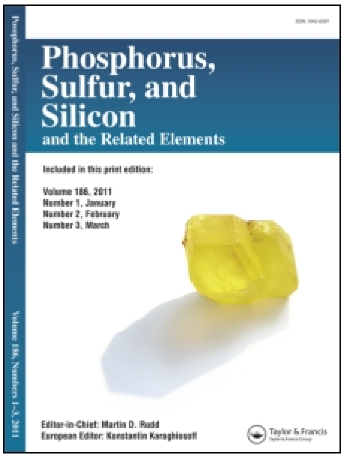


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Seven- and Eight-Membered Ring Conformations of Phosphorus Containing Heterocycles

R. P. Arshinova[a]; A. Ch. Plyamovatyi[a]; R. A. Kadyrov[a]; S. G. Gnevashev[a]; B. A. Arbusov[a]
[a] A. M. Butlerov Scientific Research Chemical Institute, Kazan State University, Kazan, USSR

To cite this Article Arshinova, R. P. , Plyamovatyi, A. Ch. , Kadyrov, R. A. , Gnevashev, S. G. and Arbusov, B. A.(1989) 'Seven- and Eight-Membered Ring Conformations of Phosphorus Containing Heterocycles', Phosphorus, Sulfur, and Silicon and the Related Elements, 41: 3, 449 — 453

To link to this Article: DOI: 10.1080/10426508908039735

URL: http://dx.doi.org/10.1080/10426508908039735

Phosphorus, Sulfur and Silica, Vol. 41, pp. 449–453
Reprints available directly from the publisher
Photocopying permitted by license only

SEVEN- AND EIGHT-MEMBERED RING CONFORMATIONS OF PHOSPHORUS CONTAINING HETEROCYCLES

R. P. ARSHINOVA, A. CH. PLYAMOVATYI, R. A. KADYROV, S. G. GNEVASHEV AND B. A. ARBUSOV
A. M. Butlerov Scientific Research Chemical Institute, Kazan State University, Kazan, USSR

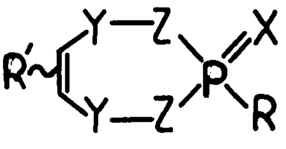
Abstract The conformational behaviour of seven- and eight-membered heterocycles based on their NMR spectrum and on a theoretical investigation is described. All possible basic conformations and their quantitative parameters have been considered. A molecular mechanics approach is applied to the calculation of the multidimensional maps of potential energy dependence on torsional angles.

INTRODUCTION

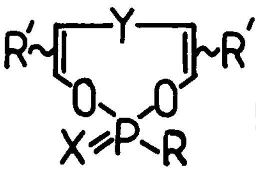
The conformational study of 7- and 8-membered cycles has been reported in great detail only for hydrocarbon ring compounds.[1] In comparison, relatively little is known about heterocyclic systems, although there have been a range of reports on their synthesis and three-dimensional structure. At the same time extensive studies have been done on both carbocyclic and inorganic 6-membered ring systems. The analysis of these results allowed us to deduce that the introduction of heteroatoms might bring a significant change in conformational behaviour. Though the conformational complexity increases rather dramatically with increasing ring size, it is interesting to investigate the structural differences between organic and inorganic ring systems of more than six members. This paper describes the conformational analysis of a series of 7- and 8-membered heterocycles.

Taking into account that the construction of a planar fragment (double bond (a,b), annulated benzene (c) or naphthyl rings

(d) etc.) in a saturated cycle reduces the conformational flexibility and the number of possible conformers, we facilitated our structural search by choosing unsaturated systems with different planar fragments and tri- and tetracoordinated phosphorus atoms in the ring (I) and (II). This enabled us to determine the effects of planar fragments, endocyclic heteroatoms and exocyclic substituents at phosphorus on the molecular conformations.



(I) Y,Z: CH_2,O,S



(II) Y: CH_2, $SiMe_2$

a, b, c, d

RESULTS AND DISCUSSION

There are two kinds of approaches for the quantitative description of ring conformations. In the first, we considered a set of a few canonical conformations on the basis of a torsion angle sign analysis and evaluated their relative energies. In the second, N-membered ring conformations were characterized by means of N-3 parameters calculated from the displacements of ring atoms from the ring mean plane,[2,3] the latter being used for the calculation of puckering parameters q_m and ψ_m. We have used the first description for saturated 8-membered systems, and the second one for unsaturated molecules (I) and (II).

Let us discuss conformations of 7-membered compounds (Ia)-(Ic). Using the second approach, the following set of four canonical conformations is defined: chair (C), boat (B), twist (T), and twist-boat (TB).[4]

C

B

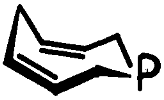
T

TB

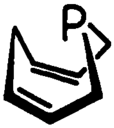
In order to determine the preferred solution state molecular conformation the results on canonical conformations are compared with the experimental data (^{1}H NMR, IR and Raman spectroscopy, dipole moments, X-ray data). They can be interpreted by considering for benzo- derivatives of 1,3,2-dioxaphosphepines (Ic) e-C $\rightleftharpoons$ T $\rightleftharpoons$ a-C equilibrium (a,e designating axial and equatorial position of R-substituents on phosphorus), while derivatives with a double bond in the ring (Ia), (Ib) adopt [T] form, where [T] is the T or TB form. The latter is the more stable according to molecular mechanics (MM) calculations,[5] however, it is difficult to distinguish between them using the above mentioned physical methods. We give here a general designation for them as [T]. 2-Phenyl-5,6-benzo-1,3,2-dioxa- and dithiaphosphepines and 6,7-benzo-1,3,5-dioxaphosphepines with different substituents on P^{IV} are characterized by equilibrium between two chair conformations. As to the orientation of exocyclic substituents on phosphorus, the tendency found for similar six-membered cycles is kept, e. g., substituents with R = AlkO, ArO prefer axial position while others NR_2 with R = Ar are situated in an equatorial site. This tendency is less manifest and that is why the three-component equilibrium a-C $\rightleftharpoons$ [T] $\rightleftharpoons$ e-C is observed for 2-methoxy-5,6-benzo-1,3,2-dioxaphosphepines with P^{III} (X is lone pair) and P^{IV} atom (X is O or S).

Investigation of a wide range of compounds permits us to elucidate the factors stabilizing particular conformations. The structure of 7-membered heterocycles with one planar fragment generally is determined by its nature: the introduction of a double bond into the ring stabilizes [T] -form, while the replacement of it by benzene stabilizes the C-conformer.

Applying the second approach to an 8-membered system (II) has for the first time made it possible to describe the set of ring structures that can be realized in these species, define them quantitatively, introduce a unified terminology, and through that give a general analysis of conformational data for this type of compound.[4,6] Calculations have shown that compounds may have the four canonical conformations: boat-chair (BC), boat-boat (BB), deformed boat (B) or twist-boat (TB).

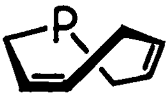


BC



BB

B



TB

The torsion angles around ring bonds and the Cremer-Pople puckering parameters for P^{III} and P^{IV} derivatives were listed earlier.[4,6] The replacement of a bridged CH_2 group by $SiMe_2$ or S groups does not considerably alter these parameters, so they may be used as quantitative criteria for conformational assignment of various kinds of heterocyclic 1,4-cyclooctadiene derivatives.

More than ten compounds that have been investigated in the crystalline state, and by using their calculated parameters, an assignment of conformation could be made. The molecules have both the BC- or deformed B-forms. Expanding the endocyclic angle of the bridged group between two arylene rings promotes the appearance of the T-conformer.[4] The analysis of 1,3,2-dioxaphosphocines (IIc) and (IId) spectral characteristics allowed us to draw conclusions on their three-dimensional structure.[6] In phosphites of series (IIc) two forms, e-BC and a-BC, are in equilibrium, the percentage of the a-BC conformer diminishes for the following R: Cl, OPh, OAr, ONf, NR_2, OEt. The e-BC conformer is also predominant in the P^{IV} compound with R=NEt_2 and X=S. However, when R = OEt the amount of the e-BC conformer decreases drastically and the favourable conformation is a-B. The 2-hydro-2-oxo- and 2-chloro-2-thiono-1,3,2-dioxaphosphocines involve a three-component equilibrium e-BC $\rightleftharpoons$ a-BC $\rightleftharpoons$ e-B with a mixture ratio 10:43:47 and 73:23:4. The presence of two bulky naphthyl fragments in series (IId) destabilizes the BC- form and therefore, the compounds typically exist as B-conformers. Their exocyclic substituent orientations depend on the substituent nature. It seems that the 1,3,2,6-dioxaphosphasilocines (Y = $SiMe_2$) (IIc) are also represented by the same equilibrium between e-B and a-B forms.

To conclude our work on the 8-membered ring conformations 2-R-thiono-1,3,2,6-dioxaphosphazocanes with saturated rings. We carried out MM calculations and obtained multi-dimensional maps of potential energy dependence on torsional angles. From this procedure, conformational energies have been found. Local minima are consistent with 39 conformations. Among them, only the BC-forms a family in full conformational variety. The most stable is the BB-conformer with one of the oxygen atoms in the flagstaff position. In each form, the preferable orientation of P=S bond is axial, and the value of the anomeric effect is determined to be about 1.2 kcal/mole. We did not find the whole range of strained conformations (TC, C, or B) to be favorable for hydrocarbon cycles. The stabilization of the CC-conformation in the crystalline state is obviously connected with the effect of crystal packing.

The present results establish that the ground-state structure and relative conformational energies differ substantially between hydrocarbon and inorganic rings.

REFERENCES

1. U. Burkert and N. L. Allinger, Molecular Mechanics, (ACS Monograph No. 177, 1982).
2. D. Cremer, and J. A. Pople, J. Amer. Chem. Soc., 97, 1354 (1975).
3. V. A. Palyulin, V. E. Shklover, Yu. T. Struchkov and N. S. Zefirov, J. Mol. Struct., 70, 65 (1981).
4. R. P. Arshinova, R. A. Kadyrov and B. A. Arbusov, Zh. Obshch. Khim., 56, 1457 (1986).
5. A. Ch. Plyamovatyi, R. R. Shagidullin, I. Ch. Shakirov and R. P. Arshinova, Izv. AN SSSR. Ser. Khim., 1817 (1986).
6. R. P. Arshinova, O. I. Danilova and B. A. Arbusov, Phosphorus and Sulfur, 34, 1 (1987).