

MOLECULAR, CRYSTAL AND ELECTRONIC STRUCTURE OF 2,2,4,4-TETRACHLORODIPHOSPHETANES

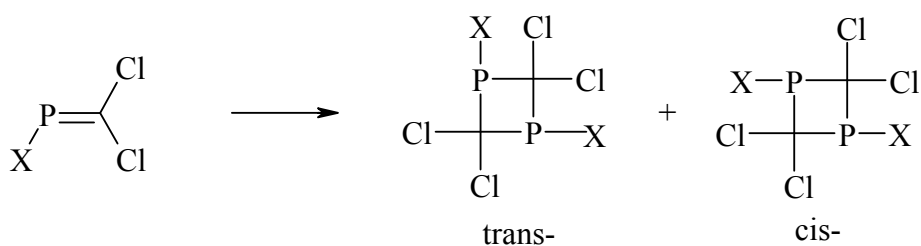
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The number of 2,2,4,4-tetrachlorodiphosphetanes (products of dimerization of kinetically unstable phosphalkenes) has been synthesized and characterised by ¹H, ¹³C, and ³¹P NMR spectroscopy and X-ray diffraction method.



X= H, Me, Et, iPr, tBu, F, Cl, Br

It has been observed that in solution diphosphetanes exist as a mixture of *trans*- and *cis*-isomers. Relation of isomers strongly depends on the substituent X nature (e.g. 96% of *trans*-isomer at X = t-Bu, and only 50% at X = Me). Moreover, it has been discovered existence of two forms of *cis*-isomers (*cis-cis* and *cis-trans*). The main peculiarities and characteristic features of molecular and electronic structure of the system investigated have been discussed on the basis of *ab initio* (RHF and DFT/6-31+G**) calculations. It has been found that *cis*- and *trans*-isomers have very close ground state energy, whereas *trans-cis* activation barrier is relatively high (e.g. 42 kcal/mol for (HPCH₂)₂).