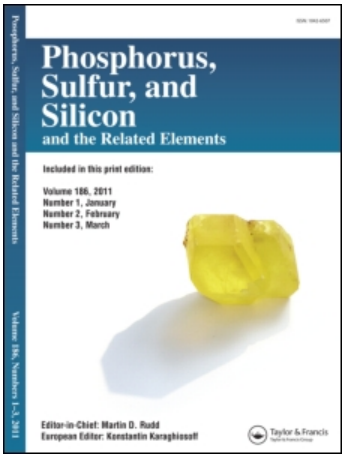

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Orbital Isomerism in the 1.3-Dphosphacyclobutane-2.4-Diyl, Quantum Chemical Investigations at MCSCF Level

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ORBITAL ISOMERISM IN THE 1.3-DIPHOSPHACYCLOBUTANE-2.4-DIYL, QUANTUM CHEMICAL INVESTIGATIONS AT MCSCF LEVEL

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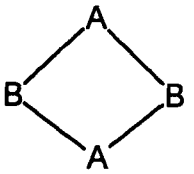
Abstract Quantum chemical calculations at open shell level (MCSCF, MP2, CISD) indicate the strong biradical nature of the title compound which is isoelectronic to the well known S_2N_2.

The delocalization of six π-electrons in a four-membered ring heterocycle has been well documented for disulfur nitride S_2N_2, 1 (A = S, B = N). Likewise for isoelectronic compounds structures have been discussed which appear to allow π-electron delocalization[1]. The first species of this type was recently synthesized and structurally characterized[2], 1 = A_2B_2 [A = Cl, B = PR, R = 2,4,6-tri-tert-butyl-phenyl].



1

Quantum chemical calculations at ab initio level and explicit electron correlation treatment (MCSCF, MP2) on the title compound, phosphetane and 1,3-diphosphetane reveal sizable energy barriers for inversion at phosphorus, making a conjugative π-delocalization of the lone pair at phosphorus within the ring system unlikely. Considerable biradical character is assigned to the energy lowest singlet state (C_i symmetry, ^1A_g), slightly below in energy with respect to the triplet state (^3A_u) and depending on the basis set and the chosen CI level (MRCI, MP4SDTQ etc., $\Delta E < 10$ kcal/mol). Substituent effects cause only a slight variation of energy differences. The title compound is an orbital isomer[2] to its bicyclic structural isomer diphosphabicyclobutane, which is lower in energy. An orbital crossing inhibits facile ring closure reaction of the former to the latter structural isomer.

References.

1. G. van Zandwijk, R.A. J. Jansen, H.M. Buck, *J. Am. Chem. Soc.*, 112 (1990) 4155. R.A. Janssen, *J. Phys. Chem.*, 97 (1993) 6384.
P.H.M. Budzelaar, D. Cremer, M. Wallasch, E.-U. Würthwein, P.v.R. Schleyer, *J. Am. Chem. Soc.*, 109 (1987) 6290.
2. E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, W.W. Schoeller, *Angew. Chem. Intern. Ed. Engl.*, 34 (1995) 555.