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Multireference Perturbation Based Quantum Chemical Investigation on Isomerization Alley of Diphosphorous Compounds

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Abstract

Methodological advances and their mathematical applications are a progressive field of study in the area of electronic structure theory dominated by molecular systems having 'quasidegeneracy'. The recently proposed Improved Virtual Orbital State Specific Multi Reference Perturbation Theory (IVO-SSMRPT) has been progressively developed into an advantageous ab initio instrument for analysing electronic states with systems prone to static and dynamic electronic correlations. This method is an alluring substitute to the broadly used MRPT methodologies and it can dodge various challenges faced by the traditional MRPTs. Even at the twisted molecular levels, IVO- Brillouin-Wigner (BW)- MRPT provides a dependable picture of quasi-degeneracy among occupied and unoccupied orbitals. The competence of IVO-SSMRPT has been explored here using highly correlated electronic systems impending from isomerization of diphosphorous compounds. IVO-SSMRPT method mimics the findings of modern age state-of-the-art methods but with depreciated computational accomplishment.

Keywords: *Ab Initio Methods; Barrier Height; Improved Virtual Orbitals; Isomerization Energy; Multireference Theory*

Introduction

Theoretical study of molecular systems having two phosphorus atoms is an arduous assignment. Analysis of these molecular systems turns into an important subject due to the miscellaneous utilizations in material science. The reactivity of diphosphenes is always an appealing dispute for both the branches of experiment and theory. It calls attention to the synthetic chemists as they are responsive to a diverse spectrum of reagents (Geoffroy *et al., 1992;* Binder *et al.,* 1996*;* Ito *et al.,*1986*;* Shah *et al.,* 2000). Diphosphenes are more inclined to reduction process than olefins or other azo compounds (Ito & Nagase,1986).

Unique photochemical behaviours shown by both diphosphines and diphosphinylidene are worth exploring in divergent field of organometallics (Pikies *et al*., 2004). Even, PP bonded molecular systems have been efficiently used in chemical hydrogen storage (Matus *et al.*, 2007). The chemical isolation process of these species is a tricky job as they have tendencies to polymerization due to thermodynamic control (Shah *et al.,* 2000). Over the last few years, P=P compounds have been combined into their conjugated counterpart to make constituent elements of molecular electronics. It is worth mentioning that for

diphosphene like systems, the PP bond distance remains in the range of 2.00 to 2.034 Å and it bears harmonic vibrational frequencies around 610 cm^{-1}. These signify the existence of a P=P double bond (Weber, 1992; Tokitoh, 2000; Hamaguchi *et al.*, 1984). Attempts have been made to study the diphosphene and diphosphinylidene class of compounds theoretically (Matus *et al.*, 2007; Ito & Nagase,1986; Tongxiang *et al.*, 2009; Allen *et al*., 1986; Lu *et al.*, 2010; Vogt-Gessie & Schaefer III, 2012; Allen *et al.*, 1990).

A depiction of the isomerization pathways of the quintessential P-P bonded compounds like diphosphinylidene (PPH_2) and diphosphene (HPPH) was extensively studied using IVO-SSMRPT formulation with minimal model space (Sinha Ray, 2020). Particular emphasis was granted to study both the transition states (TS) of two distinct isomerization pathways. The portrayal of electronic framework of TSs is usually tormented by quasidegeneracy, possessing various leading components in the total wave function. Thereby, the single reference method fails abruptly. The transition states highly need a MR study in a more notable pathway than the ground states. T_1 diagnostic test of Coupled cluster method (Lee & Taylor, 1987) shows a moderate MR character of *cis* and *trans* HPPH. Higher T_1 value of PPH_2 demonstrates higher MR nature. Maximum value of the T_1 diagnostic indicating highest MR character is due to TS between *trans* HPPH and planar PPH_2. Among the broadly applied MR methodologies, MRPT is at the arena of the techniques of selection (Chatttopadhyay *et al.,* 2016). Complete Active Space Self Consistent Field (CASSCF) is an extensively used technique to build up the unperturbed basis function in MR-correlated computations like SSMRPT method as primarily introduced by Mukherjee and co-workers (Sinha Mahapatra, 1999; Evangelista *et al.*, 2009).

But CASSCF frequently attracts problems like convergence failure, multiple solution etc. A substitute to this problem has been developed as IVO-SSMRPT method (Sinha Ray *et al.*, 2016; Sinha Ray *et al.*, 2017) and it has been widely accepted in electronic structure theory. Study on t*rans*- and *cis*-HPPH and planar PPH_2 systems with IVO-SSMRPT (Sinha Ray, 2020) is worth mentioning in this context. Results due to other *state-of-the-art* methods like State specific Multi Reference Coupled Cluster (SS-MRCC aka Mk-MRCC) (Mahapatra *et al*., 1998; Evangelista *et al*., 2006; Evangelista *et al*., 2007), Coupled Cluster Single Double and perturbative Triple (CCSD(T)) and Multi Reference Configuration Interaction (MRCI) and values are available due to the work of Schaefer and co-workers (Tongxiang *et al.*, 2009; Allen *et al*., 1986).

Results and Discussion

Correlation consistent quadruple zeta valence (cc-pVQZ) basis (Dunning Jr, 1989) has been used and have been implemented from the EMSL database (*https://bse.pnl.gov/bse*). CAS (m,n) expresses 'm' number of electrons, which are distributed in 'n' number of orbitals. For all IVO-SSMRPT cases, CAS(2,2) space has been utilised.

Trans-HPPH: Figure 1 reveals the optimized geometries of trans HPPH molecule. The structure is C_{2h} having ^1A_g symmetry. Due to the presence of bond between two phosphorous elements, its molecular framework like the P-P bond nature is appealing (Power, 2004). P-P bond length lies in the range of 2.024 Å to 2.054 Å. CAS(2,2) consists of

highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) having symmetries of a_u and b_g respectively [see Figure 4].

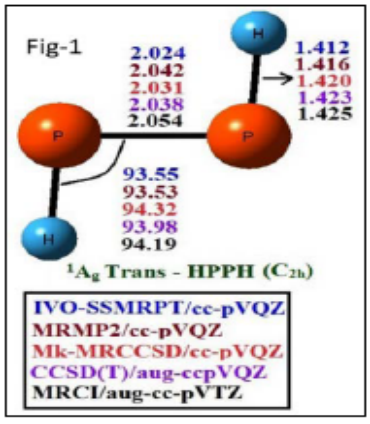

Figure 1: Geometrical Parameters of the Trans HPPH. Bond Lengths are in Angstroms (Å) and Angles are in Degrees (°)(Sinha Ray, 2020)

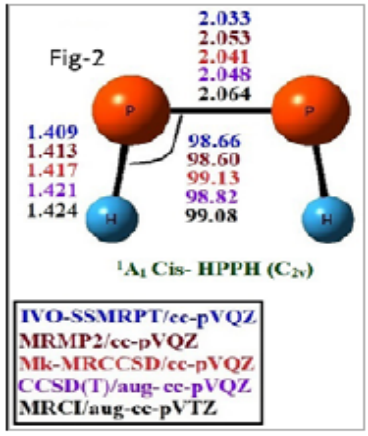

Figure 2: Geometrical Parameters of the Cis HPPH. Bond Lengths are in Angstroms (Å) and Angles are in Degrees (°) (Sinha Ray, 2020)

Cis-HPPH: Cis isomer of diphosphene has been optimized at A_1 symmetry of C_{2v} point group [see Figure 2]. The IVO-SSMRPT values are in well accord with the CCSD(T), MRMP2, Mk-MRCCSD and MRCI studies. The P-P bond length increases significantly from the trans isomer. Figure 4 describes the $2b_1$ (π) as HOMO and the $2a_2$ (π^*) as LUMO of the cis isomer.

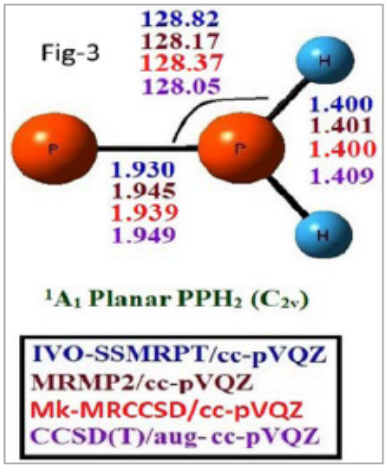

Figure 3: Geometrical Parameters of the Planar PPH_2. Bond Lengths are in Angstroms (Å) and Angles are in Degrees (°) (Sinha Ray, 2020)

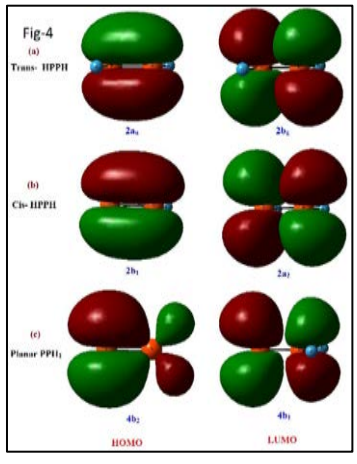

Figure 4: HOMO and LUMO of (a) Trans HPPH, (b) Cis HPPH and (c) Planar PPH^2 (Sinha Ray, 2020)

Diphosphinylidene (planar PPH_2): Another type of bonding pattern is shown in PPH_2 having $^1A_1$ symmetry at planar C_{2v} structure [see in Figure 3]. Here the P-P bond length is much shorter than both the cis and trans diphosphene anticipating a strong double bond nature. This structure also displays a greater dipole moment than the cis counterpart. HOMO and LUMO are b_2 and b_1 respectively.

TS connecting trans HPPH and planar PPH_2:This TS is found to be of singlet in nature having C_1 symmetry [Figure 5]. Analogous molecular prototypes like NPH_2 and SCH_2 show prominent 1,2 hydrogen shift (Nguyen & Ha,1989). In the TS, it is proposed that the migrating hydrogen atom behaves like a proton. The $P_1P_2H_2$ angle is calculated at 47.45 degree by IVO-SSMRPT which is almost half of the trans isomer (i,e, 93.55 degree) confirming the migration of the H atom (marked as H_2) over the P-P bond and also formation of a three-centered bond as also predicted by Schaefer III and co-workers (Tongxiang *et al.*, 2009).

TS connecting trans and cis HPPH: Trans-cis conversion of HPPH can be reached via two discrete pathways – torsional movement about P-P bond and the inversion via a linear P-P-H bond. First process is accepted due to the lower energy barrier. The TS is analysed to be in a singlet state with C_2 symmetry. The dihedral angle is found to be around 90 degree [see Figure 6] which indicates the halfway between trans and cis minima.

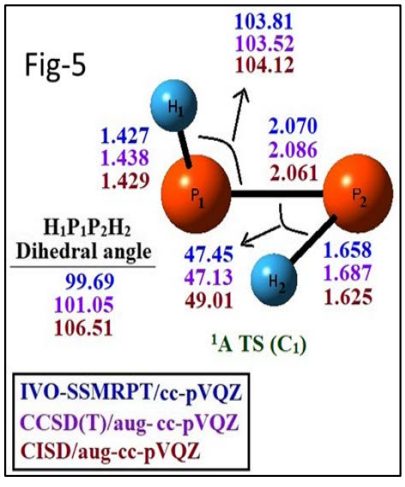

Figure 5: Geometrical Parameters of the TS between the Trans HPPH and Planar PPH2 Isomers. Bond Lengths are in Angstroms (Å) and Angles are in Degrees (°) (Sinha Ray, 2020)

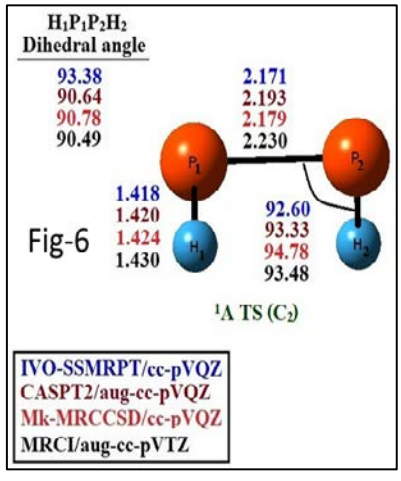

Figure 6: Geometrical Parameters of the TS between the Trans and Cis HPPH Isomers. Bond Lengths are in Angstroms (Å) and Angles are in Degrees (°) (Sinha Ray, 2020)

Relative energies and Barrier height: Geometrical optimization confirms that the trans HPPH has the lowest energy among all the isomers. In Table 1 the relative energies of other minima are represented. The 'gold standard' of quantum chemistry, CCSD(T) method indicates the geometrical isomerization energy to be 3.38 kcal/mol as compared to the 3.85 value of IVO-SSMRPT.

For structural isomerization alleyway between trans HPPH to planar PPH_2, the required energy is 24.89 which is in close proximity with the CCSD(T) estimate of 25.28 kcal/mol.

Table 1 : Relative Energies (in kcal/mol) of Different Local Minima as Compared to Global Minimum (trans-HPPH) Reflected by Different Level of Methods (Sinha Ray, 2020).

Method	Basis set	ΔE_{cis}	ΔE_{planar}
IVO-SSMRPT	cc-pVQZ	3.85	24.89
CCSD(T)	cc-pVQZ	3.38	25.28
Mk-MRCCSD	cc-pVQZ	3.32	---
MRCI	aug-cc-pVTZ	3.34	---

Table 2 : Energy Barriers (in kcal/mol) of Geometrical and Structural Isomerization Depicted Via Different Level of Methods (Sinha Ray, 2020)

Method	Basis set	TS between trans HPPH and Planar PPH_2	TS between trans HPPH and cis HPPH
IVO-SSMRPT	cc-pVQZ	51.00	39.96
CCSD(T)	cc-pVQZ	50.50	35.19
Mk-MRCCSD	cc-pVQZ	---	35.19
MRCI	aug-cc-pVTZ	----	35.05

The energy barriers related to two disparate isomerization pathways are furnished in Table (2). Trans HPPH to planar PPH_2 has a potential barrier of around 50 kcal/mol whereas the energy barrier for HPPH to cis HPPH is predicted around 35 kcal/mol. The geometrical isomerization is assuredly more attainable having lower barrier height.

Conclusion

IVO-SSMRPT deals with the two distinct isomerization paths of molecules involving two phosphorus atoms. Isomerization energy and barrier height by IVO-SSMRPT have been computed and correlated with many other refined *ab initio* approaches. The work paves the way to the use of the very promising perturbative protocol i.e. IVO-SSMRPT with very low computational cost towards the simulation of isomerization pathways containing systems with arbitrary interplay of static and dynamic electron correlation effects.

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