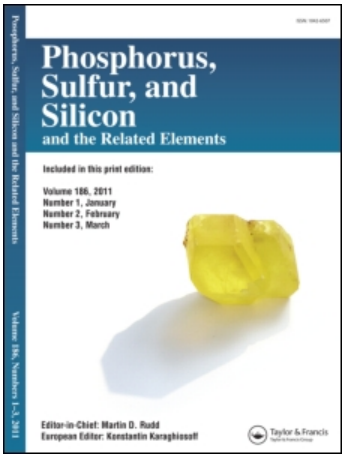


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# The Richness of Structures Available to $P_2N_2$ Inorganic Heterocycles: A Topological and Molecular' Orbital (EHMO) Analysis

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# THE RICHNESS OF STRUCTURES AVAILABLE TO $P_2N_2$ INORGANIC HETEROCYCLES: A TOPOLOGICAL AND MOLECULAR ORBITAL (EHMO) ANALYSIS (Abstract)*

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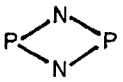
Abstract. A topological analysis, based upon Polya's theorem, was used to calculate all possible isomers of $P_2N_2$ ring derivatives, as a function of the number of substituents attached to phosphorus and nitrogen. The analysis considered four-, five- and six-coordinate phosphorus, and two-, three- and four-coordinate nitrogen. EHMO calculations established the HOMO-LUMO orbitals and the charges of variously substituted $P_2N_2$ heterocycles.



## INTRODUCTION

The four-membered ring containing alternating phosphorus and nitrogen atoms :

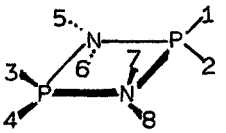



is the skeleton of a great diversity of heterocycles, in which phosphorus can be two-, three-, four-, five- and six-coordinate.

## THE TOPOLOGICAL ANALYSIS

### a) Rings containing two-, three-, four-coordinate phosphorus

In a planar $P_2N_2$ ring, with eight possible substitution sites:




* The full paper will be published in Revue Roumaine de Chimie.

the stepwise occupation of these eight sites leads to a number of ring systems which can be calculated using Polya's theorem[1] and an algoritm suggested by Dolhane[2]. The results are given in Table 1.

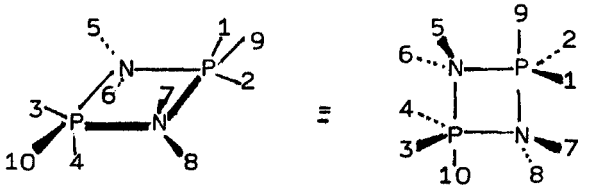
Table 1 Number of cyclic species derived from $P_2N_2$

| Number of substituents | Number of ring systems |
|---|---|
| 0 | 1 isomer |
| 1 | 2 isomers |
| 2 | 8 " |
| 3 | 10 " |
| 4 | 16 " |
| 5 | 10 " |
| 6 | 8 " |
| 7 | 2 " |
| 8 | 1 " |

Mono- and di-substituted species are not reported in the literature, but a three-substituted ring system ( a cation with two organic groups at nitrogen and one at phosphorus) is known.[3] Compounds with four, five and six substituents on the ring are also known.[4]

b) Rings containing five-coordinate phosphorus

These derive from the following skeleton, in which at least three substituents (all at phosphorus sites) are attached to the ring :



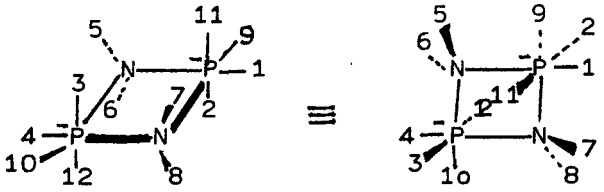

The maximum number of substituents is ten. The number of isomeric structures derived from this unit is shown in Table 2. These include geometrical isomers . Several examples of such compounds are actualy known.[4]

Table 2 Number of cyclic isomers derived from $P_2N_2$ (five coordinate phosphorus)

| Number of substituents | Number of isomers |
|---|---|
| 3 | 1 isomer |
| 4 | 2 isomers |
| 5 | 6 " |
| 6 | 6 " |
| 7 | 6 " |
| 8 | 5 " |
| 9 | 2 " |
| 10 | 1 " |

c) Rings containing six-coordinate phosphorus

The smallest number of occupied sites in this case is four and the full occupation requires 12 substituents, as can be seen from the basic unit :




The number of isomers is shown in Table 3.

Table 3 Number of isomers derived from $P_2N_2$ ring with six-coordinate phosphorus

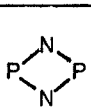
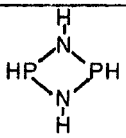
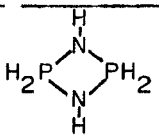
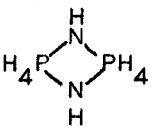
| Number of substituents | Number of isomers |
|---|---|
| 4 | 1 |
| 5 | 2 |
| 6 | 6 |
| 7 | 6 |
| 8 | 9 |
| 9 | 5 |
| 10 | 5 |
| 11 | 2 |
| 12 | 1 |

There are known examples with eigth, ten and twelve substituents in the ring.

## EXTENDED HÜCKEL CALCULATIONS

The extended Hückel method provided molecular orbital energies, and afforded the number of doubly occupied orbitals (DOO) and charge (CH). A selection of examples is given in Table 4.

Table 4 Molecular orbital energies (eV)

| |  |  |  |  |
|---|---|---|---|---|
| 1 | 30.604 | 30.663 | 30.663 | 30.665 |
| 2 | 26.629 | 27.122 | 27.121 | 27.122 |
| 3 | 19.290 | 20.450 | 21.481 | 22.243 |
| 4 | 15.917 | 18.890 | 19.957 | 20.456 |
| 5 | 15.811 | 16.710 | 17.363 | 18.089 |
| 6 | 15.790 | 16.650 | 17.172 | 17.511 |
| 7 | 14.498 | 15.920 | 16.146 | 17.011 |
| 8 | 13.273 | 15.540 | 15.917 | 16.623 |
| 9 | 13.090 | 13.470 | 15.536 | 15.927 |
| 10 | 12.670 | 13.270 | 14.557 | 14.587 |
| 11 | 11.475 | 13.130 | 13.273 | 13.273 |
| 12 | 9.650 | 11.470 | 12.928 | 12.451 |
| 13 | 2.168 | 2.168 | 2.168 | 12.264 |
| 14 | -3.602 | - | - | 11.487 |
| 15 | - | - | - | 11.417 |
| 16 | - | - | - | 11.124 HOMO |
| | | | | LUMO |
| DOO | 10 | 12 | 13 | 15 |
| CH | -4 | 0 | +2 | -2 |

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