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Theoretical Modeling of the Diphosphene (HP=PH) Ligand

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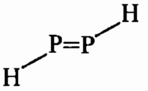
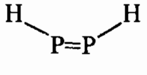
There are now several examples of compounds in which diphosphenes (RP=PR) function as η^2 ligands toward transition metals [1–4]. Moreover, the introduction of sterically demanding substituents has permitted the recent isolation of uncoordinated diphosphenes [5–11]. In view of this current interest in phosphorus–phosphorus double bonds, we report the first use of *ab initio* molecular orbital theory[**] to investigate the ground state geometry, orbital compositions, and some force constants for the prototype ligand, HP=PH.

Using the 44-31G basis set without configuration interaction (CI), we find the *trans* isomer, (*I*) (E_T = –681.74134 a.u.), to be 2.70 kcal/mol[†] more stable than the *cis* isomer, (*II*) (E_T = –681.73705 a.u.).



(*I*)



(*II*)

The computed metric parameters for (*I*) are r_{PP} = 2.121 Å, r_{PH} = 1.444 Å, and $\angle$HPH = 95.4°, while those for (*II*) are r_{PP} = 2.122 Å, r_{PH} = 1.445 Å, and $\angle$HPH = 100.4°. In view of the existence of low-lying excited states (diphosphenes are yellow-orange colored), we decided to perform CI calculations on (*I*) and (*II*). Use of the 44-31G basis set together with 7262 configurations resulted in (a) a small increase in the *trans*/*cis* energy difference (2.77 kcal/mol), and (b) geometry-optimized structures with smaller PPH angles and slightly larger P–P and P–H bond lengths for both isomers: (*I*), (E_T = –681.90186 a.u.) r_{PP} = 2.187 Å, r_{PH} = 1.469 Å, $\angle$HPH = 93.9°; (*II*) (E_T = –681.89744 a.u.) r_{PP} = 2.191 Å, r_{PH} = 1.470 Å, and $\angle$HPH = 98.9°. The *trans* isomeric preference computed for HP=PH agrees with the experimental data for $(2,4,6\text{-(t-Bu)}_3\text{-}C_6H_2)P{=}P(2,4,6\text{-(t-Bu)}_3C_6H_2)$ (*III*) (r_{PP} = 2.034(2) Å, $\angle$PPC = 102.8(1)°) [5] and $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (*IV*) (r_{PP} = 2.004(6) Å, $\angle$PPC = 108.9(4)°) [11]. Use of the 44-31G* basis set, which features *d*-type functions on phosphorus, produces a more satisfactory P=P bond length for (*I*) (r_{PP} = 1.992 Å, $\angle$HPH = 95.3°). The fact that the PPC bond angles in (*III*) and (*IV*) are larger than the HPH angle in (*I*) is presumably a consequence of steric interactions.

The molecular orbitals of (*I*) are also of interest. The two highest occupied MO's $2a_u$ (–9.23 eV) and $7a_g$ (–9.52 eV) are closely spaced and correspond to the P–P π-bond and (n_+) phosphorus lone pair combination respectively. The $2b_g$ orbital (+0.26 eV) possesses appreciable P–P π^* character and is the LUMO. The calculation of a low-lying LUMO for (*I*) is consistent with the observation that (*III*) undergoes facile one-electron reduction to produce the corresponding anion radical [6, 7] and suggests the importance of metal(nd)-π^* back donation in the η^2-binding of diphosphenes to transition metals.

The Hartree-Fock computed P–P and P–H stretching force constants for (*I*) are 3.66 and 2.86 mdyn/Å, respectively. The computed P=P stretching frequency for (*I*) is thus 633 cm^{-1}. This vibration, being of A_g symmetry, should be Raman-active, but I.R.-inactive for *trans*-HP=PH. To the best of our knowledge, no experimental data are available for the P=P stretching frequencies of diphosphenes.

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[**] The equilibrium geometries of *cis*- and *trans*-diphosphene were optimized by the gradient method [P. Pulay, G. Fogarasi, F. Pang and J. E. Boggs, *J. Am. Chem. Soc., 101,* 2550 (1979); P. Pulay, *Chem. Phys. Lett., 73,* 393 (1980)]. The *ab initio* Hartree Fock gradient program, Texas [P. Pulay, *Theo. Chim. Acta, 50,* 299 (1979)] was used for the SCF-MO calculations. A program developed by Professor H. F. Schaefer, III and co-workers was employed and included all single- and double-configurations for the CI calculations. The 44-31G basis set was taken from the literature [see R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys., 54,* 724 (1971) for hydrogen, and W. J. Hehre and W. A. Lathan, *J. Chem. Phys., 56,* 5255 (1972) for phosphorus]. The *d*-type functions for the 44-31G* basis set were also taken from the literature [W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc., 104,* 5039 (1982) and M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys., 77,* 3654 (1982). We are indebted to Professor Schaefer for permission to use his CI gradient program.

[†] 1 cal = 4.184 J.

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