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

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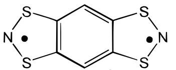
Interest in the use of 1,3,2- and 1,2,3-dithiazolyl radicals in the design of conductive[1] and magnetic[2] materials is rapidly growing.[3] For bifunctional variants, different spin and orbital arrangements are possible.[4] Thus, while the benzo-bis(1,3,2-dithiazole) **1** is biradical,[5,6] the isomeric bis-1,2,3-dithiazole **2** exhibits a quinoidal[7] rather than biradical ground state. In light of these results and the recent finding that hexa-azaanthracenes are zwitterionic,[8] we have pursued the isolation of a zwitterionic 16π-electron bis-1,2,3-dithiazole. Theoretical calculations (B3LYP/6-31G**)[9] 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**.



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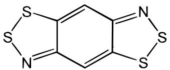

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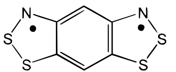

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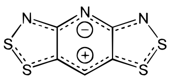

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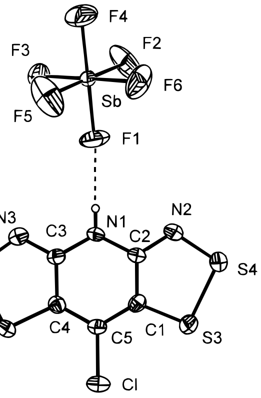
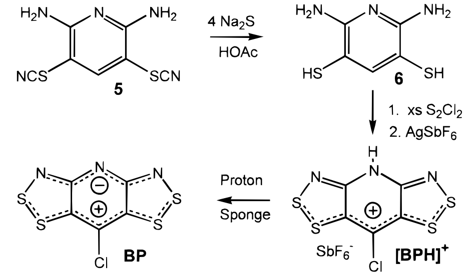


Figure 1. ORTEP drawing of a [BPH][SbF_6] cation/anion pair. Mean distances: S−C, 1.697(5); S−S, 2.070(5); S−N, 1.635(5); (S)N−C, 1.302(6); (C)N−C, 1.367(6) Å. Numbers in parentheses are the larger of the range and the ESD.

Scheme 1



Our synthetic sequence to a derivative of **4** is outlined in Scheme 1. Oxidative thiocyanation[10] of 2,6-pyridinediamine afforded the bis(thiocyanate) **5**, which was converted to the corresponding diaminodithiol **6**.[11] The latter was condensed with excess S_2Cl_2 at reflux (16 h) in chlorobenzene. The product of this cyclization was not, by analogy with the preparation of **2**,[7] the radical cation of the chlorinated bis-dithiazole $[BP]^+$, but rather the protonated, closed shell (ESR silent) cation $[BPH]^+$, 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 $[BPH]^+$ cation was established by metathesis of the insoluble, black chloride salt with $AgSbF_6$ in SO_2(l). The deep turquoise solutions ($\lambda_{max} = 661$ nm, log $\epsilon = 4.5$) so formed afforded, upon evaporation of the solvent, golden crystals of the hexafluoroantimonate salt [BPH][SbF_6] (70% yield, based on crude [BPH][Cl]).

The crystal structure[12] of this salt consists of $[BPH]^+$ cations (Figure 1) weakly hydrogen bonded to partially disordered SbF_6^- 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 $[BPH]^+$ leads to a marked stabilization of the singlet. Perhaps more notable than the singlet/triplet splittings

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(12) Crystal data for [BPH][SbF_6]: $S_4ClN_3C_5SbHF_6$, $M = 502.5$, space group $P\bar{1}$, with $a = 7.7963(6)$ Å, $b = 8.4268(7)$ Å, $c = 11.9330(9)$ Å, $\alpha = 92.806(5)°$, $\beta = 103.646(4)°$, $\gamma = 112.317(4)°$, $V = 696.36(9)$ Å^3, $Z = 2$, $D_c = 2.397$ g cm^{-3}, $\mu = 2.83$ mm^{-1}; 191 parameters were refined using 2446 unique reflections to give $R = 0.042$ and $R_w = 0.099$.

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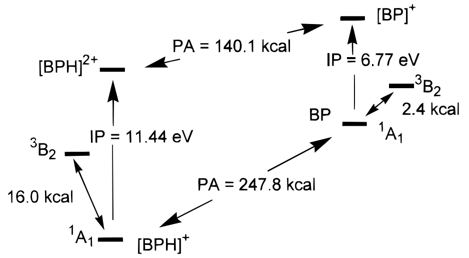

Figure 2. Computed (B3LYP/6-31G**) singlet/triplet splittings, ionization potentials (IP), and proton affinities (PA).

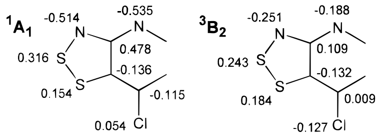

Figure 3. Mulliken charge distributions in singlet and triplet BP.

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).[13] 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[14] 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.[15] The molecules are packed in a loosely π-stacked arrangement, with cofacial pairs aligned centrosymmetrically to provide an antiparallel orientation of the molecular dipoles. There are no intermolecular S- - -S contacts inside the van der Waals separation (3.6 Å).[16]

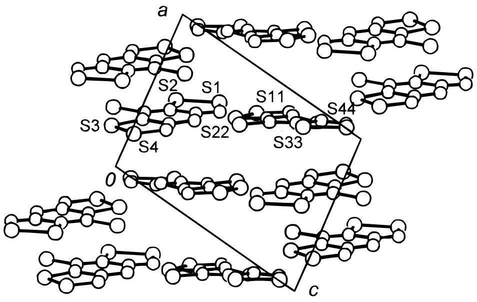

Figure 4. Layers of BP molecules in $[BP]_2\cdot CH_2Cl_2$. Mean distances: S−C, 1.70(3); S−S, 2.070(14); S−N, 1.609(10); (S)N−C, 1.33(2); (C)N−C; 1.36(2) Å. Numbers in parentheses are the larger of the range and the ESD.

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.[7,17] 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 16π-electron heterocycle BP. While a variety of antiaromatic ternary CNS heterocycles are known,[18] 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.

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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.

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[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, $\beta = 101.72(2)°$, $V = 2040(2)$ Å^3, $Z = 4$, $D_c = 2.01$ g cm^{-3}, $\mu = 1.39$ mm^{-1}; 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 ($^3B_2$).

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