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A MP2 and DFT study of the aromatic character of polyphosphaphospholes. Is the pyramidality the only factor to take into consideration?

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Abstract

A comprehensive MP2/6-311+G(d,p) and B3LYP/6-311+G(d,p) study of the aromatic character of phospholes, $P_n(CH)_{4-n}PH$ with n = 0-4 was conducted. For this purpose, the structures for these compounds were optimized at both theoretical levels and different magnetic properties (magnetic susceptibility anisotropy, χ_{anis}, and the nucleus-independent chemical shifts, NICS) were evaluated. For comparison, these magnetic properties were also calculated in the optimized structures with planarity constraints. We have also applied the ACID (anisotropy of the current-induced density) method in this analysis. The main conclusions are the aromatic character of these compounds, the relationship between aromaticity and planarity and the importance of other factors in this aromaticity.

Keywords MP2 calculations · DFT calculations · Aromaticity · Magnetic properties · Polyphosphaphospholes

Introduction

The backbone of classical heterocyclic chemistry is fundamentally formed by five-membered heterocycles such as pyrroles, furans, and thiophenes together with six-membered pyridines. Their chemistry has been continuously developed reaching huge proportions. These molecules have an essential role in biological chemistry and a recent interest in applied chemistry (as example, doped films of polypyrrole have electroconducting properties). However, the chemistry of phospholes has been underdeveloped when compared to its nitrogen, oxygen, and sulfur counterparts. In fact, the first phosphole was discovered as late as 1959 [1, 2].

The aromaticity of the phosphole and its derivatives has been one of their most analysed properties [3]. The potential aromaticity of phosphole was discussed after its first practically applicable synthesis [4, 5] was reported in the 1960s. In different reviews the nonaromatic behaviour of phospole was indicated [6-8]. This fact was explained in basis to the pyramidal preference of tricoordinate phosphorous in its compounds [9].

The planarity of the tricoordinate phosphorous can be influenced by substituents. In this sense, several cases have been studied: π-acceptor groups either at phosphorus or at the neighbouring carbon [10, 11], bulky substituents at phosphorus [12-14], etc.

Some studies have analysed the replacement of –CH= units in the phosphole by –P=, resulting polyphosphaphospholes [15, 16]. The main consequence of this replacement is the decrease of pyramidality and an enhancement of the aromatic character [15]. The recent interest in compounds with planar or partially planar tricoordinate phosphorous is focused in the relationship between aromaticity and pyramidality. In this article we discuss this fact but also introduce new important effects.

Aromaticity is a confused term due to it is not a physical observable [17]. The criterions to decide if a molecule is or not aromatic and the ways to quantify this aromaticity are innumerable [17-23].

It is well know that aromatization affects magnetic properties such as magnetic susceptibility and its anisotropy, leading to especially negative values for such properties [24-26]. These magnitudes are global properties, which can be affected by parts of the molecule not directly

implicated in the aromaticity. To avoid this problem, the Nucleus Independent Chemical Shift (NICS) proposed by Schleyer et al. is very useful. The NICS is defined as the negative of the magnetic shielding [27] and it can be evaluated at any point of the molecule, exhibiting very negatives values in the center of aromatic rings.

The ACID (anisotropy of the current-induced density) is a new method based on magnetic properties and developed by Herges and Geuenich [28]. This method allows the visualization of the ring current formed when a magnetic field is applied and allows us to study the electronic delocalization in molecules [29, 30].

Computational details

The geometry of each structure was optimized with the 6-311+G(d,p) basis set and the density functional theory (specifically, the Becke3LYP functional) [31, 32] or Møller-Plesset perturbation level with the inclusion of energy corrections through second-order (MP2). All structures were minima as frequency calculations at same level have shown. In order to evaluate the relationship of planarity with aromaticity, geometries of 1-4b structures (Fig. 1) with planarity constraints were optimized at the B3LYP and MP2 level with 6-311+G(d,p) basis set. These planar structures were transition states.

The anisotropy of magnetic susceptibility values was calculated at the B3LYP/6-311+G(d,p) level using the IGAIM (Individual Gauges for Atoms in Molecules) method [33, 34] on the B3LYP and MP2 optimized structures. In the NICS calculations, B3LYP/6-311+G(d,p) level with GIAO (Gauge-independent Atomic Orbital) method [35] were employed.

Finally, CSGT (Continuous Set of Gauge Transformations) method [33, 34, 36] at B3LYP/6-31+G(d) level of theory was employed in ACID calculations, carried out with the program supplied by Herges [28].

Quantum chemical calculations were carried out with the Gaussian98 [37] and Gaussian03 [38] program packages.

Results and discussion

<Figure 1>

Fig. 1 shows the polyphospholes studied in the present work. These structures, except for the pentaphosphole (5), are no planar. Table 1, collects the pyramidality data of these structures. The values for different magnetic properties: anisotropy of the susceptibility (we have chosen this property instead of magnetic susceptibility due to the inherent problems of this property [39]) and NICS are shown in the same Table 1. The NICS criterion is based on the negative of the magnetic shielding computed at the centre of the ring. In general [40-46], negative values imply aromaticity (diatropic ring current) and positive values imply antiaromaticity (paratropic ring current). The NICS values have been obtained at ring critical point as defined by Bader [47, 48]. NICS values at points in the ring plane (NICS(0)) contain important spurious contributions from the in-plane tensor components that are not related to aromaticity as Schleyer has indicated [49]. For this reason, NICS(1) and NICS(-1) values (1 Å above/below the plane of the ring, Fig. 2) are showed in Table 1. These values reflect π effects and they are a better indicator of the ring current than values in ring plane, because at 1 Å the effects of the local σ-bonding contributions are diminished. The result obtained by the analysis of the values for these magnetic properties is the aromatic character of all these polyphosphaphospholes.

<Table 1>

The different values of NICS(1) and NICS(-1) indicate the different aromatization in each face of the molecules and the higher aromatization in the opposite side to the hydrogen atom joined to the phosphorous atom.

<Figure 2>

Different studies have looked for a direct connection between planarity and aromaticity in these compounds. In this sense, the search of more aromatic derivatives of the phosphole was reduced many times by the search of substituents that produced more planar structures. In this work we are interested in investigating this connection between planarity and aromaticity and

if other factors should be considered. For this purpose the NICS values of all compounds are presented in Table 1 together with pyramidality data. The pyramidality at the tricoordinate phosphorous atom was measured by the sum of the bond angles around the P-H group, $\Sigma\alpha$. At first sight a good correlation between planarity and aromaticity is observed. Even so, some details attract attention: the structures of 2a and 2b at B3LYP/6-31++G(d,p) level have very similar planarity values but its NICS(0) values differ in nearly two ppm, or, in the case of structures with three phosphorous atoms, 3a and 3c have similar $\Sigma\alpha$ but very different NICS(0) values. In order to visualize the correlation between pyramidality and aromaticity, the anisotropy and NICS(1) and NICS(-1) values for all polyphospholes are plotted against the bond angle sums (Fig. 3). A rough relation between pyramidality and aromaticity is present but some facts seem indicate that a deeper analysis is recommended. If the four compounds with three phosphorous atoms are analyzed, we can observe that NICS(1) and NICS(-1) values for 3a are more negative than expected values if a perfect correlation between pyramidality and aromaticity exists at both DFT and MP2 method. This result seems to indicate that the extension of conjugation is greater when the phosphorous atoms are connected and the P-H group is an end of this connection. In this sense, 3d, structure where the three P atoms are not connected, is less aromatic than 3a, presenting a similar pyramidality.

<Figure 3>

Similar behavior is observed if compounds with two atoms of phosphorous are analyzed. So, the compound 2a with the phosphorous atom linked to P-H group is more aromatic than compound 2b, even though at B3LYP level the planarity of their structures is very similar.

We should remember that the evaluation of the absolute aromaticity of a compound remains a controversial issue [50]. The main reason to this affirmation with regard to the magnetic properties as indication of aromatic character is the lack of a reference. For this reason, we have thought in the use of some system as reference value. We have chosen the planar structures corresponding to each system as reference structure. These planar structures are transition states. Table 2 shows the differences (ΔNICS = NICS (pyramidal compound) – NICS (planar compound)) of the magnetic properties between the planar and pyramidal structures. As for the absolute values of magnetic properties, a direct relationship between pyramidality and aromaticity is not perfect. So, one of the structures with a smaller

pyramidality ($\Sigma\alpha$ = 337.8), the compound 4a, presents values even bigger than 3c, a structure with $\Sigma\alpha$ = 328.0. But, when the distance between phosphorous atoms is analyzed, the patron is the same indicated for the absolute values of NICS and even the differences are more significant (for example, the difference between ΔNICS for structure 3c and 3d is more than 3 ppm). The increase of this effect may indicate that the interaction between phosphorous atoms is larger in pyramidal structures than in planar structures.

<Table 2>

In order to carry out a deeper study of the aromaticity of the phosphole and these derivatives, the ACID method was employed. This is a relatively recently published method to investigate the delocalization and conjugation effects in molecules. It provides a powerful way to visualize the density of delocalized electrons and quantify conjugation effects. The ACID approach has several advantages: it is a scalar field which is invariant with respect to the relative orientation of the magnetic field and the molecule, it has the same symmetry as the wave function, and it can be plotted as an isosurface. In our group this method has been extensively employed in order to distinguish between pericyclic/pseudopericyclic and coarctate/pseudocoarctate reactivity, differentiation where the aromaticity has a crucial paper [51, 52].

Fig. 4 presents the ACID isosurface of the transition states for these reactions at an isosurface value of 0.03 au. Current density vectors are plotted onto the ACID isosurface. The first point to emphasize is that Fig. 4 shows a strong diatropic ring current for all these compounds, indicating their aromatic character. This affirmation is opposite to other studies that have indicated that the pyramidality of phosphole prevented the aromaticity and it is in agreement with the previously calculated NICS values. In this figure the importance of the position of the –P= units with regard to the PH group is clearly shown. In this sense, the most obvious case is the comparison between 3c and 3d. In the last case the ring current in the P=P zone is smaller than in other area of the structure. This point may be more clearly observed if the critical isosurface values, CIV, are compared. The CIV indicates the isosurface value at which the topology changes from cyclic to noncyclic. Large CIV denotes aromaticity or antiaromaticity and a small CIV denotes disconnections. So, these values are a good tool to quantify the extent of conjugation. In this case and as an example, the structure 3d exhibits the smallest CIV (0.034) indicating a smaller aromaticity than other structures with similar $\Sigma\alpha$

(the CIV for the 3a structure is 0.041). This result is in agreement with result obtained in the analysis of the NICS values and it confirms the important role of the position of P atoms.

<Figure 4>

Conclusions

This work allows to us to indicate the aromatic character of the phosphole and the studied polyphospholes. This aromaticity is shown by the negative values of the magnetic properties, and the ACID figures.

It is also interesting to notice the qualitative agreement between MP2 and DFT results.

In order to avoid the problem of lack of reference of the magnetic properties as indicator of the aromaticity, a model was employed: the magnetic properties of the structures are compared with the magnetic properties of these planar structures.

The relationship between aromaticity and pyramidality is showed through graphics of magnetic properties versus $\Sigma\alpha$. But the main conclusion of this work is the importance for the aromaticity of these compounds of other aspects besides the pyramidality. In this sense, the influence of the position of –P= units has been clearly indicated.

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Tables

Table 1 Values of Σα and magnetic properties for the optimized structures at B3LYP and MP2 level

	Σα(°)		χ_{anis} /cgs-ppm		NICS (0)/ppm		NICS (1)/ppm		NICS (-1)/ppm	
	DFT	MP2	DFT	MP2	DFT	MP2	DFT	MP2	DFT	MP2
1	292.4	294.1	-42.5	-44.0	-5.9	-6.2	-5.6	-5.9	-6.1	-6.5
2a	300.7	308.8	-53.2	-54.6	-7.8	-8.7	-7.2	-7.8	-7.4	-8.4
2b	300.4	302.6	-50.8	-52.5	-5.6	-6.0	-6.7	-7.1	-7.2	-7.6
3a	309.1	318.0	-65.9	-67.9	-8.3	-9.6	-8.2	-9.0	-8.9	-9.9
3b	312.6	321.4	-63.5	-66.0	-7.8	-9.2	-8.3	-9.2	-8.8	-9.9
3c	316.8	328.0	-67.3	-68.7	-9.6	-11.1	-9.0	-9.9	-9.1	-10.4
3d	310.9	317.2	-64.4	-67.6	-6.7	-7.8	-7.9	-8.7	-8.6	-9.4
4a	324.6	337.8	-83.1	-87.4	-10.2	-12.7	-10.0	-11.3	-11.0	-12.5
4b	329.0	339.7	-83.7	-85.8	-11.3	-13.0	-10.7	-11.6	-11.2	-12.4
5	360.0	359.9	-113.0	-111.9	-17.7	-17.6	-15.1	-15.0	-15.1	-15.2

Table 2 Difference between NICS for planar and pyramidal structures

	⊿NICS (1)/ppm		⊿NICS (-1)/ppm	
	DFT	MP2	DFT	MP2
1	5.0	4.8	4.5	4.2
2a	4.6	4.0	4.4	3.4
2b	4.4	4.1	3.9	3.5
3a	4.6	3.8	3.9	2.9
3b	3.9	3.1	3.4	2.4
3c	3.5	2.6	3.4	2.2
3d	4.3	3.8	3.6	3.1
4a	3.8	2.5	2.8	1.3
4b	2.9	1.9	2.4	1.2

Figure captions

Fig. 1 The polyphosphaphospholes object of the study

Fig. 2 Figure indicating the position where NICS is evaluated

Fig. 3 Plots of NICS values versus $\Sigma\alpha$. The area corresponding to structures 3a, 3b, 3c and 3d is magnified

Fig. 4 ACID figures for the studied structures

Figure 1
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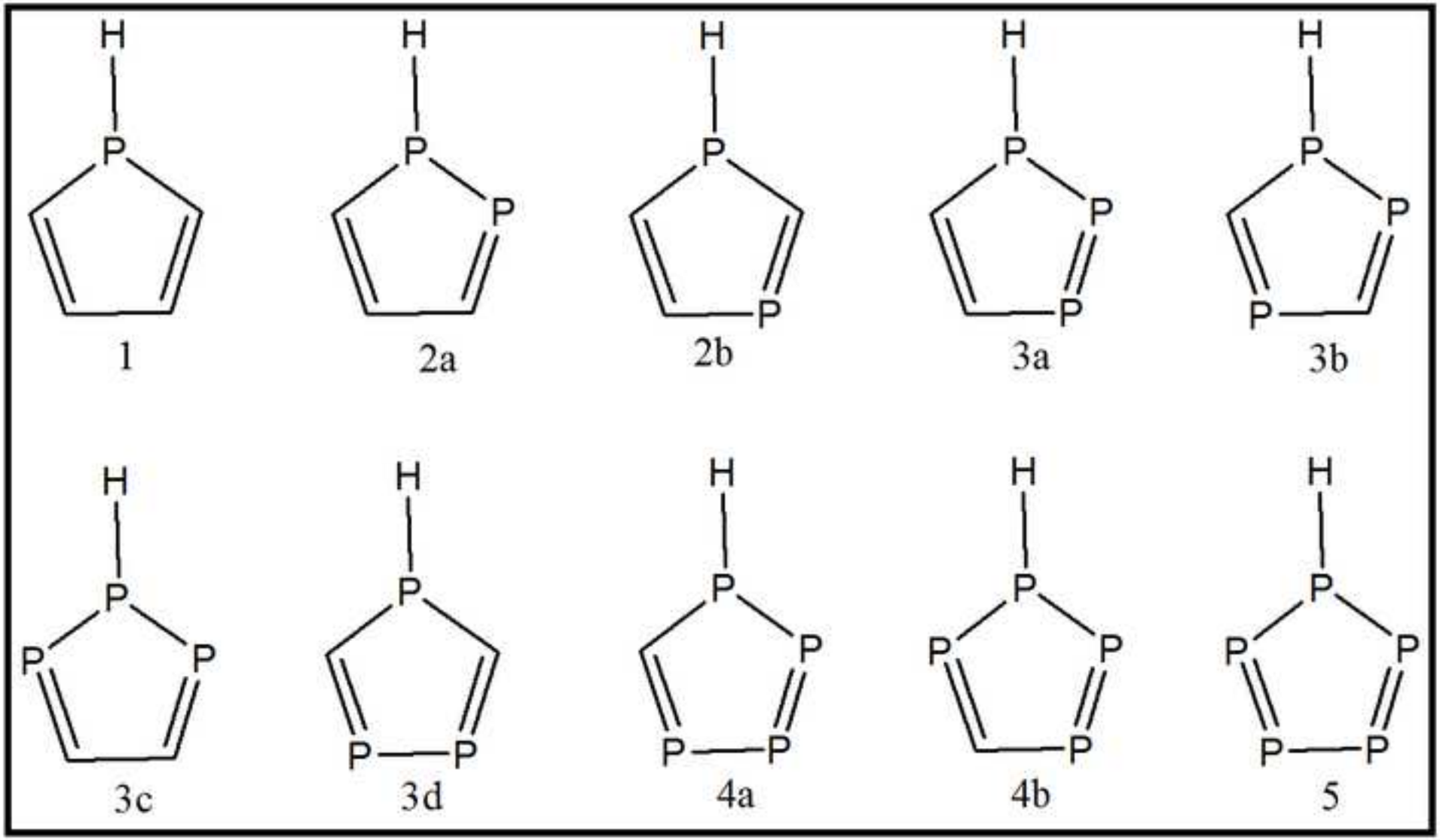

Figure 2
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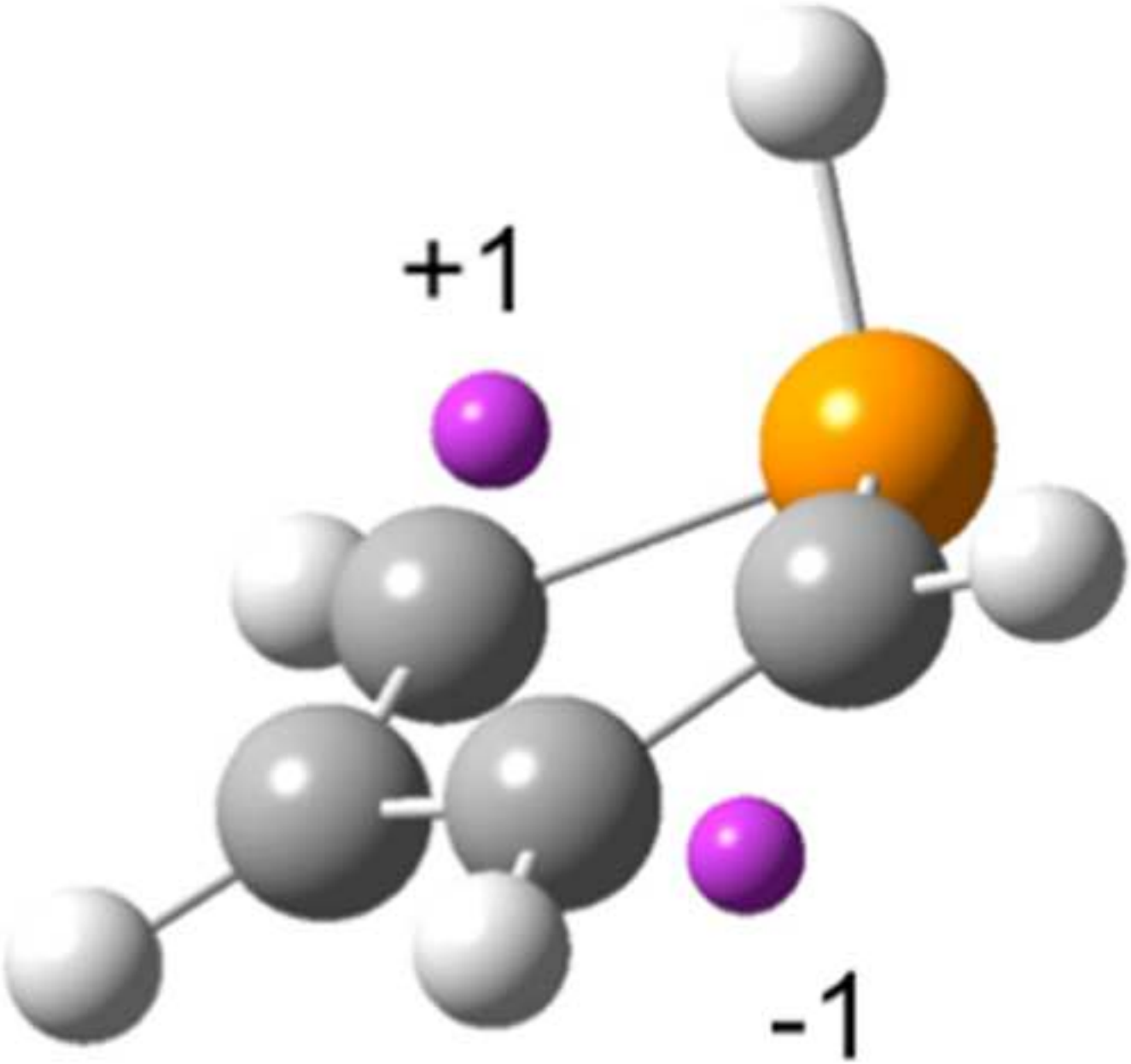

Figure 3

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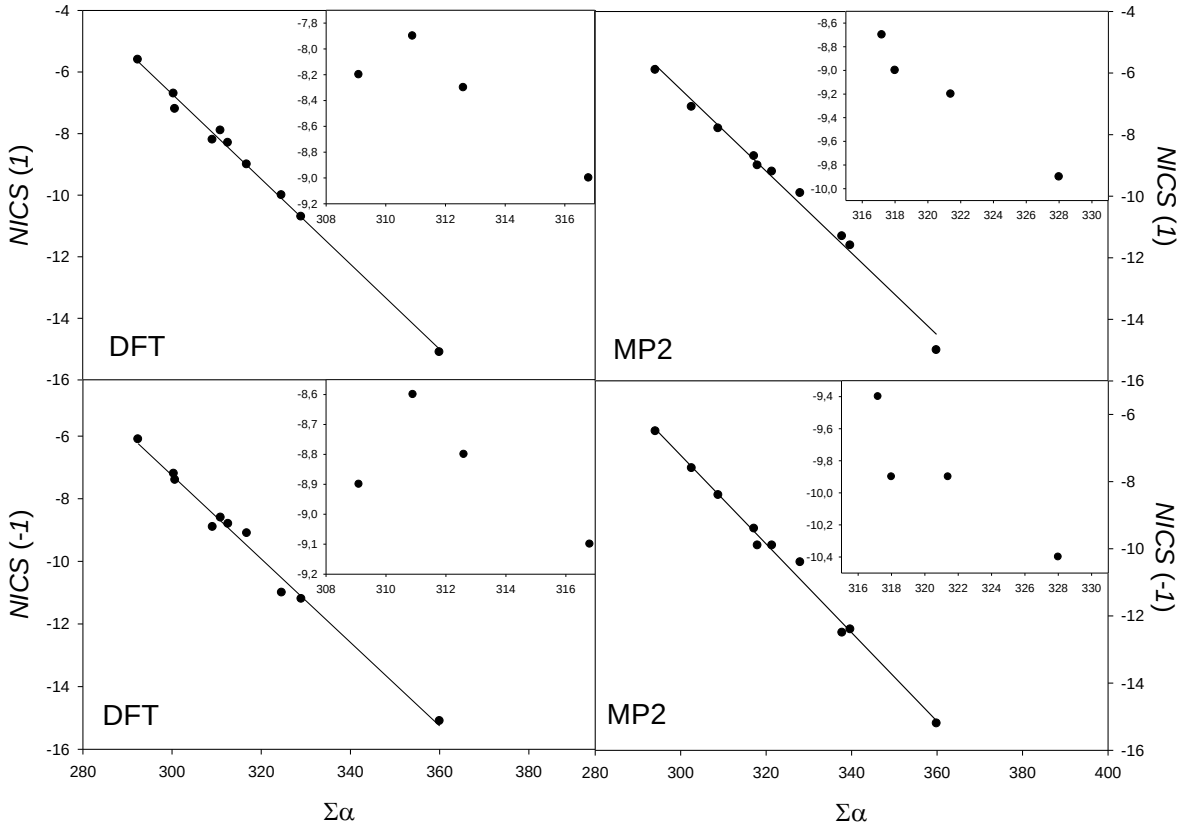
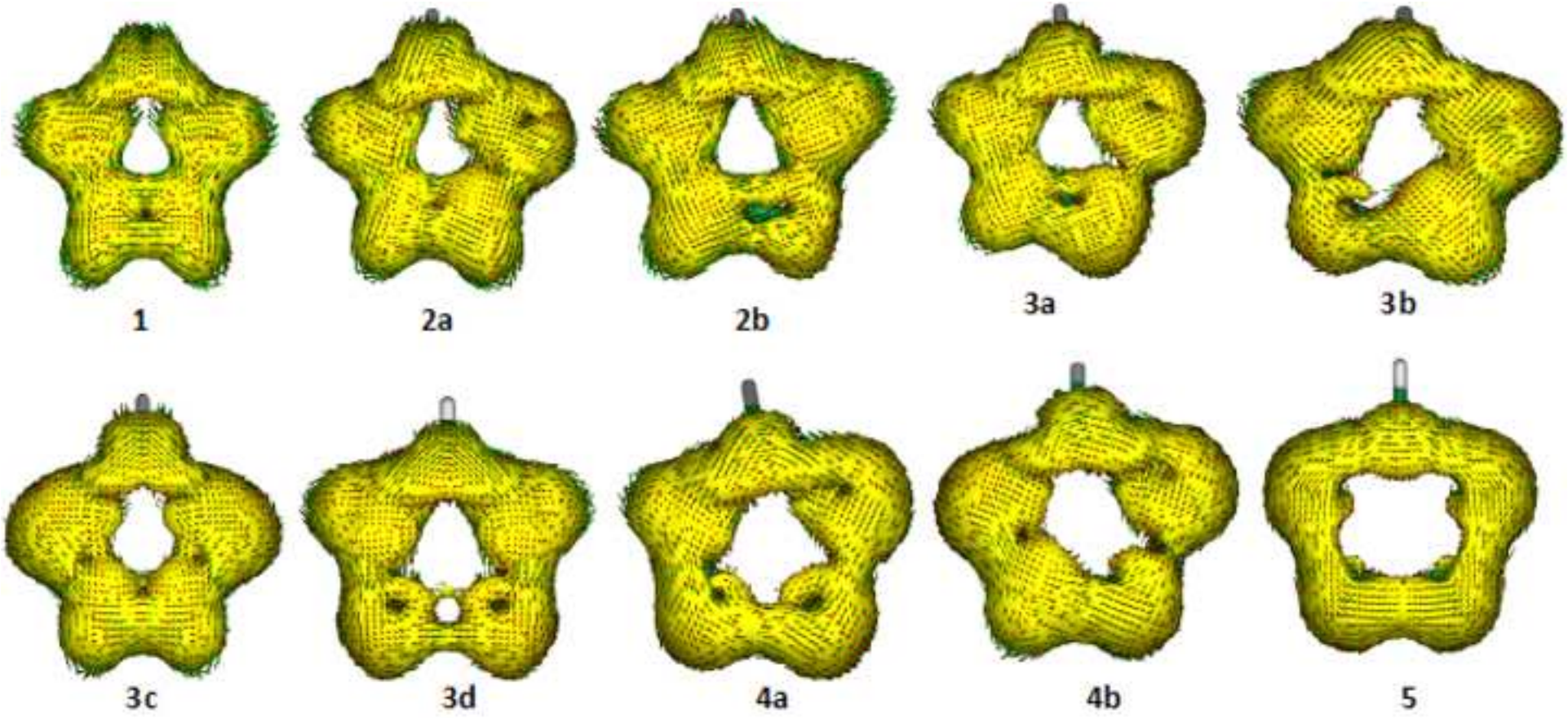
Figure 4
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