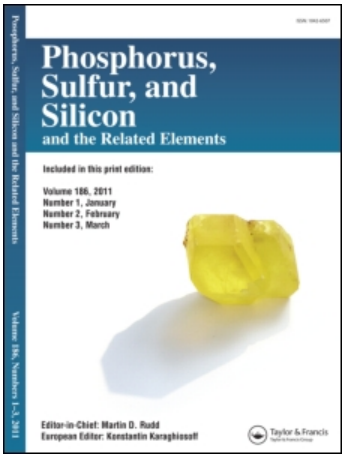

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Nonbonded P···P and P···Se Interactions in Naphthalene 1,8-Positions: Role of Lone-Pair Orbitals

Warô Nakanishi[a]; Satoko Hayashi[a]
[a] Department of Chemistry, Faculty of Systems Engineering, Wakayama University, Wakayama, Japan

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NONBONDED P···P AND P···Se INTERACTIONS IN NAPHTHALENE 1,8-POSITIONS: ROLE OF LONE-PAIR ORBITALS

Warô Nakanishi and Satoko Hayashi
Department of Chemistry, Faculty of Systems Engineering, Wakayama University, Wakayama, Japan

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The lone pair–lone pair repulsion plays an important role in the nonbonded P···P interaction in naphthalene 1,8-positions. The conformations around P and Se in 8-(PhSe)-1-(Ph_2P═O)$C_{10}H_6$ are determined by the attractive O···Se—C 3c–4e type interaction. The P···Se interaction in the 1,8-positions is also discussed.

Keywords: Ab initio MO calculations; lone pair; naphthalene 1,8-positions; nonbonded interactions; phosphorus; selenium

Nonbonded interactions play an important role in determining fine structures of compounds and/or to create high properties of materials. Since nonbonded interactions are so weak, it is important to set up the system to show detectable interactions. Naphthalene 1,8-positions should serve a good system to investigate such interactions since the nonbonded distances at the positions are suitably short.[1–4] Ab initio MO calculations are necessary to support the experimental results. Much attention has been paid to the role of lone pairs in the nonbonded interactions. The group 15 elements such as phosphorus have only one *s*-type lone pair. Therefore, the structure around the atom in the compounds containing group 15 elements will be determined by the behavior of the *s*-type lone-pair orbital in the nonbonded interactions. We investigated the role of lone-pair orbitals in the nonbonded P···P and P···Se interactions on the structures of **1–6**, together with models **a–c** (Figure 1).

Address correspondence to Warô Nakanishi, Department of Chemistry, Faculty of Systems Engineering, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan. E-mail: nakanisi@sys.wakayama-u.ac.jp

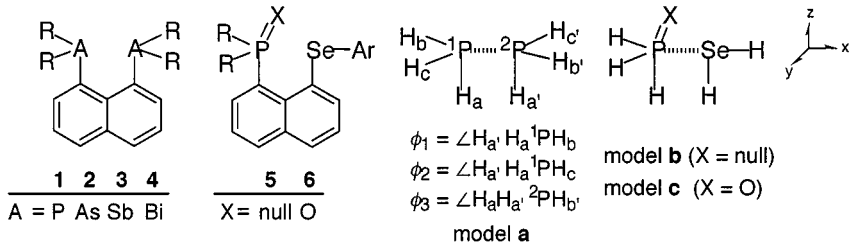

FIGURE 1

RESULTS AND DISCUSSION

Nonbonded P···P and the Related Interactions

Ab initio MO calculations are performed on 1,8-$(R_2A)_2C_{10}H_6$ (**1–4**; R = H, Me, and Ph) using the Gaussian 94 and/or 98 programs. Table I shows the results. The methods of calculations are shown in the table. The observed structures[5–7] are well reproduced by the calculations. The cis and trans conformers are predicted to be stable. The trans conformers are more stable than cis. The deviation of the heteroatoms from the naphthyl plane is larger in trans than in cis conformers, and the deviation is largest when R = Me. The energy difference [$\Delta E = E$(cis) − E(trans)] is largest when R = Me, if the heteroatom is the same. The trend is almost the same for **1–3**, if R is the same. However, the cis conformers of **4** would not be so stable.

In order to reveal the role of the lone pairs in the nonbonded P···P interaction, model calculations are performed on model **a**, $H_aH_bH_c{}^1P\cdots{}^2PH_{a'}H_{b'}H_{c'}$, where the aryl or alkyl groups in **1** are replaced by hydrogen atoms and the nonbonded P···P distance is fixed at the observed value of 3.052 Å.[5] The ^{1}P atom of model **a** is placed at the origin and the ^{2}P atom on the x axis and the ^{1}P–H_a and ^{2}P–$H_{a'}$ bonds in the z direction. Ab initio MO calculations were performed on model **a** with the B3LYP/6-311++G(3df,2pd) method. The cis and trans conformers (**A** and **B**, respectively) are shown to be stable and the energies are well separated in model **a**. In order to shed light on the nature of the nonbonded interaction, the torsion angular dependence of the energy of model **a** is calculated with variously fixed $\phi_1(= \angle H_{a'}H_a{}^1PH_b)$. The conformer with $\phi_1 = \phi_2(= \angle H_{a'}H_a{}^1PH_c)$ is called **C**. The torsion angular dependence of the energy is also calculated with variously fixed $\phi_3(= \angle H_aH_{a'}{}^2PH_{b'})$ under the conditions $\phi_1 = \phi_2$. The results are shown in Figure 2.

TABLE I Energies (E) and Energy Differences (ΔE) Between cis and trans Conformers, Together with the Predicted Nonbonded Distances Between Heteroatoms in 1,8-$(R_2A)_2C_{10}H_6$ Calculated at the B3LYP Level

	Basis set 6-311 + G(2d, p)			Basis set LANL2DZ		
AR_2	E(cis)[a] r(A, A)[c]	E(trans)[a] r(A, A)[c]	ΔE[b]	E(cis)[a] r(A, A)[c]	E(trans)[a] r(A, A)[c]	ΔE[b]
PH_2	−1069.9286 3.1008	−1069.9313 3.0173	7.1	−399.9594 3.1643	−399.9632 3.0901	10.0
PMe_2	−1227.2419 3.2006	−1227.2532 3.0443	29.7	−557.2220 3.2414	−557.2315 3.1232	24.9
PPh_2				−1324.0269 3.2220	−1324.0337 3.0993	17.9
AsH_2	−4858.9180 3.2083	−4858.9201 3.1389	5.5	−399.2118 3.2437	−399.2150 3.1703	8.4
$AsMe_2$	−5016.2337 3.2810	−5016.2426 3.1683	23.4	−556.4801 3.3186	−556.4882 3.2103	21.3
$AsPh_2$				−1323.2822 3.3010	−1323.2889 3.1821	17.6
SbH_2				−397.7603 3.4737	−397.7636 3.4072	8.7
$SbMe_2$				−555.0382 3.5379	−555.0455 3.4430	19.2
$SbPh_2$				−1321.8358 3.5250	−1321.8418 3.4033	15.8
BiH_2				−397.8397 3.5176	−397.8418 3.4768	5.5
$BiMe_2$				−555.1164 3.5591	−555.1208 3.5107	11.6
$BiPh_2$				−1321.9133 3.5537	−1321.9178 3.4541	11.8

The cis conformer has C_s symmetry or is close to that symmetry and the trans conformer has C_2 symmetry or is close to it. $\Delta E = E(\text{cis}) - E(\text{trans})$. The 3-21G* and DSS basis sets are applied to **1–3** (A = P, As, and Sb) and **1–4** (A = P, As, Sb, and Bi), respectively. The results are essentially the same as those shown here. Only one conformer is predicted for A = N, which reproduces the observed structure of R = Me and Ph.

[a] In atomic units, All.

[b] In kJ/mol.

[c] In angstroms, Å.

The *s*-type lone pairs of P atoms are not directed to the P—H bonds with each other in conformers **A** and **B** of model **a**. The lone-pair orbital will overlap effectively with the σ^*(P—H) in conformer **C**, but it is not the stationary point. While the lone-pair orbitals are directed with each other in conformer **D**, it is most unstable among the four. Compilation of these results lead us to the conclusion that the lone pair–lone pair

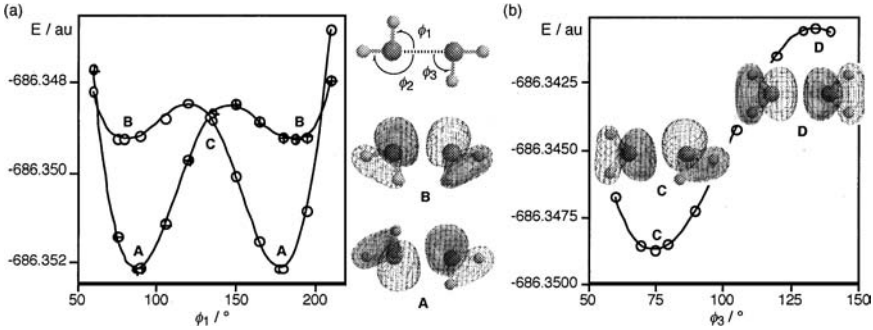

FIGURE 2 Plots of energy of model **a**: (a) versus torsion angle ϕ_1 ($\oplus$) ($\bigcirc$ for ϕ_2) and (b) versus ϕ_3 under $\phi_1 = \phi_2$.

repulsion must be more important than the n(P)···σ^*(P—H) interaction in the nonbonded P···P interaction. The role of the lone-pair orbitals in the nonbonded As···As, Sb···Sb, and Bi···Bi interactions is in the same line to determine the structures around the heteroatoms of **2–4**.

Nonbonded P···Se Interaction in 5

Compound **5**, 8-(PhSe)-1-(Ph_2P)$C_{10}H_6$, is prepared.* The phosphine oxide of **5** (**6**)† is also obtained during the isolation of single crystals of **5**. The following conclusions are obtained based on the MO calculations performed on 8-(MeSe)-1-(Me_2P)$C_{10}H_6$ and on model **b**, $H_3P\cdots SeH_2$: (a) The lone pair–lone pair repulsion is important. (b) The n(Se)···σ^*(P—H) and n(P)···σ^*(Se—H) 3c–4e type attractive interactions would also be comparably contribute to the nonbonded P···Se interaction.

Figure 3 shows the structure of **6**, determined by x-ray crystallographic analysis. The three O···Se—C atoms in **6** align linearly ($\angle$OSeC = 168.8° and $\angle$POSe = 88.8°). Ab initio MO calculations are performed on 1-(MeSe)-8-(Me_2PO)$C_{10}H_6$ (**7**) and on model **c**, $H_3P(O)\cdots SeH_2$. The structure around the P and Se in **6** is well reproduced by the calculations. The most stable conformers of **7** and model **c** are shown in Figure 4, together with the HOMO-1 and HOMO-3 of model **c**. The MOs demonstrate that the 3c–4e type interaction is predominant in the linear O···Se—H alignment. Therefore, the structure of **6** is determined by the 3c–4e type interaction of the linear O···Se—C atoms.

*δ(P) = −12.51, δ(Se) = 446.2, ^4J(P, Se) = 380.9 Hz.
†δ(P) = 37.47, δ(Se) = 457.9.

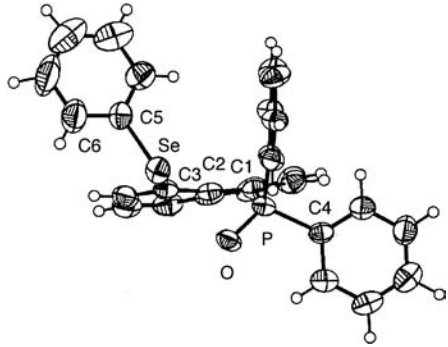

FIGURE 3 Ortep drawing of **6**. Selected bond lengths (Å): P–Se, 3.220(1); P–O, 1.486(2): P–C1, 1.823(4); Se–O, 2.887(2); Se–C3, 1.935(3); Se–C5, 1.922(4). Selected angles (°): P–O–Se, 88.8(2); C1–P–O, 112.3(2); O–Se–C5, 168.8(3); C3–Se–C5, 97.2(2). Selected torsion angles (°): C2–C1–P–O, 24.9; C2–C1–P–C4, 144.4; C2–C3–Se–C5, 117.0; C3–Se–C5–C6, 109.9.

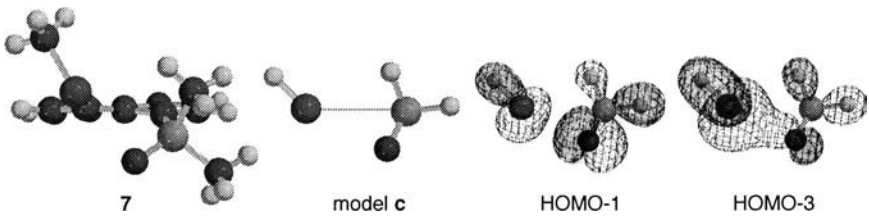

FIGURE 4 Optimized structures for **7** and model **c**, together with HOMO-1 and HOMO-3 of model **c**.

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