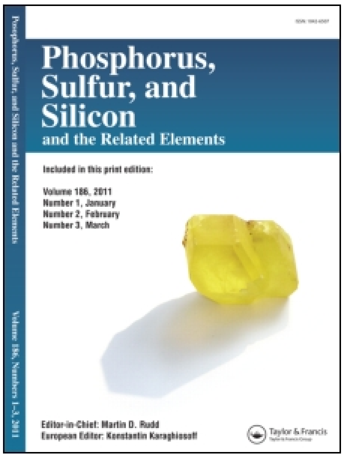

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PM3 STUDY OF PHOSPHINES AND PHOSPHINE CHALCOGENIDES. CONFORMATIONAL AND CONFIGURATIONAL PROPERTIES OF TRI-*O*-TOLYL PHOSPHINE AND ITS CHALCOGENIDES

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PM3 STUDY OF PHOSPHINES AND PHOSPHINE CHALCOGENIDES. CONFORMATIONAL AND CONFIGURATIONAL PROPERTIES OF TRI-*O*-TOLYL PHOSPHINE AND ITS CHALCOGENIDES

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An investigation employing the PM3 semiempirical self-consistent field molecular orbital method to calculate structure optimization and pyramidal phosphorus atom inversion barriers for phosphines and phosphine chalcogenides **1–16** has been undertaken. The calculated structural parameters (for **1–12**) and inversion barriers (for **13–16**) are in good agreement with experimental results. The conformational interconversion pathways for tri-*o*-tolylphosphine (**9**), tri-*o*-tolylphosphine oxide (**10**), tri-*o*-tolylphosphine sulfide (**11**) and tri-*o*-tolylphosphine selenide (**12**) were investigated in detail. For compounds **9–12**, four rotamers are possible with respect to the position of the methyl groups. In the most stable geometry of **9**, two of the methyl groups are close to the phosphorus lone pair. In **10**, the methyl groups assume the paddle conformation, having all methyl groups close to the oxygen atom. In **11**, the most stable rotamer is similar to that in **9**. In the most stable rotamer of **12**, all methyl groups are far from the selenium atom.

Keywords: Phosphine; Stereochemistry; Semiempirical calculations; conformational analysis; Pyramidal inversion

INTRODUCTION

Phosphorus compounds of the type PX_3 and PX_3Y with X = H, alkyl, aryl, halogen, and Y = O, S, or Se, have attracted interest particularly because

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* To receive any Correspondence.

there exists the possibility of charge transfer within the P-Y linkages[1,2]. The distance between the atoms of a given type are found to vary, with differences reflecting both the number and electronegativities of other atoms bonded to phosphorus atom. Thus, the P-F bonds in PF_3 are longer than in POF_3 and the P-O bond in the latter is shorter than in $POCl_3$[3,4]. There have been a number of experimental and theoretical studies on the conformations of tertiary phosphine oxides. The conformations about the PC bond of trialkylphosphine chalcogenides have been examined using various physical techniques[1–4].

While, the *ab initio* calculations have been reported for simple phosphines[3,4], computational limitations restricted detailed studies of geometry and conformational features of arylphosphines. Inversion barriers in phosphines and the factors affecting the size of the barriers were also discussed in earlier studies[3–7]. In particular, the much larger barrier to inversion in phosphines than in amines has been explained.

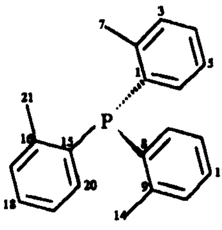
We wish to report a Parametric Method Number 3 (PM3)[8] study of phosphines and phosphine chalcogonides **1–16**. The equilibrium geometries of **1–16** are calculated for comparison with the electron diffraction results[9–11] and X-ray structural data[12–16]. Detailed semiempirical self-consistent field (SCF) molecular orbital (MO) calculations on the ground-state geometries, conformational and configurational interconversion pathways in tri-*o*-tolylphosphine (**9**) and its chalcogenides **10–12** are also reported.

PROCEDURE

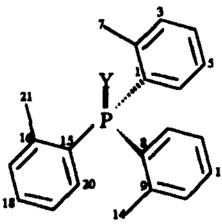
Semiempirical calculations were carried out using the PM3 method[8] with the MOPAC 6.0 program[17,18] implemented on a VAX 4000–300 computer. Energy-minimum geometries were located by minimizing the energy with respect to all geometrical coordinates, and without imposing any symmetry constraints. The structures of the transition-state geometries were obtained using the optimized geometries of the equilibrium structures according to the procedure of Dewar *et al*[19] (using the keyword SADDLE). The configurational racemization energy barriers for P-C bond rotation pathways were estimated by reaction coordinate procedure. All structures were characterized as stationary points, and true local

$R_3P = Y$

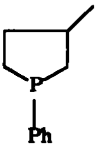
	R	Y
1	CH_3	-
2	CH_3	O
3	CH_3	S
4	CH_3	Se
5	C_6H_5	-
6	C_6H_5	O
7	C_6H_5	S
8	C_6H_5	Se



9



10, Y = O
11, Y = S
12, Y = Se



13

$(Me)(C_6H_5)(t\text{-}Bu)P$ **14**

$(Me)(C_6H_5)(o\text{-}CH_3\text{-}C_6H_4)P$ **15**

$(Me)(C_6H_5)(CH_2{=}CHCH_2)P$ **16**

energy-minima and energy-maxima on the potential energy surface were found using the keyword FORCE. All energy-minimum and energy-maximum geometries obtained in this work were calculated to have 3*N*-6 and 3*N*-7 real vibrational frequencies, respectively[20,21].

TABLE I Calculated and experimental (electron diffraction, ED, and X-ray) structural parameters (bond lengths, r in Å; bond angles, θ in degrees) in some phosphines (R_3P) and phosphine chalcogenides ($R_3P = Y$; $Y = O$, S, or Se)

Compound	*Method*	*r (P=Y)*	*r (P-C)*	*θ (YPC)*	*θ (CPC)*
$(CH_3)_3P$ (**1**)[a]	PM3	–	1.87	–	101
	ED	–	1.85	–	99
$(CH_3)_3P{=}O$ (**2**)[b]	PM3	1.48	1.82	115	104
	ED	1.48	1.81	114	104
$(CH_3)_3P{=}S$ (**3**)[b]	PM3	1.94	1.83	116	102
	ED	1.94	1.82	114	105
$(CH_3)_3P{=}Se$ (**4**)[c]	PM3	2.10	1.83	115	104
	ED	2.09	1.82	114	105
Ph_3P (**5**)[d]	PM3	–	1.86	–	103
	X-ray	–	1.83	–	103
$Ph_3P{=}O$(**6**)[e]	PM3	1.56	1.83	114	105
	X-ray	1.48	1.80	112	107
$Ph_3P{=}S$ (**7**)[f]	PM3	1.96	1.83	114	104
	X-ray	1.95	1.82	113	106
$Ph_3P{=}Se$ (**8**)[g]	PM3	2.11	1.80	113	106
	X-ray	2.11	1.83	113	106
(*o*-Me-$C_6H_4)_3P$ (**9**)[h]	PM3	–	1.87	–	104
	X-ray	–	1.84	–	102
(*o*-Me-$C_6H_4)_3P{=}O$ (**10**)[h]	PM3	1.51	1.83	113	106
	X-ray	1.47	1.81	113	106
(*o*-Me-$C_6H_4)_3P{=}S$ (**11**)[h]	PM3	1.97	1.84	113	105
	X-ray	1.95	1.82	113	106
(*o*-Me-$C_6H_4)_3P{=}Se$ (**12**)[h]	PM3	2.12	1.82	113	106
	X-ray	2.12	1.83	113	106

a. Ref.[9].
b. Ref.[10].
c. Ref.[11].
d. Ref.[13].
e. Ref.[14].
f. Ref.[15].
g. Ref.[16].
h. Ref.[12].

RESULTS AND DISCUSSION

Simple phosphines and phosphine chalcogenides

Trimethylphosphine (**1**) and trimethylphosphine chalcogenides (**2–4**) have been the subject of electron diffraction studies. The X-ray crystallographic results are available for triphenylphosphine (**5**) and tri-*o*-tolylphosphine (**9**) and their chalcogenides (**6–8** and **10–12**). In order to guage PM3 reliability for the phosphines and phosphine chalcogenides, we have optimized the geometry of compounds **1–12** without restriction. As shown in Table I, the agreement between the experimental data and the calculated quantities is generally quite good.

Dynamic NMR spectroscopic results for pyramidal phosphorus atom inversion have been reported for some suitably substituted phosphines. The calculated and experimental results for pyramidal phosphorus atom inversion in phosphines **13–16** are shown in Table II. The agreement between calculated and experimental quantities is fairly good.

TABLE II Calculated and Experimental (Dynamic NMR) barriers for pyramidal inversion in some phosphines (kJ mol^{-1})

Compound	*PM3*	*Experimental*
P(Me)(Ph)(t-Bu) (**13**)	139.5	137[a]
P(Me)(Ph)(MeO-C_6H_4) (**14**)	138.6	129[a]
P(Me)(Ph)($CH_2CH=CH_2$) (**15**)	142.6	135[a]
3-Methyl-1-phenylphospholane (**16**)	156.6	150[b]

a. Ref.[7].
b. Ref.[6].

Tri-o-tolyl-phosphine (9)

The conformational possibilities available to **9** are four energy-minimum rotamers and three distinct energy-maximum geometries. The energy surface for the interconversion of energy-minimum conformations of **9** was investigated in detail by changing different torsional angles (see Figure 1).

By changing $\phi_{14,10,1,2}$ from −88° to 35° a smooth change occurred leading to a transition state [**9**-TS(A)] which is 11.6 kJ mol^{-1} higher in energy

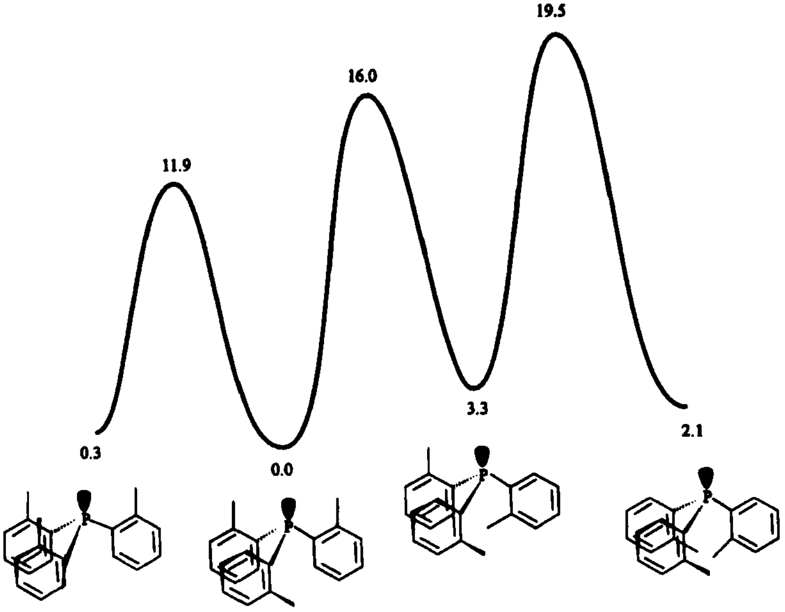


FIGURE 1 Calculated strain energy (kJ mol^{-1}) profile for conformational interconversion of tri-*o*-tolylphosphine (**9**)

than **9**-↑↑↑ rotamer. Upon further change of the same torsional angle, another energy-minimum conformation (**9**-↑↑↓) was obtained, which is the most stable geometry of **9**. In this conformation, two of the methyl groups are on the same side of with the phosphorus lone-pair. By changing $\phi_{12,9,1,2}$ and $\phi_{3,2,1,9}$, respectively, two other rotamers (**9**-↑↓↓ and **9**-↓↓↓) were obtained. The results of semiempirical PM3 calculations for various molecular geometries of tri-*o*-tolylphosphine (**9**) are shown in Figure 1 and Table III.

Tri-o-tolylphosphine chalcogenides (10–12)

Altoghether seven geometries were found to be important for a description of the conformational features of tri-*o*-tolylphosphine oxide (**10**), sulfide (**11**) or selenide (**12**). Four of these geometries correspond to energy minima and three are energy maxima as shown in Figures 2–4 and Tables IV–VI. In the most stable rotamer of tri-*o*-tolylphosphine oxide (**10**-↑↑↑)

the methyl groups in each molecule are close to the phosphoryl oxygen atom. By changing $\phi_{16,15,P,1}$ a conformational change occurred leading to a transition state **10**-TS(A), which is 14.9 kJ mol^{-1} higher in energy than **10**-↑↑↑. Upon further changing the same torsional angle, another energy-minimum geometry (**10**-↑↑↓) was obtained. By changing $\phi_{19,8,P,1}$ and $\phi_{O,,P,1,2}$, conformational changes occurred leading to other rotamers, namely, **10**-↑↓↓ and **10**-↓↓↓ (see Figure 1). The calculated energy barriers for interconversion of these conformations, are 14.9, 13.6, 19.3 kJ mol^{-1}, respectively.

TABLE III Calculated heats of formation (kJ mol^{-1}) and selected structural parameters (bond lengths r in Å bond angles θ and dihedial angles ϕ in degrees) for tri-*o*-tolylphosphine (9)

Feature	9-↑↑↑	*9-TS(A)*	9-↑↑↓	*9-TS(B)*	9-↑↓↓	*9-TS(C)*	9-↓↓↓
ΔH°_f	306.4	318.0	306.1	322.1	309.4	325.6	308.2
$\Delta\Delta H^\circ_f$[a]	0.3	11.9	0.0	16.0	3.3	19.5	2.1
Dipole (D)	0.12	0.26	0.33	0.52	0.69	0.85	0.93
$r_{P\text{-}C1}$	1.87	1.87	1.87	1.86	1.87	1.88	1.87
$r_{P\text{-}C8}$	1.87	1.89	1.87	1.88	1.87	1.87	1.87
$r_{P\text{-}C15}$	1.87	1.88	1.87	1.87	1.87	1.87	1.87
$\theta_{8,P,15}$	102	108	106	105	104	106	107
$\theta_{1,P,15}$	102	101	103	103	105	106	107
$\theta_{1,P,8}$	102	103	103	108	107	110	107
$\phi_{P,15,16,21}$	2	10	3	−1	−1	11	6
$\phi_{P,1,2,7}$	3	1	−3	−9	−4	2	6
$\phi_{P,8,9,14}$	2	−3	−4	6	6	11	6

a. The standard strain energy in each geometry of a molecule is defined as the difference between the standard heats of formation (ΔH°_f) for that geomety and the most stable conformation of the molecule [22].

The most stable conformation of **11** and the starting geometry for semiempirical calculations, has two of the methyl groups in the same side of the molecule with the sulfur atom. The energy barriers for interconversion of various conformations of **11** are 10.9, 5.7, 20.9 kJ mol^{-1}, respectively. Therefore, the energy barrier required for interconversion of these conformations are quite low and the geometry having two methyl groups up and one methyl group down is the most stable conformation (see Figure 3 and Table V).

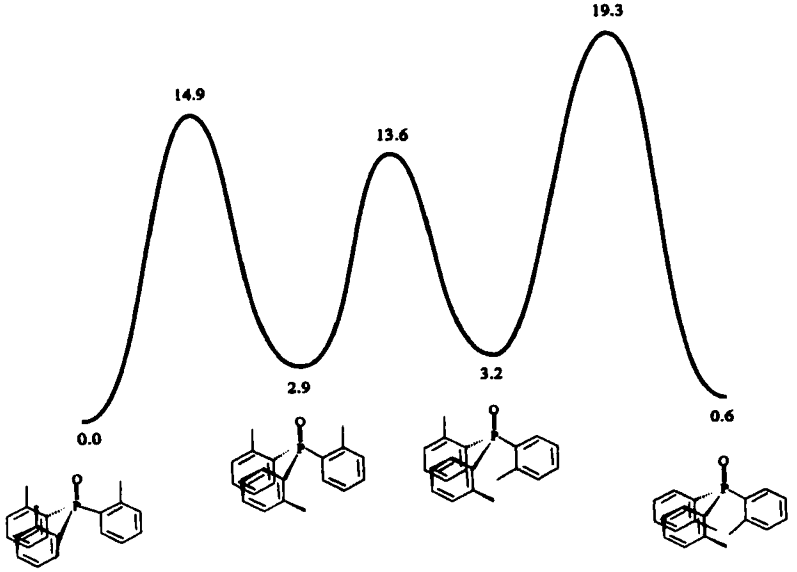


FIGURE 2 Calculated strain energy (kJ mol^{-1}) profile for conformational interconversion of tri-*o*-tolylphosphine oxide (**10**)

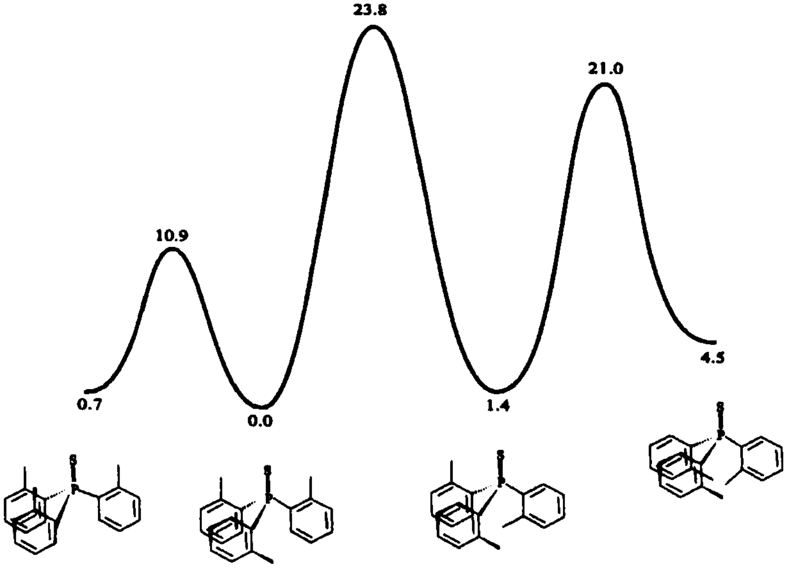


FIGURE 3 Calculated strain energy (kJ mol^{-1}) profile for conformational interconversion of tri-*o*-tolylphosphine sulfide (**11**)

TABLE IV Calculated heats of formation (kJ mol^{-1}) and selected structural parameters (bond lengths r in Å bond angles θ and dihedial angles φ in degrees) for tri-*o*-tolylphosphine oxide (**10**)

Feature	*10-↑↑↑*	*10-TS(A)*	*10-↑↑↓*	*10-TS(B)*	*10-↑↓↓*	*10-TS(C)*	*10-↓↓↓*
ΔH°_{f}	92.1	107.0	95.1	105.8	95.4	111.4	92.8
$\Delta\Delta H^{\circ}_{f}$[a]	0.0	14.9	2.9	13.6	3.2	19.3	0.6
Dipole (D)	2.85	3.14	3.23	3.49	3.50	3.78	3.77
$r_{\mathrm{P\text{-}O}}$	1.51	1.49	1.49	1.49	1.48	1.48	1.48
$r_{\mathrm{P\text{-}C1}}$	1.83	1.84	1.84	1.85	1.84	1.85	1.85
$r_{\mathrm{P\text{-}C8}}$	1.83	1.84	1.84	1.84	1.85	1.87	1.85
$r_{\mathrm{P\text{-}C15}}$	1.83	1.85	1.86	1.86	1.85	1.86	1.85
$\theta_{8,\mathrm{P},15}$	106	106	107	104	104	107	108
$\theta_{1,\mathrm{P},15}$	106	110	105	107	106	107	108
$\theta_{1,\mathrm{P},8}$	106	103	107	104	110	112	108
θ_{OPC}	113	113	112	112	112	110	111
$\varphi_{\mathrm{P},15,16,21}$	−1	6	2	1	−1	−1	5
$\varphi_{\mathrm{P},1,2,7}$	0	7	2	0	8	5	5 5
$\varphi_{\mathrm{P},8,9,14}$	−1	−2	−2	−5	−1	3	5

a. See footnote *a*,Table III.

TABLE V Calculated heats of formation (kJ mol^{-1}) and selected structural parameters (bond lengths r in Å, bond angles θ and dihedral angles φ in degrees) for tri-*o*-tolylphosphine sulfide (**11**)

Feature	*11-↑↑↑*	*11-TS(A)*	*11-↑↑↓*	*11-TS(B)*	*11-↑↓↓*	*11-TS(C)*	*11-↓↓↓*
ΔH°_{f}	370.6	380.8	369.9	393.7	371.3	390.8	374.4
$\Delta\Delta H^{\circ}_{f}$[a]	0.7	10.9	0.0	5.7	1.4	20.9	4.5
Dipole (D)	5.67	5.74	5.92	6.06	6.11	6.33	6.33
$r_{\mathrm{P\text{-}S}}$	1.97	1.96	1.97	1.98	1.97	1.98	1.98
$r_{\mathrm{P\text{-}C1}}$	1.85	1.85	1.84	1.84	1.83	1.84	1.85
$r_{\mathrm{P\text{-}C8}}$	1.85	1.85	1.84	1.83	1.84	1.83	1.85
$r_{\mathrm{P\text{-}C15}}$	1.85	1.85	1.85	1.85	1.86	1.85	1.85
$\theta_{8,\mathrm{P},15}$	104	105	106	105	105	105	108

Feature	*11*-↑↑↑	*11-TS(A)*	*11*-↑↑↓	*11-TS(B)*	*11*-↑↓↓	*11-TS(C)*	*11*-↓↓↓
$\theta_{1,P,15}$	104	107	104	106	106	106	108
$\theta_{1,P,8}$	104	99	106	109	109	109	108
$\theta_{S,P,C}$	114	115	113	112	112	112	111
$\varphi_{P,15,16,21}$	−4	0	1	−2	−1	−2	4
$\varphi_{P,1,2,7}$	−4	−1	−2	−2	3	−2	4
$\varphi_{P,8,9,14}$	−4	−4	−3	−5	0	5	4

a. See footnote *a*, Table III.

TABLE VI Calculated heats of formation (kJ mol^{-1}) and selected structural parameters (bond lengths r in Å, bond angles θ and dihedral angles φ in degrees) for tri-*o*-tolylphosphine selenide (**12**)

Feature	*12*-↑↑↑	*12-TS(A)*	*12*-↑↑↓	*12-TS(B)*	*12*-↑↓↓	*12-TS(C)*	*12*-↓↓↓
ΔH°_f	339.2	372.8	337.0	365.3	336.0	358.0	335.5
$\Delta\Delta H^\circ_f{}^a$	3.7	36.9	1.5	29.8	0.5	22.5	0.0
Dipole (D)	5.42	5.50	5.66	5.82	5.88	6.15	6.10
$r_{P\text{-}Se}$	2.12	2.13	2.13	2.13	2.13	2.13	2.13
$r_{P\text{-}C1}$	1.82	1.83	1.82	1.83	1.81	1.82	1.83
$r_{P\text{-}C8}$	1.82	1.84	1.82	1.84	1.82	1.84	1.83
$r_{P\text{-}C15}$	1.82	1.81	1.83	1.81	1.83	1.84	1.83
$\theta_{8,P,15}$	106	106	107	106	108	108	110
$\theta_{1,P,15}$	106	109	106	109	107	108	110
$\theta_{1,P,8}$	106	104	107	105	110	113	110
$\theta_{Se,P,C}$	113	112	112	112	111	109	109
$\varphi_{P,15,16,21}$	4	10	2	−10	−1	−2	3
$\varphi_{P,1,2,7}$	4	7	−2	−7	4	8	3
$\varphi_{P,8,9,14}$	4	1	−4	−1	0	4	4

a. See footnote *a*, Table III.

In the most stable form of compound **12**, all methyl groups are far from the phosphoryl selenide bond, that is, the anti geometry (three methyl groups down) is more stable relative to the other forms. Important equilib-

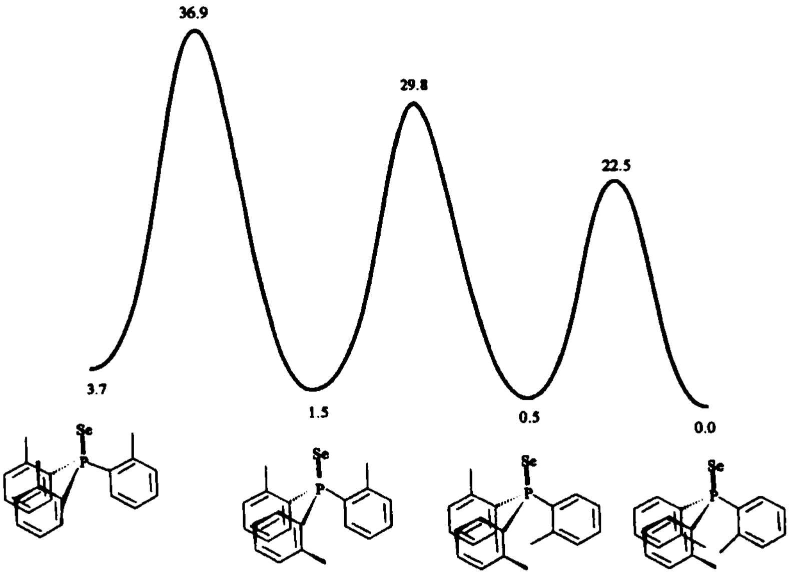


FIGURE 4 Calculated strain energy (kJ mol^{-1}) profile for conformational interconversion of tri-*o*-tolylphosphine selenide (**12**)

rium and transition-state geometries and selected parameteres for these conformers of tri-*o*-tolylphosphine selenide (**12**) are shown in Figure 4 and Table VI.

CONCLUSION

PM3 semiempirical SCF MO calculations provide a fairly clear picture of conformational properties of tri-*o*-tolylphosphine (**9**) and its chalcogonides (**10–12**) from both structural and energetic points of view. For compounds **9–12**, four energy minimum conformations and three transition state geometries are important. In the most stable form of **10**, all methyl groups are close to the oxygen atom, while in the best conformation of **12**, all methyl groups are far from the selenium atom. In the most stable geometry of **9**, two of the methyl groups are close to the phosphorus lone pair. In **11**, the most stable form is similar to that in **9**.

References

[1] L. D. Quin, *A Guide to Organophosphorus Chemistry*, Wiley, New York, 2000.

[2] D. E. C. Corbridge, *Phosphorus. An Outline of Its Chemistry, Biochemistry, and Technology*, 4th. ed., Elsevier, Amsterdam, 1990.

[3] D. G. Gilheany, in *The Chemistry of Organophosphorus Compounds*, Vol. 1, F. R Hartley, ed., 1990, Wiley, New York, ch. 2.

[4] D. B. Chesnut and A. Savin, *J. Amer. Chem. Soc.*, **121**, 2335 (1999); D. B. Chesnut, *J. Amer. Chem. Soc.*, **120**, 10504 (1998); D. G. Gilheany, in *The Chemistry of Organophosphorus Compounds*, Vol. 2, F.R. Hartley, ed., 1992, Wiley, New York, ch. 1.

[5] M. J. Gallagher, in *The Chemistry of Organophosphorus Compounds*, Vol. 2, F. R. Hartley, ed., 1992, Wiley, New York, ch. 2.

[6] W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **92**, 1442 (1970).

[7] R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **93**, 773 (1971).

[8] J. J. P. Steward *J. Comput. Chem.*, **10**, 209 (1989) (see also p. 221).

[9] C. J. Wilkins, K. Hagen, L. Hedberg, Q. Shon, and K. Hedberg, *J. Am. Chem. Soc.*, **97**, 6352 (1975).

[10] I. S. Bartell and L. O. Brockway, *J. Phys. Chem.*, **32**, 512 (1960).

[11] E. J. Jacob and S. Samdal, *J. Am. Chem. Soc.*, **99**, 5656 (1977).

[12] T. S. Cameron and B. Dahlen, *J. Chem. Soc., Perkin Trans, 2*, 1737 (1975).

[13] J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

[14] L. M. Engelhardt, C. L. Raston, C. R Whitaker, and A. H. White, *Aust. J. Chem.*, **39**, 2151 (1986).

[15] P. W. Codding and K.A. Kerr, *Acta Crystallogr. Sect. B*. **34**, 3785 (1978).

[16] P. W. Codding and K. A. Kerr, *Acta Crystallogr. Sect. B*. **35**, 1261 (1979).

[17] J. J. P. Stewart, *J. Comput. Aid. Mol. Des.*, **4**, 1 (1990).

[18] J. J. P. Stewart, QCPE, 581, Department of Chemistry, Indiana University, Bloomington, IN, USA.

[19] M. J. S. Dewar, E. F. Healy, J. J. P. Stewart, *J. Chem. Soc., Faraday Trans.*, **80**, 227 (1984).

[20] O. Ermer, *Tetrahedron*, **31**, 1849 (1975).

[21] J.W. McIver Jr. *Acc. Chem. Res.* **7**, 72 (1974).

[22] E. M. Arnett, J. C. Sanda, J. M. Bollinger, M. Barber, *J. Am. Chem. Soc.*, **89**, 5389 (1967).