]: S<sub>4</sub>C<sub>13</sub>N<sub>5</sub>S<sub>6</sub>H<sub>6</sub>F<sub>6</sub>,  $M = 502.5$ , space group  $P1$ , with  $a = 7.7963(6) \text{ Å}$ ,  $b = 8.4268(7) \text{ Å}$ ,  $c = 11.9330(9) \text{ Å}$ ,  $\alpha = 92.806(5)^\circ$ ,  $\beta = 103.646(4)^\circ$ ,  $\gamma = 112.317(4)^\circ$ ,  $V = 696.36(9) \text{ Å}^3$ ,  $Z = 2$ ,  $D_c = 2.397 \text{ g cm}^{-3}$ ,  $\mu = 2.83 \text{ mm}^{-1}$ ; 191 parameters were refined using 2446 unique reflections to give  $R = 0.042$  and  $R_w = 0.099$ .



**Figure 2.** Computed (B3LYP/6-31G\*\*) singlet/triplet splittings, ionization potentials (IP), and proton affinities (PA).



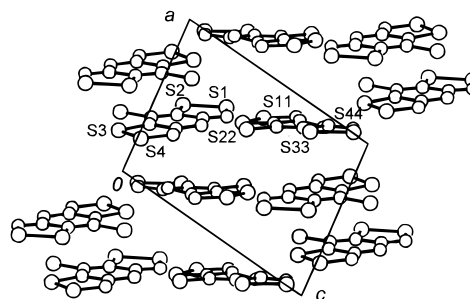
**Figure 3.** Mulliken charge distributions in singlet and triplet BP.

is the proton affinity (PA) of BP which, at 247.8 kcal/mol, makes BP a comparable gas-phase base to proton sponge (246 kcal/mol).<sup>13</sup> Indeed, even the radical cation  $[BP]^+$  retains basic properties.

The strongly basic character of BP is a manifestation of its zwitterionic nature. The calculated charge distribution (Figure 3) in the singlet quantifies the degree of polarization; the positive charge is carried mainly by the sulfur atoms at each end of the molecule while the negative charge is localized over the five-atom NCNCN fragment, particularly the central nitrogen. In the triplet, charge on the central nitrogen is markedly reduced. The dipole moments, 4.4 D ( $^1A_1$ ) and 2.8 D ( $^3B_2$ ), follow suit.

Given the computational evidence we explored the use of proton sponge to liberate the free base from its  $SbF_6^-$  salt. When a solution of  $[BPH][SbF_6]$  in acetonitrile was added slowly to an *unstirred* solution of proton sponge in  $CH_2Cl_2$ , green/black needles of the solvate  $[BP]_2 \cdot CH_2Cl_2$  grew at the interface of the two solutions. These crystals dissolve sparingly in  $CH_2Cl_2$  to give pale yellow solutions that are ESR silent, that is, BP is a diamagnetic zwitterion.

The crystal structure<sup>14</sup> of  $[BP]_2 \cdot CH_2Cl_2$  contains two independent BP molecules (Figure 4) in the asymmetric unit; both are planar to within 0.079(11) Å, and the dihedral angle between the planes is 7.77(8)°. Most bond lengths vary little from those in the  $[BPH]^+$  cation. However, the short S—C bonds in BP are notable and are consistent with a singlet rather than a triplet state.<sup>15</sup> The molecules are packed in a loosely  $\pi$ -stacked arrangement, with cofacial pairs aligned centrosymmetrically to provide an



**Figure 4.** Layers of BP molecules in  $[BP]_2 \cdot CH_2Cl_2$ . Mean distances: S—C, 1.70(3); S—S, 2.070(14); S—N, 1.609(10); (S)N—C, 1.33(2); (C)N—C, 1.36(2) Å. Numbers in parentheses are the larger of the range and the ESD.

antiparallel orientation of the molecular dipoles. There are no intermolecular S—S contacts inside the van der Waals separation (3.6 Å).<sup>16</sup>

Cyclic voltammetry on a solution of BP in  $CH_3CN$  (Pt electrodes, 0.1 M  $Bu_4NPF_6$ , ref S.C.E.) reveals a reversible oxidation wave and an irreversible reduction wave. Similar behavior is observed for **2** and related compounds.<sup>7,17</sup> However,  $E_{1/2}^{ox}$  for BP (0.71 V) is lower than that found for **2** (0.93V), while the cathodic peak potential  $E_{pc}^{red}$  (−0.50 V) is higher than that seen in **2** (−0.95 V). These trends again reflect the zwitterionic nature of BP.

In summary we have prepared and structurally characterized the 16 $\pi$ -electron heterocycle BP. While a variety of antiaromatic ternary CNS heterocycles are known,<sup>18</sup> BP is the first to exhibit a zwitterionic ground state. Exploration of the charge transfer and acid/base chemistry of BP and related compounds is underway.

**Acknowledgment.** We acknowledge the Natural Science and Engineering Council of Canada (NSERCC) and the State of Arkansas for financial support. We also thank the NSERCC for a post-graduate scholarship to K.E.P., and Professor T. B. McMahon for useful discussions.

**Supporting Information Available:** Crystallographic details for the two structures reported (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0016497

(13) Maier, J. P. *Helv. Chim. Acta*, **1974**, *57*, 994.

(14) Crystal data for  $[BP]_2 \cdot CH_2Cl_2$ :  $S_8Cl_4N_6C_{11}H_2$ ,  $M = 616.5$ , space group  $P2_1/c$ ,  $a = 7.889(4)$  Å,  $b = 25.456(14)$  Å,  $c = 10.377(5)$  Å,  $\beta = 101.72(2)^\circ$ ,  $V = 2040(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.01$  g cm<sup>−3</sup>,  $\mu = 1.39$  mm<sup>−1</sup>; 262 parameters were refined using 2430 unique observed reflections ( $I > 0.7\sigma(I)$ ) to give  $R = 0.104$  and  $R_w = 0.111$  ( $R = 0.052$  for  $I > 3\sigma(I)$ ).

(15) There are few computed structural differences between the  $^1A_1$  and  $^3B_2$  states of BP and  $[BPH]^+$  (at the B3LYP/6-31G\*\* level). The largest is in the S—C distance, which is 1.712 Å ( $^1A_1$ ) and 1.755 Å ( $^3B_2$ ).

(16) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 41.

(17) Barclay, T. M.; Cordes, A. W.; Oakley, R. T.; Preuss, K. E.; Reed, R. W. *Chem. Mater.* **1999**, *11*, 164.

(18) (a) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299. (b) Boeré, R. T.; French, C. L.; Oakley, R. T.; Cordes, A. W.; Privett, J. A. J.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 7710. (c) Hoffmeyer, R. B.; Chan, W.-T.; Goddard, J. D.; Oakley, R. T. *Can. J. Chem.* **1988**, *66*, 2279. (d) Cordes, A. W.; Hojo, M.; Koenig, H.; Noble, M. C.; Oakley, R. T.; Pennington, W. T.; *Inorg. Chem.* **1986**, *25*, 1137.