Calculations on the Group 15 Intraring Substituted Benzenes (Pyridine to Bismin Series) and Their Datively Bonded Oxides and Sulfides

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Received: July 22, 2004; In Final Form: June 11, 2005

The series of heterocyclic compounds pyridine, phosphorin, arsenin, antimonin, bismin, and the related series of pyridine oxide, etc., and pyridine sulfide, etc., were investigated using density functional theory. In addition to molecular geometries and energies, the nucleus independent chemical shift (NICS) values were calculated for each ring, and the CHELPG atomic charges were calculated. Calculated heats of formation are: pyridine +133, phosphorin +181, arsenin +231, antimonin +329, bismin +468, pyridine oxide +143, phosphorin oxide +1, arsenin oxide +183, antimonin oxide +344, bismin oxide +570, pyridine sulfide +252, phosphorin sulfide +205, arsenin sulfide +328, antimonin sulfide +435, and bismin sulfide + 642 kJ/mol. The question of aromaticity for these heterocycles was discussed. On the basis of hydrogenation energies, NICS values, and lack of bond alternation, the entire series from pyridine to bismin appears to be aromatic and to a roughly equal degree. The situation for the oxides and sulfides of pyridine, phosphorin, and arsenin is much the same, but bismin oxide and bismin sulfide are nonplanar and according to NICS nonaromatic. Antimonin oxide is aromatic by some of the criteria and nonaromatic by others.

Introduction

The peculiar properties of benzene, as compared to other unsaturated hydrocarbons, have led to the concept of aromaticity. The similar behavior of certain heterocycles indicates that these, too, can be “aromatic.” Pyridine in particular is exhibited as an example of aromaticity in heterocyclic compounds.

It is interesting to compare the chemistry of P, As, Sb, and Bi with that of N. One sees both the similarities that led to them being placed in the same column of the periodic table, and the differences that often occur between the first row of main group elements and the other rows. Many of these differences are related to the “unusually” strong π bonding of the first-row elements, so the series C_5H_5N (pyridine), C_5H_5P (phosphorin), C_5H_5As (arsenin), C_5H_5Sb (antimonin), and C_5H_5Bi (bismin)[1] is likely to provide interesting comparisons and contrasts.

Pyridine was described in 1851,[2] but the other members of the C_5H_5E series were not prepared until ∼1970.[3] The reactions of the heavier pnictabenzenes resemble pyridine in that they can undergo electrophilic substitution and in that they can act as a Lewis base using either the lone pair of the E atom or the π system of the ring. Unlike pyridine, the heavier pnictabenzenes readily participate in Diels−Alder reactions. The self-condensation of bismin is rapid enough to make it only a transient species. The computational studies of members of the pnictabenzene series have been too many to list exhaustively, but those of Berger et al.,[4] Bachrach,[5] Mracec et al.,[6] Priyakumar et al.,[7] and Saieswari et al.[8] are relatively recent and discuss at least two members of the series.

The analogues of pyridine *N*-oxide have received much less attention. The dative bond in these molecules might be expected to effect a larger perturbation of the π system of the six-membered ring than would an ordinary substituent: perhaps phenoxide is the closest carbocyclic analogue. It is possible that, in the more “fragile” aromatic systems, such perturbation may be strong enough to destroy aromaticity found in the unsubstituted heterocycle or perhaps even bring about aromaticity which is absent in the parent heterocycle. Additionally, many of the pnictabenzene oxides and sulfides are unknown to science (or at least to *Chemical Abstracts* as of March 4, 2004): these include C_5H_5PS, C_5H_5AsO, C_5H_5AsS, C_5H_5SbO, C_5H_5SbS, C_5H_5BiO, and C_5H_5BiS. Pyridine sulfide, C_5H_5NS, has been the subject of one theoretical study, Fabian,[9] who predicted that this compound would be deeply colored. Borisov[10] performed a PPP calculation, and earlier with Kornienko[11] a CNDO/2 calculation on C_5H_5PO and some of its isomers. Thus only pyridine oxide itself is experimentally known.

Computational Details

The calculations were performed using the Gaussian 98W suite of programs.[12] The hybrid density functional method B3LYP[13] was used. All molecules and ions had their geometry optimized at the B3LYP/cc-pvdz[14] level. Energies were computed at the B3LYP/aug-cc-pvtz[14] level. For the heavier elements As, Sb, and Bi, the pseudopotential versions of these basis sets (cc-pvdz-pp and aug-cc-pvtz-pp)[15] were used. Certain one- and two-heavy-atom species were also calculated at the CCSD(T)/aug-cc-pvtz//B3LYP/cc-pvdz level.

Nucleus independent chemical shift (NICS) calculations were performed using the GIAO method and the B3LYP/aug-cc-pvtz wave function. NICS(0) values were calculated at the center of the ring, found by averaging the coordinates of the six atoms forming the ring. NICS(1) values were calculated at a point 1 Å away from the center of the ring, in a direction perpendicular to the plane of the ring. When the ring is nonplanar, the point at which to calculate NICS(1) is not well defined. In these cases, the pair of opposite directions perpendicular both to the C4−pnictogen axis and the C2−C6 axis were chosen. NICS(+1)

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10.1021/jp046733d CCC: $30.25

TABLE 1: Gas-Phase Ion Energetics of the Pnictabenzenes[a]

	E = N	E = P	E = As	E = Sb	E = Bi
IE, eV	9.01 (9.26)	8.86 (9.0)	9.38 (8.6)	7.99 (8.3 vert.)	7.69 (7.9)
EA, eV	< 0	0.07	0.26	0.58	0.64
PA, kJ/mol	932 (930)	819 (817.7)	768 (784.8)	766	763

[a] NIST WebBook values are in parentheses where available.

TABLE 2: Heats of 3,4-Hydrogenation and Bond-Dissociation Enthalpies (BDE) at 298.15 K for the Pnictabenzenes and Their Oxides and Sulfides

	E = N	E = P	E = As	E = Sb	E = Bi
$\Delta H(+H_2)$ for C_5H_5E	35	38	38	38	37
$\Delta H(+H_2)$ for C_5H_5EO	33	34	35	29	17
$\Delta H(+H_2)$ for C_5H_5ES	29	33	35	32	19
BDE(C_5H_5E-O), B3LYP, kJ/mol	260	435	277	208	126
BDE(C_5H_5E-S), B3LYP, kJ/mol	160	257	181	155	95
BDE(C_5H_5E-O), corrected, kJ/mol	241	430	297	234	145
BDE(C_5H_5E-S), corrected, kJ/mol	158	254	180	171	103

and NICS(−1) are taken at the points 1 Å from the ring center in this pair of opposite directions; the ring center and NICS(0) evaluation point still defined as the average of the coordinates of the ring atoms. NICS(+1) is the point further from the oxygen or sulfur in the nonplanar pnictabenzene chalcogenides. NICS(−1) is the point taken in the other direction from the ring center.

Atomic charges were calculated according to the CHELPG procedure, developed by Breneman and Wiberg.[16] This procedure is based on fitting charges in order to reproduce as closely as possible the external electric field generated by the charge distribution in the molecule. To fit only the external electric field, exclusion radii are set for each atom, within which the electric field is not evaluated. In this study, the exclusion radii were 0.2 Å plus the van der Waals radius of the atom. More precisely, the exclusion radii were: 1.40 Å for H, 1.90 Å for C, 1.75 Å for N, 2.00 Å for P, 2.05 Å for As, 2.25 Å for Sb, 2.35 Å for Bi, 1.72 Å for O, and 2.00 Å for S. Consistency within the current study was considered to be more important than exactly matching the radii used by Breneman and Wiberg, who actually used two sets of exclusion radii and found the results were not highly dependent on the exact magnitude of the radii.

Results

Geometrical data for the pnictabenzenes, their pnictogen-protonated conjugate acids, and their oxides and sulfides optimized at the B3LYP/cc-pvdz level are given in Tables S1−S4 in the Supporting Information. All the pnictabenzenes themselves are planar, with C_{2v} symmetry. The geometric parameters are in agreement with previous experimental[17] and computational[18] studies. Among the conjugate acids, pyridinium and phosporinium are planar, but the arsenic, antimony, and bismuth analogues are nonplanar with $\angle C4-E-H = 130.2$, 109.5, and 93.8°, respectively. Priyakumar and Sastry[19] found that the nonplanarity of arseninium was greater at the B3LYP/6-31G* level than at the MP2/6-31G** level, both in terms of equilibrium geometry and in terms of energy required for planarization. Berger et al.[18] found arseninium to be planar at the PM3 level, but antimoninium is nonplanar at that level. The oxides and sulfides of pyridine, phosphorin, arsenin, and antimonin are also planar with C_{2v} symmetry, but bismin oxide and bismin sulfide are nonplanar with C_s symmetry.

The ionization energies (IE), electron affinities (EA), and proton affinities (PA) were calculated by comparing B3LYP/aug-cc-pvtz//B3LYP/cc-pvdz energies of the neutral pnictabenzenes with the energies of the radical cations, radical anions, and conjugate acids at the same level (see Table 1). These are thus adiabatic rather than vertical values. The radical cations and anions share the C_{2v} symmetry of the neutral pnictabenzenes. One observes that the electron affinities increase in the pyridine to bismin series, and the ionization energies increase then decrease, arsenin having the highest value. The proton affinities decrease gradually from pyridine to bismin.

Heats of formation have been calculated using the reaction $C_6H_6 + EH_3 \rightarrow C_5H_5E + CH_4$. This reaction was chosen because of availability of thermochemical data and the fact that, although the reaction is not isodesmic, at least the bonds being broken and then formed are to elements with similar electronegativities. For E = N, the calculated reaction enthalpy at 298.15 K is 21 kJ/mol, giving for pyridine a heat of formation of +133 kJ/mol. This is close to the tabulated experiment-derived value of +140.6 kJ/mol.[20] For the rest of the series, the calculated heats of reaction at 298.15 K are: C_5H_5P +2, C_5H_5As +14, C_5H_5Sb +29, and C_5H_5Bi +34 kJ/mol. This leads to the following calculated enthalpies of formation: phosphorin +181, arsenin +231, antimonin +329, and bismin +468 kJ/mol. The bismin heat of formation is based on 278 kJ/mol[21] for the heat of formation of BiH_3. These may be compared to previously published PM3 calculations,[18] in which the heats of formation are phosphorin 180, arsenin 264, and antimonin 313 kJ/mol.

To quantify the effect of the cyclic conjugation in these six-membered rings, the heat of hydrogenation to the 3H,4H-dihydro compounds were calculated. The results are in Table 2. The 3H,4H-dihydro compounds were chosen because hydrogenation at these positions breaks the cyclic conjugation without changing the coordination of either the group 15 atom or the carbons directly attached to the group 15 atom. The calculated heats of hydrogenation at 298.15 K are: pyridine 35, phosphorin 38, arsenin 38, antimonin 38, and bismin 37 kJ/mol. One may compare these with the 45 kJ/mol value calculated for the hydrogenation of benzene to 1,3-cyclohexadiene. Note that all six of these hydrogenations are endothermic. The hydrogenation energies should not be taken as direct measures of aromaticity, as the addition of hydrogen may increase or decrease the strain energy of the ring, and the hybridization of atoms changes as well. Regarding the latter, the gross hybridization changes are controlled for by hydrogenating at corresponding positions which are remote from the heteroatom, but more subtle effects of the changes in hybridization may still affect the comparability of the hydrogenation energies.

The heats of hydrogenation of the 3H,4H-dihydropnictabenzene oxides and sulfides are also without exception endo-

TABLE 3: NICS(0) and NICS(1) Values[a]

	E = N	E = P	E = As	E = Sb	E = Bi
NICS(0), C_5H_5E	−6.53	−6.64	−7.35	−5.91	−6.40
NICS(0), C_5H_5EO	−5.88	−8.18	−7.33	+1.54	−1.18
NICS(0), C_5H_5ES	−4.00	−6.58	−5.83	−5.34	−1.54
NICS(1), C_5H_5E	−10.08	−9.35	−10.05	−8.54	−8.28
NICS(1), C_5H_5EO	−7.21	−8.15	−8.28	+0.13	(+1) −3.37
					(−1) −4.96
NICS(1), C_5H_5ES	−6.51	−7.46	−7.52	−6.96	(+1) −3.85
					(−1) −5.06

[a] Compare with values for benzene: NICS(0) = −7.96 and NICS(1) = −9.85.

TABLE 4: Dipole Moments of Pnictabenzenes and Their Oxides and Sulfides

	E = N	E = P	E = As	E = Sb	E = Bi
dipole of C_5H_5E, Debye	2.28	1.61	0.91	0.44	−0.29
dipole of C_5H_5EO, Debye	4.13	4.08	4.48	4.63	4.64
dipole of C_5H_5ES, Debye	5.55	3.91	4.13	4.14	4.22

thermic. Moreover, the heats of hydrogenation of C_5H_5EO and C_5H_5ES are only slightly lower than those for C_5H_5E where E = N, P, or As. For E = Sb and Bi, the heats of hydrogenation of the oxides and sulfides are noticeably less than those of C_5H_5E itself. The heats of hydrogenation of the pnictabenzene oxides and sulfides are tabulated in Table 2, along with the bond dissociation enthalpies $C_5H_5E{-}O$ and $C_5H_5E{-}S$. Since B3LYP/aug-cc-pvtz bond dissociation enthalpies are not highly accurate, a correction was made equal to the difference in calculated bond dissociation enthalpies at absolute zero for $H_3E{-}O$ and $H_3E{-}S$ calculated at B3LYP/aug-cc-ptvz and CCSD(T)/aug-cc-pvtz. Details can be found in Tables S5 and S6 in the Supporting Information. By application of these corrections, we get for the heats of formation: C_5H_5NO +143, C_5H_5PO +1, C_5H_5AsO +183, C_5H_5SbO +344, C_5H_5BiO +570, C_5H_5NS +252, C_5H_5PS +205, C_5H_5AsS +328, C_5H_5SbS +435, and C_5H_5BiS +642 kJ/mol.

The NICS metric was introduced by Schleyer et al. in 1996[22] as a measure of the ring current in aromatic and antiaromatic systems. NICS(0) is defined as the negative of the isotropic magnetic shielding at the center of the ring, the center in turn being defined as the point whose coordinates are the (nonmass-weighted) mean of the coordinates of the ring atoms. NICS(1), calculated at a point 1 Å "above" the ring, appears to be a more satisfactory metric for (anti)aromaticity; for a discussion of the positional dependence of NICS in aromatic and antiaromatic rings, see Schleyer et al. (2001).[23] Here NICS(0) and NICS(1) values are given in Table 3. Because bismin oxide and bismin sulfide are nonplanar, these species have two distinct NICS(1) values which are labeled (+1) and (−1) as described in the Computational Details section.

The dipole moments of the pnictabenzenes and their oxides and sulfides are given in Table 4. One will note the steady decline in dipole moment as one progresses from pyridine to bismin; the last is shown as negative because the dipole points in the opposite direction from the others in the series. All the oxides and sulfides have large dipoles and are of similar magnitude (and all in the same direction). This is an expected result since we have introduced a "formal" dipole into the formula: $E^{+-}O^{-}$ or $E^{+-}S^{-}$ respectively. Atomic charges according to the CHELPG procedure were also calculated, and these are arranged in Tables 5−7. There is significant variation in the series, but the CHELPG charges of the oxygen atoms in the pnictabenzene oxides are all in the neighborhood of −0.6, and the CHELPG charge of the sulfur atoms in the pnictabenzene sulfides are all in the neighborhood of −0.3. One might also note the tendency to charge alternation in the ring atoms of the pnictabenzenes; this is not so evident in the oxides and sulfides.

TABLE 5: CHELPG Atomic Charges of the Pnictabenzenes

atom	E = N	E = P	E = As	E = Sb	E = Bi
E	−0.665	−0.208	−0.079	+0.031	+0.140
C2	+0.497	+0.154	+0.055	−0.006	−0.124
C3	−0.512	−0.384	−0.328	−0.315	−0.223
C4	+0.280	+0.181	+0.125	+0.123	+0.051
H2	+0.005	+0.059	+0.073	+0.077	+0.100
H3	+0.173	+0.155	+0.144	+0.138	+0.120
H4	+0.057	+0.058	+0.066	+0.057	+0.063

TABLE 6: CHELPG Atomic Charges of the Pnictabenzene Oxides

atom	E = N	E = P	E = As	E = Sb	E = Bi
E	+0.558	+0.890	+0.867	+0.958	+0.496
O	−0.568	−0.577	−0.580	−0.602	−0.546
C2	−0.169	−0.469	−0.450	−0.484	−0.017
C3	−0.116	+0.086	+0.072	+0.076	−0.367
C4	−0.148	−0.316	−0.296	−0.294	+0.219
H2	+0.153	+0.203	+0.203	+0.203	+0.105
H3	+0.143	+0.110	+0.111	+0.108	+0.166
H4	+0.134	+0.144	+0.137	+0.131	+0.060

TABLE 7: CHELPG Atomic Charges of the Pnictabenzene Sulfides

atom	E = N	E = P	E = As	E = Sb	E = Bi
E	−0.188	+0.220	+0.282	+0.407	+0.368
S	−0.360	−0.283	−0.313	−0.341	−0.399
C2	+0.328	−0.077	−0.089	−0.141	−0.130
C3	−0.334	−0.111	−0.133	−0.142	−0.149
C4	+0.059	−0.134	−0.103	−0.081	+0.014
H2	+0.028	+0.099	+0.104	+0.113	+0.125
H3	+0.168	+0.129	+0.132	+0.131	+0.118
H4	+0.109	+0.116	+0.106	+0.094	+0.090

Discussion

A number of indices of aromaticity have been proposed. Most of these are based on bond alternation, thermochemistry, or magnetic (ring current) properties.

It is in general difficult to quantify bond alternation when heteroatoms are involved. However, with these molecules it is evident that bond alternation would result in breaking the C_{2v} (or for the nonplanar species C_s) symmetry. As this is not observed, all the pnictabenzenes, pnictabenzene oxides, and pnictabenzene sulfides have no bond alternation and are thus "aromatic" according to this criterion.

The heats of hydrogenation to the 3H,4H-dihydropnictabenzenes are endothermic for all five pnictogens. They are in fact nearly identical, 35−38 kJ/mol, for the entire series. This is only somewhat lower than the 45 kJ/mol value calculated for benzene. The heats of hydrogenation for the pnictogen oxides and pnictogen sulfides are somewhat lower but still positive. As mentioned in the Results section, hydrogenation energies include effects not related to aromaticity; nonetheless, the calculated results suggest that the cyclical conjugation lowers the energy of these molecules. Thus by this criterion also, the entire series of pyridine, phosphorin, arsenin, antimonin, bismin, and their oxides and sulfides are "aromatic," although the nonplanar bismin oxide and bismin sulfide are perhaps "less aromatic" than the others.

The NICS(0) and NICS(1) values for the pnictabenzenes and their oxides and sulfides are given in Table 3. When comparing NICS values to those from the literature, one should remember that there is substantial basis set dependence in the calculated values. Generally one compares with the NICS values for benzene at the same level of theory. The NICS(0) values calculated here for benzene (−7.96), pyridine (−6.53), phosphorin (−6.64), and arsenin (−7.35) should thus be compared *as a series* to the NICS(0) values of Saieswari et al.:[24] benzene (−11.5), pyridine (−9.6), phosphorin (−9.5), and arsenin (−9.4). The Saieswari et al. calculations are at the HF/6-31G* level. One also can compare the NICS(0) to the NICS(RCP) values calculated by Bachrach:[25] benzene (−7.4), pyridine (−6.3), and phosphorin (−6.4). NICS(RCP)—note that this is my designation, not theirs—is calculated at the ring critical point, which will normally be near the ring center used in NICS(0) calculations. The NICS(1) values calculated here for the series benzene (−9.85), pyridine (−10.08), phosphorin (−9.35), and arsenin (−10.05) should likewise be compared to the series calculated at HF/6-31G* by Saieswari et al.: benzene (−12.8), pyridine (−12.4), phosphorin (−11.4), and arsenin (−11.4). Thus the conclusion to draw from Table 7 is in agreement with Bachrach and with Saieswari et al.: pyridine, phosphorin, and arsenin have somewhat lower NICS values than benzene. According to these calculations, NICS values for antimonin and bismin are somewhat lower than those for pyridine, phosphorin, and arsenin. The oxides of pyridine, phosphorin, and arsenin have NICS(0) and NICS(1) values which are somewhat less negative than those of pyridine, phosphorin, and arsenin themselves; the sulfides have NICS values which are somewhat less negative than those of the oxides. However, the NICS values of these species are all indicative of aromaticity. Antimonin sulfide likewise appears to be aromatic, but antimonin oxide is nonaromatic by the NICS criterion. Bismin oxide and bismin sulfide are borderline and could be classed as either weakly aromatic or nonaromatic.

It is impossible to conclusively demonstrate aromaticity for any species in the absence of a precise and agreed-upon definition. Nonetheless, the preponderance of the evidence—geometric, energetic, and magnetic—suggests that the entire series from pyridine to bismin is aromatic. The same can be said for the oxides and sulfides of pyridine, phosphorin, and arsenin; the evidence for aromaticity of the antimonin and bismin oxides and sulfides is less compelling, and perhaps these should be regarded as nonaromatic. Thus it appears that all five of the Group 15 elements are capable of participating in aromatic bonding, despite the lower strength of π bonds relative to σ bonds for the heavier elements in this column. This is not to say that the weaker π bonding of the heaver elements is not reflected in the chemistry of the pnictabenzene series: the fact that the heavier pnictabenzenes participate in Diels−Alder reactions would be attributable to this effect. The addition of a datively bonded oxygen or sulfur appears to diminish the ability of the pnictogen to participate in an aromatic system; the magnitude of this effect seems to be slight for E = N, P, and As but substantial for Sb and Bi. The marked contrast between arsenin oxide and antimonin oxide is particularly interesting.

Conclusion

Computations were performed on the pnictabenzene series (C_5H_5E: pyridine, phosphorin, arsenin, antimonin, bismin) and some of their derivatives including radical cations, radical anions, protonated species, E-oxides, and E-sulfides. Results are generally consistent with previous experimental and computational studies, where available. All five members of the C_5H_5E series are aromatic according to geometric, energetic, and NICS criteria, and there seems to be little or no diminishment of aromaticity as one moves down the series from N to Bi. Many of the pnictabenzene oxides and sulfides (C_5H_5EO for E = N, P, and As and C_5H_5ES for E = N, P, As, and Sb) are also aromatic by these criteria, although perhaps to a lesser degree. Antimonin oxide, paradoxically, is aromatic by geometric and energetic criteria, but the NICS indicates nonaromaticity. Bismin oxide and bismin sulfide are nonplanar and have borderline NICS values, but there is no bond alternation, and the addition of H_2 is endothermic.

Supporting Information Available: Tables showing geometrical data for the pnictabenzenes, their pnictogen-protonated conjugate acids, their oxides, and their sulfides optimized at the B3LYP/cc-pvdz level and bond dissociation enthalpies for H_3E-O and H_3E-S. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) These names are formed "irregularly" in the IUPAC-approved Hantzsch−Widman system in order to avoid confusion with established trivial names for PH_3, AsH_3, and SbH_3. In another variant of the Hantzsch−Widman system, the series of names is: pyridine, phosphinine, arsinine, stibinine, bismine.

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