THEO
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# Pnicogen heterobenzenes

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## Abstract

The behavior of the group 15 heterobenzenes is analyzed from a theoretical point of view (BPW91/6-311-G** level) and compared with the very well-known behavior of pyridine. Special emphasis is deserved to the problems of aromaticity and geometry, which can be useful to explain why stybitine is unstable and bismutinine does not exist as an isolated molecule. In general the lability of all the members of this family (with the exception of pyridine) in normal conditions is also analyzed.
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## 1. Introduction

Pyridine is a very useful compound in organic synthesis and one of the most important model compounds for theoretical and academic purposes. All the pyridine-like systems are aromatic molecules classified as $\pi$ deficient compounds [1] since the pnicogen atom (in this case nitrogen) plays the role of a very electronegative center compared with carbon.

The other heteroarenes belonging to the pnicogen family are very poorly known [2]. Phosphinine is the only one (with the exception of pyridine) that has been studied within the context of organic, organometallic and coordination chemistry [3].

Phosphinine and arsinine are air-sensitive compounds but they have a reasonably stability, stibinine is unstable and spontaneously polymerize and bismutinine has not been synthesized as an isolated species due to its high reactivity [1]. The main question about these compounds is why they are not as stable as pyridine if the structure is almost the same.

The aim of this work is to study the five structures of the pnicogen heteroarenes of six members looking for their similarities and their intrinsic characteristics that cause the stability and reactive differences outlined above. In this sense, the geometry and aromaticity of these rings have been

calculated. The geometries have been approximated with a very powerful DFT method and with a large basis set. In the case of aromaticity homodesmic reactions and NICS, indices have been used.

It is important to point out that there are several theoretical studies that are dealing with the topic of pnicogen heterocycles. Veszprémi [4] and coworkers carried out a comparative study on P=C, C=C and N=C double bonds in order to establish a reactivity trend, they designed homodesmic reactions in which heteroaromatic rings were included, they used the MICROMOL method with a 4-31G basis. The group of Borden [5] studied directly phosphinine in comparison with silabenzene in stability toward dimerization, their calculations were carried out by the hybrid B3LYP method included in the Gaussian98 package with a 6-31G* basis set. Chamizo and coworkers [6] included phosphinine, arsinine and stibinine in their work about organometallic aromaticity accomplished into the Extended Hückel scheme. Schleyer and Wang [7] studied the aromatic or ylidic nature of $\lambda^5$-phosphorins, a very interesting point of this work is that they calculated the NICS(1) value of the phosphinine ($-10.8$), which is very important to the present study because this is one of the first quantitative estimation of the aromaticity on one of the molecules under study.

Phosphinine have been more extensively studied than the other molecules of the family in experimental as well as theoretical fashions, in this point it is very important to refer

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the excellent review by Nyulászi about the aromaticity of phosphorus heterocycles [8]. In this paper several results about phosphinine are shown and in some cases we compare with those obtained in the present paper.

Finally Baldridge and Gordon [9] carried out a very valuable work, they indirectly estimated the aromaticity of pyridine, phosphinine, arsinine and stibinine in a very elegant thermochemical work in which some homodesmic reactions were designed. It is important to note the experimental works of LeFloch [3] and Ashe [10], who synthesized and characterized many of the molecules under study and provided experimental data that is very useful.

## 2. Theoretical methods

All calculations were carried out using the GAUSSIAN98 quantum chemical package [11]. A pure DFT method containing the Becke's gradient corrections [12] for exchange and Perdew–Wang's for correlation [13] were used for the optimization of all the geometries and energy evaluation with the basis set 6-311-G**, in the cases of molecules with antimony and bismuth, a pseudopotentials LAN2DZ were applied including the relativistic effects. Furthermore frequency calculations were carried out in all cases in order to get the needful thermochemical values for the homodesmic reactions analysis, these calculations were carried out in the same conditions. Therefore all these parts of the work were performed at BPW91/6-311G** level and LAN2DZ pseudopotentials in two cases. The NICS values were used as an aromaticity index and were obtained on the optimized structures following the methodology developed by Schleyer and his coworkers [14] at the same level as in their original work, i.e. HF/6-31 + G* and pseudopotentials for the indicated atoms.

## 3. Results and discussion

The analysis of the geometry yields a good estimation on the quality of the employed method. Baldridge and Gordon [9] reports a complete set of theoretical results (HF/3-21G*) on geometrical parameters and compare with their experimental results [15] and those obtained by Ashe [10] with a reasonable match. The same comparison is presented in this work. In this case obtained results compare well with experimental data, considering the high level of the theory for calculation. Results and comparisons are shown in Table 1 and the optimized structures are shown in Fig. 1.

There are some important items to note about the optimized geometries of these species. First all the molecules of this family are planar as Ashe probed [10] and belong to the *C2v* symmetry point group. The second point is the progressive deformation of the ring mainly shown by the C–E–C angle that tends to close, in this sense the closest angle is the one of the bismutine in which it is

Table 1
Geometrical parameters

| Atom | C–E length | C–E–C angle | Baldridge and Gordon, Ashe length | | Bldridge and Gordon, Ashe angle | |
|------|-----------|-------------|--------|--------|--------|--------|
| N  | 1.332 | 117.2 | 1.330 | 1.370 | 116.8 | 117.0 |
| P  | 1.734 | 100.2 | 1.718 | 1.730 | 100.8 | 101.0 |
| As | 1.868 | 96.4  | 1.850 | 1.850 | 97.2  | 97.0  |
| Sb | 2.056 | 91.9  | 2.060 | 2.040 | 93.2  | 93.0  |
| Bi | 2.121 | 90.4  |       |       |       |       |

found almost an straight angle. And finally the match of the C–E bonds lengths with experimental data, the obtained values suggest that there are appreciable multiple bond character.

With respect to chemical behavior, there are some interesting features to consider. Pyridine is a basic molecule due to the presence of the heteroatom. However, phosphinine is a negligible basis and the tendency becomes progressive when going down in the periodic table, i.e. it is expected that arsinine will be amphoteric as well as stybine and bismutinine, even more it could be expected acid character for the last three cases.

Mulliken charge values for the heteroatoms are shown in Table 2, the change from the negative charge of nitrogen or the almost neutral of the phosphorus to the very positive of arsenic, antimony and bismuth is dramatic. This phenomenon has been indicated by Ashe [10] and he suggests it can be explained on the basis of the deformation of C–E–C angle indicated above, this point is assessed by the charge results obtained in this work, however, it is important to note the strong change on electronegativity when going from nitrogen to bismuth and other electronic effect concerning to the localization and influence of the intrinsic lone pair of these atoms that will be carefully explained below.

The atomic orbitals have the tendency to mix among them (hybridization) when the atoms bind together. However, this tendency is low in accordance with the rising of the atomic weight. Therefore the lone pair intrinsic of the elements of this family is approximately localized on one hybridized orbital in pyridine but tends to localize it in the low mixed s orbital in phosphinine as it was observed by Oehling and Schweig [16]. It was found here that this effect is even more marked for arsinine, stybinine and bismutine as it can be seen with the nature of the HOMO and the electronic population of s atomic orbital (Table 2). The HOMO for pirydine is localized mainly in the lateral C–C bonds of the ring, the nitrogen atom with its lone pair and some peripheral hydrogen atoms. This wavefunction belongs to the a1 irreducible representation. It can be seen that the heteroatom has a large participation into a hybrid scheme (Fig. 2). However, the other four molecules have a very different HOMO but similar among them that belong to the b2 irreducible representation with an increase on the separation of the atomic orbital s (see Fig. 2).
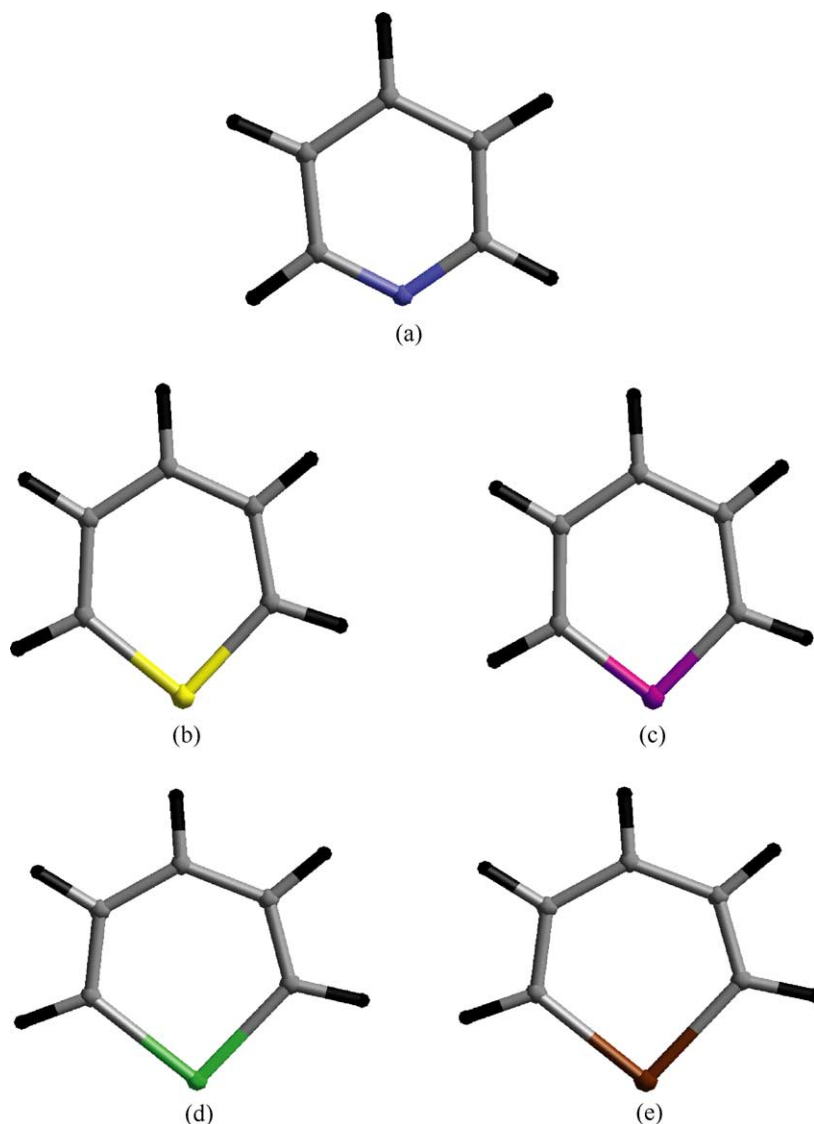
Fig. 1. Molecules under study: (a) pyridine; (b) arsinine; (c) phosphinine; (d) stybine and (e). bismuthine.

All these arguments show that the localization of the lone pair in the atomic orbital s of the atoms heavier than nitrogen enable this pair to be shared with other chemical species. For this reason the large rings are poorly basic or not basic at all.

Baldridge and Gordon [9] carried out a thermochemical study mainly based on a reaction designed by them called superhomodesmic reaction. The situation is almost different in this case in which a new homodesmic reaction similar to that proposed by the same authors for group IV hetero-benzene was designed. The scheme of this reaction is shown in Fig. 3.

All energy values were corrected for zero-point vibrational energies (ZPE) obtained by the frequencies calculations. The $\Delta U$ values obtained by the homodesmic reaction analysis are shown in Table 3, these results are useful to estimate the aromaticity of the rings, for this reason the results of the analysis of NICS are shown in the same table. In the case of phosphinine the results differ slightly with respect to those already reported [8], but the homodesmic reaction is different in the present case and the correction for the ring strain was not considered here.

Table 2
Mulliken charges and s atomic orbital populations

| Atom | Charge | Population |
|------|--------|-----------|
| N | $-0.28$ | 1.372 |
| P | $-0.012$ | 1.543 |
| As | 0.82 | 1.628 |
| Sb | 0.85 | 1.688 |
| Bi | 0.71 | 1.770 |

Fig. 2. Homodesmic reaction.

Table 3
Aromaticity results

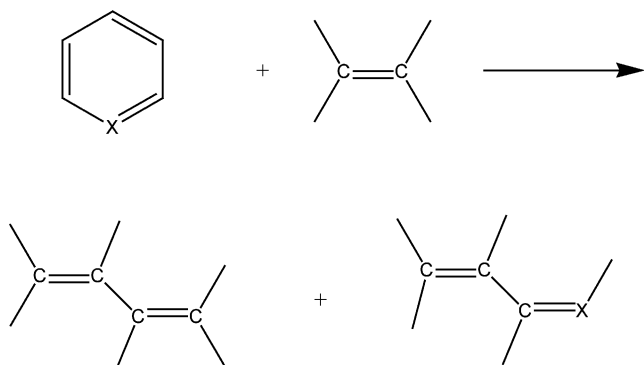| Atom | Homodesmic reaction (kcal/mol) | NICS (ppm) |
|------|-------------------------------|-----------|
| N | − 17.68 | − 8.17 |
| P | − 20.71 | − 8.43 |
| As | − 17.43 | − 7.95 |
| Sb | − 15.30 | − 7.85 |
| Bi | − 13.70 | − 8.15 |

There are two important points to note. First, in both cases, the homodesmic reactions as well as NICS analysis, the phosphinine is the most aromatic ring. On the other hand the NICS analysis shows a very appreciable value for the bismutine. These results are not expected.

A simple explanation for the large aromaticity in phosphinine is based in the low participation of its lone pair. The location of these electrons on a low hibridized and very diffuse s orbital gives place to a better electron current in the ring than in the pyridine case. This effect makes the phosphorus atom to have a behavior 'almost as a carbon atom' with respect to aromaticity, therefore the Hückel structure of the phosphinine ring is assessed. However, the presence of this lone pair prevents an electrophilic aromatic substitution as it was early indicated [8].

This phenomenon is not important in the cases of arsenic and antimony rings because the mix of s and p orbitals in the hybridization is poor compared with nitrogen and phosphorus. This result on the phosphorus heterobenzene is very interesting because the versatility of this ring in organic synthesis can be improved with the respect of pyridine, in one sense the aromatic ring can participate in electrophilic aromatic substitutions almost as it would be other homocyclic compound and in other sense, the low charged
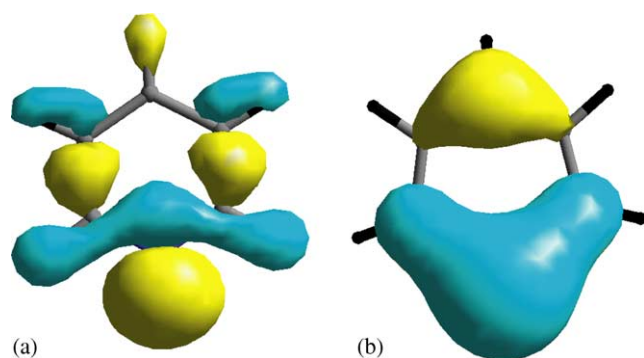
heteroatom is a good target for reactions with bases and nucleophilic reagents.

The second phenomenon has a more complicated explanation. Relativistic effects lead to substantial differences between the chemistry of bismuth and the other pnicogens. One important difference in this respect is the high ability of bismuth to develop $\pi$ bonds in spite of its poor hybridization [17]. Recently it was synthesized the $Bi_2$ unity [18] and the double bond character is evident. Hence the bismuth atom has the capability to generate better $\pi$ bonds than arsenic and antimony with the concomitant improve in the electronic delocalization and finally better aromaticity value. This result should be handled very carefully because the bismutinine has not been isolated to date, indeed the structure of the more stable aromatic bismuth ring is a Diels–Alder adduct [10,19]. It is important to realize the value obtained by the homodesmotic reaction method is the lowest of all i.e. the stability of the correspondent aromatic ring is the poorest. In other words bismutinine would be a medium aromatic compound if it would be possible to prepare as a planar species.

## 4. Conclusions

Pnicogen heterobenzenes present a large diversity of behaviors depending on the nature of the heteroatom in spite that all belong to the same family in the periodic table. There are several reasons for this variety, one of them is the behavior of the lone pair that is a common feature of the group 15 elements, this electronic pair is found progressively localized in diffuse s orbitals in such a way that its participation in chemical reactions is almost restricted to the pyridine, other one is the strong relativistic effect present in bismuth. The aromaticity analysis carried out with NICS and homodesmotic reactions techniques shows that phosphinine is the more aromatic member of the family due to the almost neutral character of the phosphorus. Bismuthine shows a very appreciable value of aromaticity into the context of the NICS analysis but a low value in the thermochemical one, this phenomenon should be assessed to the strong relativistic effect on bismuth which can make good $\pi$ bonds.



Fig. 3. (a) HOMO of pyridine; (b) HOMO of bismuthine; (the corresponding HOMO's for phosphinine, arsinine and stybine have the same shape that the shown HOMO of bismuthine).

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