Tetrahedron Letters,Vol.25,No.31,pp 3321-3324,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

ab initio CALCULATIONS OF ISOMERIZATION REACTION OF DIPHOSPHENE 1-SULFIDE TO THIADIPHOSPHIRANE

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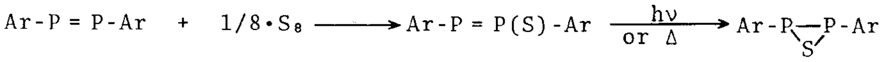
ab initio Calculations of the isomerization reaction of diphosphene 1-sulfide (**2'**) to thiadiphosphirane (**3'**) suggest that the energy barrier of the reaction in the ground state is 25 kcal/mol and that **2'** lies 21 kcal/mol above **3'**, while the calculations show that there exists one local minimum on the lowest triplet energy surface.

We reported that bis(2,4,6-tri-t-butylphenyl)diphosphene (**1**) reacts with one equivalent of sulfur to give the diphosphene monosulfide (**2**) which isomerizes thermally or photochemically to the corresponding thiadiphosphirane (**3**).[1] The X-ray crystallography of **1**,[2] **2**,[1] and **3**[3] indicated striking features that the o-t-butyl groups in these molecules protect each reactive site very nicely with an accompanying rotation of the phenyl rings. It should be noted that the sulfur atom in **2** is located on the CPPC plane defined by two ipso-carbons of the aryl groups and two double bonded phosphorus atoms but that the PSP plane in **3** is perpendicular to the CPPC plane.



$$\text{Ar-P=P-Ar} + 1/8\cdot S_8 \longrightarrow \text{Ar-P=P(S)-Ar} \xrightarrow[\text{or }\Delta]{h\nu} \underset{\text{S}}{\text{Ar-P—P-Ar}}$$

(**1**) [Ar = 2,4,6-$Bu^t_3C_6H_2$] (**2**) (**3**)

We now report our preliminary results on ab initio calculations of this interesting isomerization reaction. In the calculations, each aryl group was replaced by hydrogen atom for the simplification of the system as has been applied for diphosphene (**1'**)[4] (Fig. 1). The calculations were performed for the ground and lowest triplet states starting from the ground states of both **2'** and **3'**. The geometries were optimized by the energy gradient method using 3-21G[5] + polarization functions (3-21G*) on both sulfur (0.6) and phosphorus (0.5) atoms. The energies of stationary points were recalculated at 6-31G**[6] (exponent 1.1 on hydrogen atom).[7] To obtain better energetics for the ground state, GVB-(5)$_{pp}$[8] calculations were carried out with this 6-31G** basis set at SCF/3-21G*-optimized geometries.

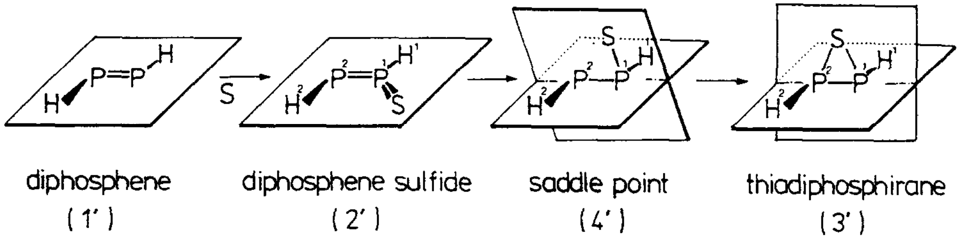


Fig. 1. Schematic drawings of the isomerization reaction of **2**' to **3**'.

Table 1 shows the results on the optimized geometries of the reactant and product together with those at a saddle point (transition state). The calculated ground-state geometries (bond lengths and angles) agree well with the experimental values for **2** and **3**, taking steric repulsion caused by the extraordinarily bulky groups into account. A hypervalent P-S bond in **2**' can be formed by the donation from the σ-type phosphorus lone pair to the vacant 3p orbital of the sulfur atom and the back donation from the 3p π-orbital of the sulfur atom to the π* orbital of the P=P part. The predicted saddle-point structure in the ground state (**4**') lies in the middle location between **2**' and **3**' but is rather close to **3**'. One might expect that the transition state is located in an early stage of the reaction, as has been proposed for exothermic reactions,[9] however, **4**' is rather contrary to this prediction:[10] the P^1-S bond length, SP^{1}P^2 bond angle, and H^{2}P^2-P^{1}S dihedral angle change very much, whereas the P^1-P^2 bond length remains unaltered during the process from **2**' to **4**'. Furthermore, it should be noted that the P^2···S distance does not change very much from **2**' (3.618 Å) to **4**' (3.100 Å) compared with that from **4**' to **3**' (2.117 Å). It is interesting to mention that the HPPH plane is almost maintained (174.1°) even in **4**'. However, this planarity could be deformed by the steric hindrance between the bulky aryls in the actual isomerization reaction, **2** to **3**. A sulfur atom might approach to the less hindered site of one of the phosphorus atoms along the CPPC plane in **1** to give **2** and then the sulfur atom in **2** shifts vertically accompanied with rotation of the phenyl rings to avoid steric hindrance during the isomerization to **3**.

The calculated SCF and GVB energies of the ground state are shown in Table 2. At all levels of theory the energy separation between monosulfide (**2**') and thiadiphosphirane (**3**') consistently lies in the range of 19 - 21 kcal/mol. But, the energy barriers of the rearrangement **2**' → **3**' and **3**' → **2**' are reduced to 24.8 and 45.3 kcal/mol, respectively, by the GVB calculations. A favorable phase relation in **4**' is shown in the right.[11] Although these values should be taken only semiquantitatively, one can say that the reverse reaction **3**' → **2**' does not occur. This is consistent with the experimental fact.[3]

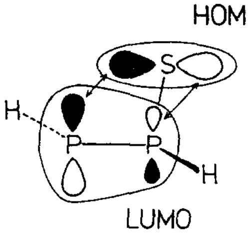


Table 3 shows the calculated energies for the lowest triplet states: the $^3A'$ and $^3A''$ states of **2**' are the (π → π*)

Table 1. Computed geometries for H_2P_2S isomers.

Diphosphene monosulfide (C_s): **2**'			Thiadiphosphirane (C_2): **3**'		
P^1P^2	1.993 Å	(2.054(2) Å)[a]	P^1P^2	2.176 Å	(2.249(3) Å)[b]
P^1S	1.907 Å	(1.931(2) Å)[a]	P^1S	2.117 Å	(2.103(3) Å)[b]
P^1H^1	1.391 Å		P^1H^1	1.405 Å	
P^2H^2	1.406 Å		P^2P^1S	59.08°	(57.7(1)°)[b]
P^2P^1S	136.11°	(129.0(1)°)[a]	$H^1P^1P^2$	95.56°	(106.7(1)°)[b]
$H^1P^1P^2$	107.63°	(106.1(1)°)[a]	H^1P^1S	98.43°	(99.9(2)°)[b]
$H^2P^2P^1$	94.20°	(99.9(1)°)[a]			

Saddle point (C_1): **4**'				Lowest triplet state (C_1): T_1[c]			
P^1P^2	2.053 Å	P^2P^1S	97.59°	P^1P^2	2.194 Å	P^2P^1S	105.92°
P^1S	2.068 Å	$H^1P^1P^2$	100.90°	P^1S	2.046 Å	$H^1P^1P^2$	98.86°
P^1H^1	1.401 Å	$H^2P^2P^1$	93.72°	P^1H^1	1.407 Å	$H^2P^2P^1$	93.50°
P^2H^2	1.399 Å	$SP^1P^2H^2$	60.92°[d]	P^2H^2	1.399 Å	$SP^1P^2H^2$	65.99°[d]
		$SP^1P^2H^1$	113.20°[d]			$SP^1P^2H^1$	106.08°[d]

a) Obsd (**2**): H^1 and H^2 should read ipso-carbons of the Ar groups; data taken from Ref. 1. *b*) Obsd (**3**): H^1 and H^2 should read ipso-carbons of the Ar groups; data taken from Ref. 4. *c*) Optimized structure of the lowest triplet state, see also Table 3. *d*) Dihedral angle.

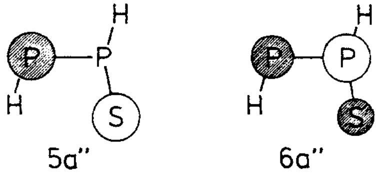
Table 2. SCF and GVB total energies and ΔE values for the lowest singlet states.

Species	State	SCF/3-21G* (a.u.)	ΔE (kcal/mol)	SCF/6-31G** (a.u.)	ΔE (kcal/mol)	GVB/6-31G** (a.u.)	ΔE (kcal/mol)
2'	$^1A'$	-1074.9700	0.0	-1080.0912	0.0	-1080.1557	0.0
3'	^1A	-1075.0009	-19.4	-1080.1241	-20.7	-1080.1884	-20.5
4'	S_0	-1074.9025	42.4	-1080.0263	40.7	-1080.1162	24.8

Table 3. SCF total energies and VE values for the lowest triplet states.

Species	State	3-21G*(a.u.)	VE (kcal/mol)	6-31G**(a.u.)	VE (kcal/mol)
2'	$^3A'$	-1074.9242	28.8	-1080.0469	27.8
	$^3A''$	-1074.8833	54.4	-1080.0067	53.1
3'	^3A	-1074.8527	92.9	-1079.9779	91.8
	^3B	-1074.8403	100.8	-1079.9655	99.6
T_1	^3A	-1074.9728	----	-1080.0974	----

and ($n_S \rightarrow \pi^*$) states, respectively. The ^3A state of 3' corresponds to the excitation from the lone pair orbital of the sulfur atom to the P-S antibonding orbital. The vertical excitation energy (VE) of the $^3A'$ of 2' is small (27.8 kcal/mol) compared with ^3A of 3', because the 5a'' orbital is nonbonding orbital. We find only one local minimum (T_1) on the lowest triplet energy surface, the structure of which is very similar to that at the ground-state saddle point (4') except for the P^1-P^2 distance ($S \cdots P^2$, 3.386 Å). The planarity of the HPPH moiety is also maintained (172.0°) similarly to 4'. The deformation to this structure is understandable by assumption of the singly occupied molecular orbitals: the 5a'' orbital has no amplitude on P^1, while 6a'' has large amplitude on P^1. According to Walsh's rule,[12] the excitation from 5a'' to the 6a'' orbital leads to a bent-out plane of the P^1SH^1 part. Furthermore, the antiphase combination of 6a'' on P^1 and P^2 atoms gives rise to lengthen the P-P distance.



If the reaction, 2' $\rightleftarrows$ 3', proceeds on the lowest triplet surface, the intersystem crossing to the ground-state surface would also afford the isomerization product. The reverse reaction, 3' → 2', might not occur even in the lowest triplet state, because the large excitation energy of the ^3A state in 3' is required.

The authors thank the Computer Center, Institute for Molecular Science, Okazaki, Japan, for the use of a HITAC M200H computer and the Library Programs IMSPACK written by Prof. K. Morokuma and his coworkers (IMS) and GAMESS written by Dr. M. Dupuis (NRCC).

References

1. M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Chem. Soc., Chem. Commun., 1983, 862; Heterocycles, 22, 681 (1984).
2. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Am. Chem. Soc., 103, 4587 (1981); 104, 6167 (1982).
3. M. Yoshifuji, K. Ando, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, Angew. Chem., Int. Ed. Engl., 22, 418 (1983).
4. M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita, and K. Nishimoto, J. Am. Chem. Soc., 105, 2495 (1983).
5. M. S. Gordon, S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, J. Am. Chem. Soc., 104, 2797 (1982).
6. M. M. Francl, W. J. Pietro, W. J. Hehre, S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, J. Chem. Phys., 77, 3654 (1982).
7. P. C. Hariharan and J. A. Pople, Theor. Chim. Acta, 28, 213 (1973).
8. F. W. Bobrowicz and W. A. Goddard, "Method of Electronic Structure Theory," Ed. by H. F. Schaefer, Plenum, New York (1977), Chap. 7.
9. G. S. Hammond, J. Am. Chem. Soc., 77, 334 (1955).
10. Y. Osamura, J. D. Goddard, H. F. Schaefer, and K. S. Kim, J. Chem. Phys., 74, 617 (1981). We should reserve quantitative discussion on the energy and structure of the real transition state of isomerization of 2 to further experimental and theoretical studies.
11. K. Fukui, "Theory of Orientation and Stereoselection," Springler-Verlag, New York (1975).
12. A. D. Walsh, J. Chem. Soc., 1953, 2260.

(Received in Japan 26 March 1984)