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Aromatic behaviour of benzene and naphthalene upon pnictogen substitution

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Dedicated to Professor José Elguero on the occasion of his 80th anniversary

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ABSTRACT

A thorough study of the structural and aromatic properties of derivatives of benzene and naphthalene where one or more –CH– groups have been substituted by a nitrogen, phosphorous or arsenic atom has been carried out at B3LYP/6-311++G(d,p) level. Relative energies between isomers range from 5.0 to 294 kJ mol^{-1} finding the largest relative energies in compounds with nitrogen substitutions. In general, most of the compounds show to be planar with a few exceptions, which exhibit twisted structures. Wiberg bond indexes as well as bond distances indicate that in almost all the cases the bond nature is benzene-like. Aromatic characteristics have been addressed calculating NICS values, profiles, isosurfaces and HOMA indexes. NICS(1) and (2) present values close to those of benzene showing aromatic behaviour, confirmed by NICS profiles and 3D NICS isosurfaces. HOMA indexes obtained for those compounds with reported parameterized bonds are in agreement with their corresponding aromatic nature.

1. Introduction

Aromaticity is one of the pillar concepts in organic chemistry that continues unabated.[1–7] There is not a single measure of aromaticity, but in order to have an insight of this characteristic, we associate to aromaticity properties such as planarity, resonance stabilization and magnetic effects due to the electron delocalization (current) along the π-orbitals. Several experimental techniques have been developed to assess aromaticity; thus, energy-based measurements such as empirical resonance energy (ERE) from heat of reaction[8–10] or equilibria[11–13] are just a few examples found in the literature. In parallel, several theoretical approaches have been developed in the last decades to address the problem of measuring aromaticity. Amongst them, some of the most popular are the Krygowsky HOMA indexes,[14,15] Bird Structural Indexes[16] and NICS values,[17] including some description within a 3D molecular space by Kleinpeter et al.,[18–24] Martin et al.,[25–29] Rodríguez-Otero et al.[30] and Sebastiani et al.[31]

Probably the most studied and representative aromatic molecule is benzene,[32,33] and it has been the reference in any study of aromaticity. However, several heterocyclic systems have also been intensively studied. Amongst the vast research devoted to heteroaromaticity and considering the aim of the present manuscript, it is worth noting those studies involving nitrogen and phosphorous derivatives. The works of Bachrach,[34] Sastry[35,36] or Kassaee[37] are just a few examples of studies of these benzene derivatives at different computational levels.

Regarding the benzene nitrogen derivatives, pyridine has been the subject of numerous papers in the last decades. Pyridine and its polysusbtituted nitrogen derivatives are not only experimentally well-known compounds,[38–40] but also a large number of theoretical studies on the aromaticity and stability of nitrogen heterocycles, including azabenzenes, di- tri- and tetrazabenzenes, can be found in the literature.[41–50] A very good example of an exhaustive and remarkable study is that of Fabian and Lewars[51] who theoretically analyzed pyridines and related six-membered rings ($C_xH_xN_{(6-x)}$, x=0–5) in terms of structure, homodesmotic stabilization energy and NICS values. Another article by Galeev et al.[52] involving benzene phosphorous derivatives presents the structural data and aromaticity of different $C_xH_xP_{(1-x)}$ isomers, including benzvalene, prismane and benzene-like structures. In fact, the aromaticity of phosphorous heterocycles, including different size rings, was previously reviewed in detail by Nyulászi[53] and Katritzky.[54]

Syntheses and applications of phosphinines[55] and arsinines[56,57] have been previously described in the literature. It has been shown

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that phosphinine derivatives can be used as tunable molecules for multi-electron donor systems,[58] and more recently,[59] unprecedented P(π)-donor properties have been found in pyridyl analogues of phosphinine, which made them very promising molecules for absorption–emission materials.

In the present paper, a systematic computational study of Z pnictogen derivatives (Z=N, P and As) of benzene and naphthalene (Fig. 1) has been carried out paying special attention to their structural and aromatic properties. The main objective of this study is to consolidate previous data found in the literature and to extend the study to larger systems including bicyclic systems (naphthalene) and phosphorous and arsenic derivatives. This is a need to establish a rational comparison between similar structures containing N, P and As and to homogenize the data.

2. Computational details

The geometry of the systems has been optimized at the B3LYP[60,61]/6-311++G(d,p)[62] computational level. Frequency calculations have been carried out to confirm that the structures obtained correspond to energetic minima.

NICS values[17] were calculated using the GIAO method[63,64] on the B3LYP/6-311++G(d,p) geometries. To obtain the spatial distribution of the NICS, its values have been calculated on a 3D cubic grid of 12 Å size following the procedure described in our previous work.[65–67] The points in the grid are located at 0.2 Å one from other in the three spatial directions. The result is a cube of 226,800 NICS values, which in the next step are represented over the 0.001 a.u. electron density isosurface using the WFA program.[68] All the

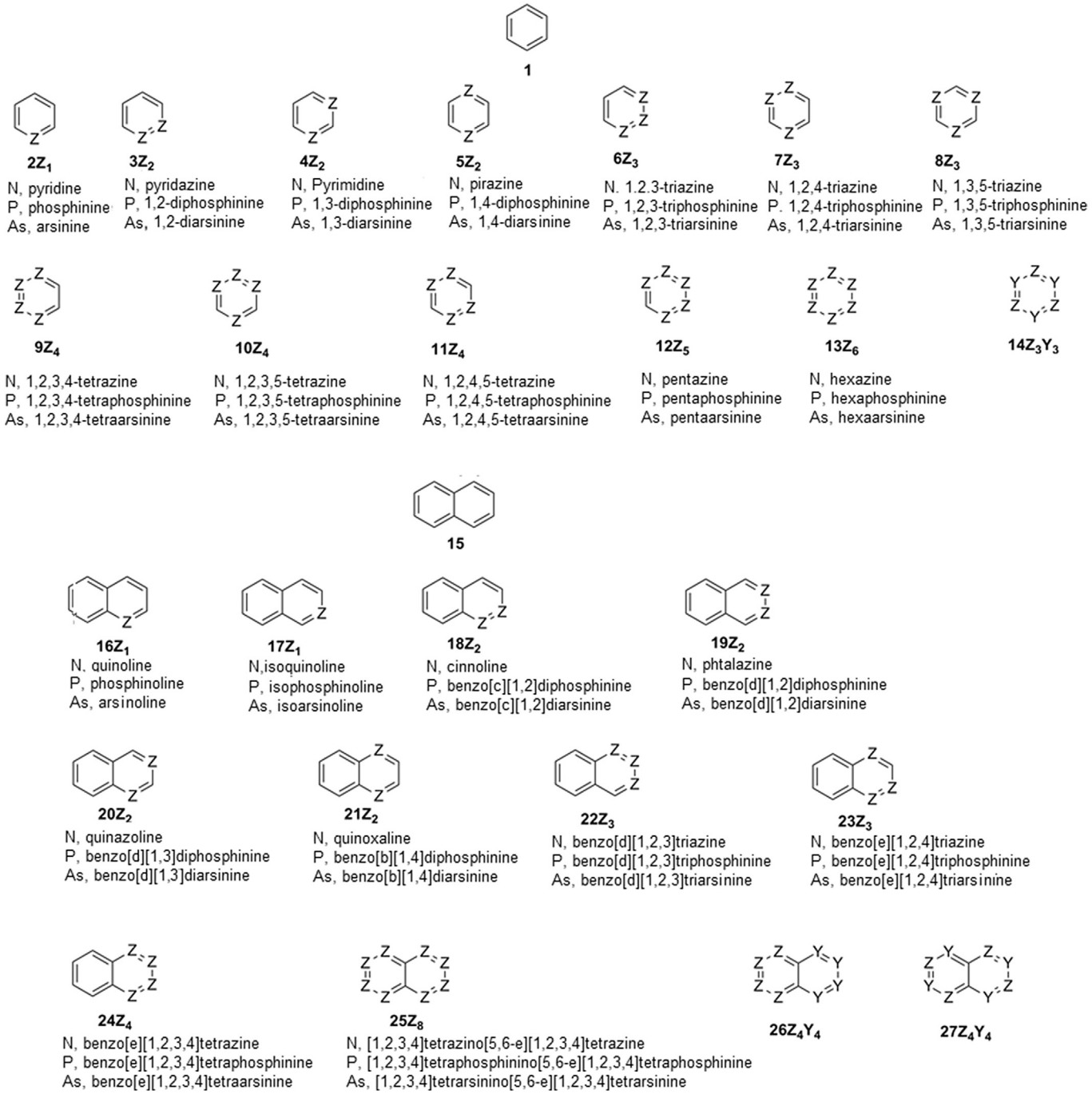

Fig. 1. Mono and bicyclic benzene derivatives containing nitrogen, phosphorous and arsenic ($C_xH_xZ_{(6-x)}$; Z,Y=N, P and As).