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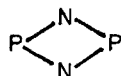
THE RICHNESS OF STRUCTURES AVAILABLE TO P_2N_2 INORGANIC HETEROCYCLES: A TOPOLOGICAL AND MOLECULAR²₂ ORBITAL (EHMO) ANALYSIS (Abstract)*

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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 :

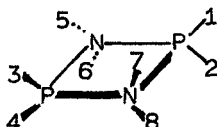


is the skeleton of a great diversity of heterocycles, in which phosphorus can be two-, three-, four-, five- and six-coordinate.

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 theorem¹ and an algorithm suggested by Dolhane². The results are given in Table 1.

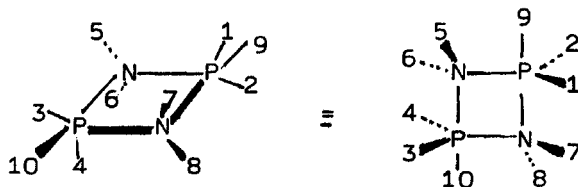
Table 1 Number of cyclic species derived from P_2N_2

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 :



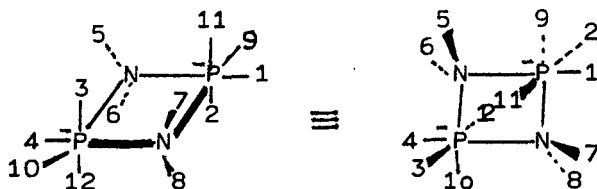
The maximum number of substituents is ten. The number of isomeric structures derived from this unit is shown in Table 2. These include geometrical isomers. Several examples of such compounds are actually known.⁴

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


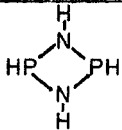
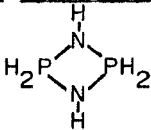
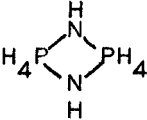
Number of substituents	Number of isomers
4	1
5	2
6	6
7	6
8	9
9	5
10	5
11	2
12	1

There are known examples with eighth, 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
DOO	10	12	13	15	LUMO
CH	-4	0	+2	-2	

REFERENCES

1. A.T. Balaban, Chemical Applications of Graph Theory, Academic Press, London, 1976.
2. H. Dolhane, Computers & Chemistry, **5**, 41 (1981).
3. A.H. Cowley, M. Lattman and J.C. Wilburn, Inorg. Chem., **21**, 2916 (1981).
4. I. Haiduc, The Chemistry of Inorganic Ring Systems, Wiley-Interscience, London, 1970; I. Haiduc and D.B. Sowerby, Eds., The Chemistry of Inorganic Homo- and Heterocycles, Academic Press, London, 1987.