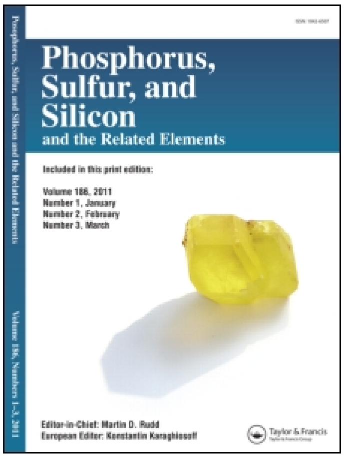

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COMPARATIVE PM3-MO STUDY OF THE E_2O_2 AND E_2N_2 (E=P,As) FOUR MEMBERED RING SYSTEMS.

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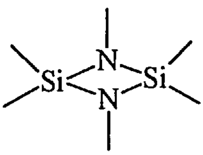
It seems that the relative stability of the E_2O_2 and E_2N_2 (E=P,As) rings is mainly determined by the different weights of the oxygen and nitrogen p orbitals to the HOMO's of these systems which in turn reflects a more favourable orbital mixing in the rings where the difference of the electronegativity of the constituents is smaller.This might explain the great diversity of the cyclodiphosphazane (arsazane) rings comparatively to the cyclodiphosphoxane (arsoxane) rings.

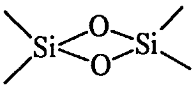
Keywords: cyclodiposphazanes, cyclodiphosphoxanes, cyclodiarsoxanes, cyclodiarsazanes, PM3 molecular orbital calculations.

INTRODUCTION

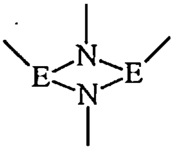
Contrastingly to the great variety of cyclodisilazanes[1] (**a**), cyclodisiloxanes (**b**) have only a few well characterized reprezentatives[2]. Similar observation holds for cyclodiphosph(III)azanes[3] (**c**) and cyclodiphosph(III)oxanes[4] (**d**) and also for the cyclodiars(III)azane-cyclodiars(III)oxane (**e**,**f**) pairs as well[5].



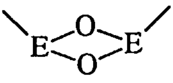
a



b



c (E=P)
e (E=As)



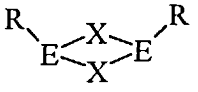
d (E=P)
f (E=As)

Based on qualitative molecular orbital arguments we have shown[6] that the main difference between (**a**) and (**b**) comes from the shape and relative composition of their HOMO orbitals. In this paper we use the results of the semiempirical PM3 molecular orbital method to get further insight into the bonding of the (**c-f**) cyclic systems. The preference for one of the *cis* or *trans* isomers of **c-f** will be discussed and a possible explanation for the above mentioned contrasts will be stressed on the basis of orbital interactions in these systems.

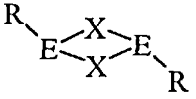
PM3 molecular orbital calculations[7] have been carried out with full optimisation of the geometry for $(REO)_2$ and $(RENH)_2$ (E=P,As,R=H, CH_3,CF_3,F,Cl) by using the PC version of the MOPAC6 package[8].

RESULTS AND DISCUSSION

Depending on the position of the R groups toward the mean plane of the ring, the $(REX)_2$ systems have two possible conformations: *cis* (g) and *trans* (h)



g



h

Table I lists the enthalpies of formation of the $(REX)_2$ (E=P, As R= H, CH_3, CF_3, F, Cl) dimers, the difference between the enthalpies of formation of the *cis* and *trans* conformers ($\Delta H = H^f_{cis} - H^f_{trans}$) and the enthalpies of dimerization ($\Delta H_{dim} = H^f_{(REX)2} - 2H^f_{REX}$) of the presumable precursors, R-E=X of these rings.

TABLE I PM3 calculated enthalpies of formation (kcal/mol) of $(REX)_2$ systems and related data.

R		CH_3	H	CF_3	F	Cl
$(RPO)_2$	*cis*	-173.59	-147.81	-441.84	-328.72	-229.07
	trans	-171.83	-146.72	-441.77	-327.51	-230.59
	$\Delta H_{dim.}$	-81.59	-87.73	-74.08	-80.74	-76.81
	ΔH	-1.76	-1.09	-0.07	-1.21	1.52
$(RAsO)_2$	*cis*	-96.90	-73.47	-342.61	-214.44	-138.95
	trans	-93.46	-71.02	-342.48	-212.61	-137.54
	$\Delta H_{dim.}$	-85.76	-90.13	-77.91	-83.34	-81.65
	ΔH	-3.44	-2.45	-0.13	-1.83	-1.41
$(RAsNH)_2$	*cis*	-16.22	8.74	-274.90	-134.07	-65.29
	trans	-13.03	9.34	-267.63	-128.08	-60.47
	$\Delta H_{dim.}$	-75.89	-77.73	-72.56	-74.54	-74.17
	ΔH	-3.19	-0.60	-7.27	-5.99	-4.82

With one exception [$(ClPO)_2$], these data show a slight preference for the *cis* conformation for all rings and all substituents investigated. Similar results have been obtained earlier in the study of cyclodiphosphazanes by using both MNDO and RHF/3-21G* molecular orbital treatments[9]. It seems thus that there might be an inherent thermodynamic preference of these four membered rings for the *cis* conformation of the substituents on the heavier elements. Note also the somewhat larger ΔH values for the arsenic containing rings than for those containing phosphorus.

This behaviour can be understood by a simple model which takes the interaction of an E_2X_2 bare ring with a pseudomolecule R..R (Figure 1).

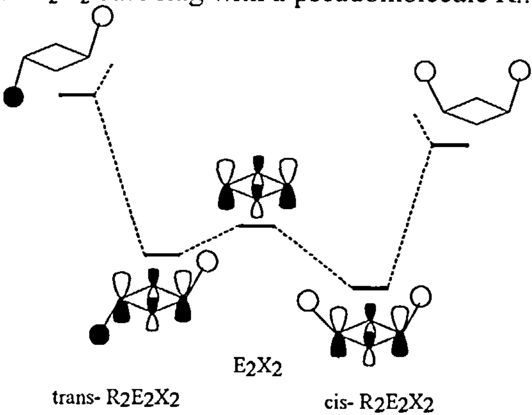


FIGURE 1 The interaction diagram between the HOMO orbital of a bare E_2X_2 (E=P,As) ring and an R...R pseudomolecule.

Due to the lower energy of the in-phase combination of the σ orbitals of R in the *cis* conformation, the bonding interaction with the HOMO orbital of the E_2X_2 systems is better (Figure 1 right) than in the *trans* conformation (Figure 1 left) and the HOMO of the $(REX)_2$ system goes lower for the *cis* than for the *trans* conformers. The HOMO energies listed in Table II support this model. Thus, if the R groups interact with their σ type orbitals, the *cis* conformation will be always preferred over the *trans* one. R ligands bearing also occupied π type orbitals have a more subtle effect on the conformations[9] and this might be responsible for the inversion noticed above for the chlorine which is predicted to adopt *trans* positions in $(ClPO)_2$.

TABLE II The HOMO energies of $(REX)_2$ systems (eV)

R	CH_3	H	CF_3	F	Cl
$(RPO)_2$ *cis*	-8.49	-7.99	-10.12	-9.68	-9.80
trans	-8.20	-7.93	- 9.83	-9.23	-9.52
$(RAsO)_2$ *cis*	-9.85	-9.00	-10.70	-10.48	-9.85
trans	-9.52	-8.97	-10.41	-9.98	-9.52

Since a less electronegative element has higher contribution to the HOMO of the E_2X_2 system, it follows that the HOMO of the naked As_2X_2 ring interacts better with the R groups than that of the P_2X_2 rings and hence the larger (absolute) ΔH values for the arsenic than for phosphorus compounds (Table I). This is again reflected in the lower energies of the HOMO for $(RAsX)_2$ than for $(RPX)_2$ (Table II). Electronegativity differences suggest also a greater weight of the nitrogen orbitals (in P_2N_2) than of oxygen orbitals (in P_2O_2) to the HOMO of the bare P_2X_2 ring. This means that the corresponding bonding π orbital is more stabilised for X=N than for X=O and one might expect better bonding interactions in cyclodiphosphazane than in cyclodiphosphoxane rings. Similarly, the bonding in cyclodiarsazanes should be more favourable than in cyclodiarsoxanes.

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