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Orbital Isomerism in the 1,3-Diphosphacyclobutane-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

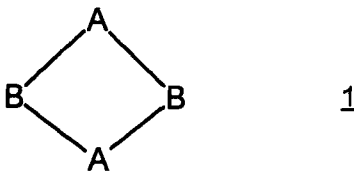
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Abstract Quantum chemical calculations at open shell level (MCSCF, MP2, CISD) indicate the strong biradical nature of the title compound which is isoelectronic to the well known S_2N_2 .

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 delocalization¹. The first species of this type was recently synthesized and structurally characterized², **1** = A_2B_2 [A = Cl, B = PR, R = 2,4,6-tri-tert-butyl-phenyl].



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_g) 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 isomer² 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.

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