Do Distibene (HSb=SbH) and Dibismuthene (HBi=BiH) feature Double Bonding? A Theoretical Comparison with Diphosphene (HP=PH) and Diarsene (HAs=AsH)

Shigeru Nagase,* Satoshi Suzuki and Toshiya Kurakake

Department of Chemistry, Faculty of Education, Yokohama National University, Yokohama 240, Japan

Ab initio calculations suggest that the Sb and Bi atoms in group 15 form double bonded compounds, as do the lighter P and As atoms, unlike the heavier Sn and Pb in group 14; dibismuthenes are the heaviest example of double bonding between main group elements.

Compounds featuring double bonding between the heavier group 15 elements are of current interest.[1] In 1981, the first stable P–P double bonded compound, a diphosphene derivative (RP=PR), was synthesized and isolated.[2] Since then, many schemes have been revised and diphosphenes are now commonplace.[1] In addition, compounds with an –As=As– linkage, diarsenes, have also been successfully synthesized and isolated.[3–5] However, attempts to prepare the heavier analogues, distibenes (RSb=SbR) and dibismuthenes (RBi=BiR), have all been unsuccessful up to now, except for the metal-coordinated distibene complexes, but these lose double bond character because of side-on η^2 coordination.[6–9]

The lighter Si and Ge atoms in group 14 can form isolable ethene analogues,[10] disilenes ($R_2Si{=}SiR_2$)[11] and digermenes ($R_2Ge{=}GeR_2$).[12] However, the heavier Sn is reluctant to form double bonds in distannenes ($R_2Sn{=}SnR_2$),[13,14] while Pb does not form a diplumbene ($R_2Pb{=}PbR_2$) structure at all.[15,16] From this point of view, it is important to determine if the heavier atoms in group 15 are also incapable of forming double bonded compounds. For this purpose, we have undertaken the first *ab initio* calculations of the parent compounds, HSb=SbH **3** and HBi=BiH **4**.

Geometries were fully optimized at the Hartree–Fock (HF) level with relativistic effective core potentials (ECP)[17] on Sb and Bi using the double-zeta (DZ) basis sets[17] augmented by a set of d-type polarization functions [d exponents[18] 0.211 (Sb) and 0.185 (Bi)]. The DZ basis set[19] for H was scaled by a factor of 1.2 and augmented by a set of p-type polarization functions (p exponent 1.0).

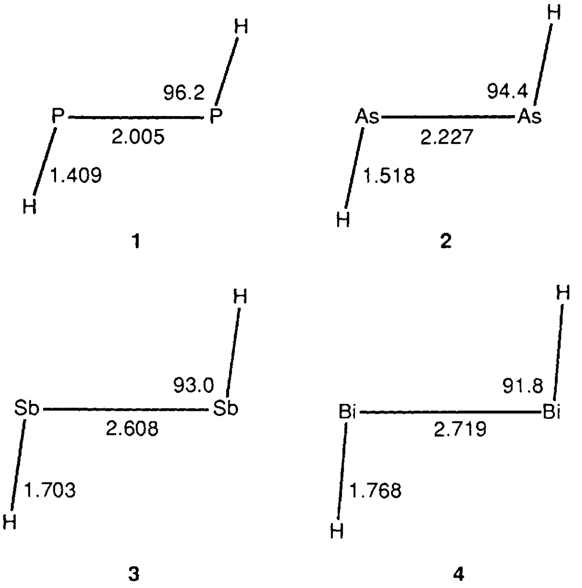

Fig. 1 Optimized structures of the *trans* C_{2h} forms in Å and (°) at the HF/DZ(d,p) level. Total energies of **1–4** are −13.82439, −13.06697, −11.63640, and −11.70925 au, respectively.

Fig. 1 shows the optimized geometries of **3** and **4**. The harmonic vibrational frequencies are summarized in Table 1. The vibrational frequencies are all real, confirming that the planar *trans* structures of C_{2h} symmetry are at energy minima on the H_2Sb_2 and H_2Bi_2 potential energy surfaces; the *cis* forms of C_{2v} symmetry were also located as minima but less stable than the *trans* forms by 2.3 kcal mol^{-1} for **3** and 2.4 kcal mol^{-1} for **4**.

For comparison, similar calculations were carried out for HP=PH **1** and HAs=AsH **2** with ECP at the same level [d exponents 0.55 (P) and 0.293 (As)], as shown in Fig. 1. The *trans* C_{2h} forms of **1** and **2** were 3.3 and 2.7 kcal mol^{-1} more stable than the *cis* C_{2v} forms, respectively. The optimized P–P bond distance of 2.005 Å in **1** agrees well with the previous calculated values of 2.004 Å (HF/6-31G** and HF/DZ + P) in all-electron calculations[20,21] and the experimental values of 2.001–2.034 Å for the derivatives of **1**.[2,3,22–25] The optimized As–As bond distance of 2.227 Å in **2** also agrees reasonably well with the experimental values of 2.224–2.245 Å for the derivatives of **2**.[3–5]

As shown in Fig. 1, the Sb–Sb and Bi–Bi bond distances are calculated to be 2.608 in **3** and 2.719 Å in **4**. An important finding is that the bond distances are 9.0% (0.257 Å) and 8.9% (0.264 Å) shorter than the Sb–Sb and Bi–Bi single bond distances in $H_2Sb{-}SbH_2$ (2.865 Å) and $H_2Bi{-}BiH_2$ (2.983 Å), respectively. These bond shortenings are comparable to the P–P and As–As bond shortenings of 9.2% (0.203 Å) in **1** from $H_2P{-}PH_2$ (2.208 Å) and 9.7% (0.239 Å) in **2** from $H_2As{-}AsH_2$ (2.466 Å), suggesting that Sb and Bi atoms are capable of forming double bonds, as are P and As atoms. This is in sharp contrast with the Sn and Pb cases in group 14; distannene and diplumbene structures suffer from strong pyramidalization at the Sn and Pb atoms and the Sn–Sn and Pb–Pb bond distances become only slightly shorter and much longer, respectively, than the corresponding single bond distances.

The Sb–Sb and Bi–Bi bond stretching frequencies of 254 and 180 cm^{-1} in **3** and **4** are 40.3 and 39.5% higher than the corresponding frequencies in $H_2Sb{-}SbH_2$ (181 cm^{-1}) and $H_2Bi{-}BiH_2$ (129 cm^{-1}), respectively. These frequency-shifts compare favourably with those of 40.8% in **1** from $H_2P{-}PH_2$ (498 cm^{-1}) and 44.1% in **2** from $H_2As{-}AsH_2$ (272 cm^{-1}). In an attempt to characterize the bonding, bond indices (B)[26] were also calculated and compared. The calculated values of B(Sb=Sb) 1.98, and B(Bi=Bi) 2.03, are close to those of B(P=P) 2.01, and B(As=As) 1.93.

As measured by bond distances, stretching frequencies, and bond indices, **3** and **4** feature double bonding between the Sb or Bi atoms. In fact, internal rotations around the Sb–Sb and Bi–Bi bonds were hindered by significant barriers of 16.4 kcal mol^{-1} in **3** and 14.2 kcal mol^{-1} in **4**; the free energy barriers ($\Delta G^{\ddagger}$) at room temperature were 15.4 **3** and 13.3 **4** kcal mol^{-1}. (For these energy and frequency calculations as well as for the geometrical optimizations, two-configuration self-consistent-field theory was used to describe correctly the

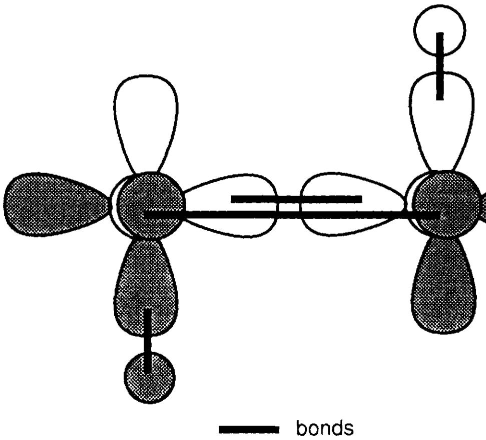

Fig. 2 A simplified description of bond formation by heavier group 15 atoms with the $(ns)^2(np)^3$ valence electron configuration. Double occupied ns atomic orbitals are omitted for simplicity. According to generalized valence bond (GVB) calculations, overlaps between the optimized np_π-like GVB orbitals forming π bonds are 0.55, 0.51, 0.45, and 0.44 in **1**–**4**, respectively.

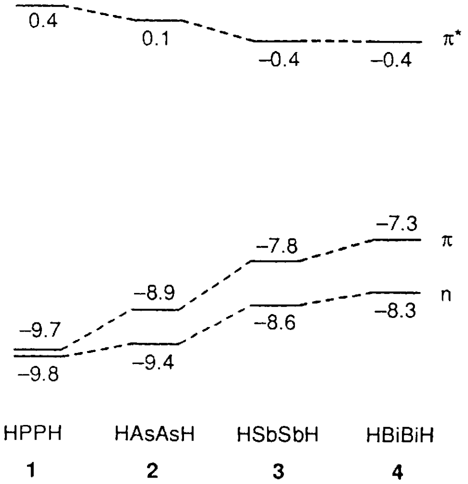

Fig. 3 Frontier orbital energy levels (eV) for the *trans* C_{2h} forms at the HF/DZ(d,p) level

Table 1 Harmonic vibrational frequencies (cm^{-1}) of HM=MH (M = P, As, Sb and Bi) in the *trans* C_{2h} form at the HF/DZ(d,p) level

	M = P **1**	As **2**	Sb **3**	Bi **4**
MH a-stretch (b_u)	2547	2306	2030	1908
MH s-stretch (a_g)	2537	2298	2022	1896
s-bend (a_g)	1074	921	742	688
torsion (a_u)	867	742	599	560
a-bend (b_u)	761	644	496	439
MM stretch (a_g)	701	392	254	180

Table 2 The relative energies (kcal mol^{-1}; 1 cal = 4.184 J) of HMMH, H_2MM, and the transition structure (TS) for the isomerization calculated on the HF/DZ(d,p) optimized geometries at several levels of theory[a]

	HF	MP2	MP3	MP4
HPPH **1**	0.0	0.0	0.0	0.0
H_2PP (C_{2v})	23.8	26.1	27.4	27.3
TS (C_1)	53.9	54.8	55.2	54.9
HAsAsH **2**	0.0	0.0	0.0	0.0
H_2AsAs (C_{2v})	30.1	33.4	34.2	34.1
TS (C_1)	47.6	48.8	48.9	48.6
HSbSbH **3**	0.0	0.0	0.0	0.0
H_2SbSb (C_{2v})	31.3	34.7	35.2	35.1
TS (C_1)	38.0	39.9	39.9	39.6
HBiBiH **4**	0.0	0.0	0.0	0.0
H_2BiBi (C_s)	22.3	37.5	35.1	36.7
TS (C_1)	32.5	36.2	35.9	35.6

[a] Nonplanar, pyramidalized structures of C_s symmetry were located for H_2AsAs, H_2SbSb and H_2BiBi at the HF/DZ(d,p) level, unlike the planar C_{2v} structure of H_2PP. However, electron correlation made the planar C_{2v} structures more stable by 5.2 and 0.6 kcal mol^{-1} in H_2AsAs and H_2SbSb at the MP4 level, respectively. The nonplanar C_s structure of H_2BiBi was 5.9 kcal mol^{-1} more stable even at the MP4 level.

scission of the π-bonds upon rotation, *i.e.*, the biradical transition states for *trans–cis* isomerization.)[†]

The H–M–M (M = P, As, Sb, Bi) bond angles in **1**–**4** (Fig. 1) are much smaller than the H–N–N bond angle of 107.6° (HF/6-31G**) in HN=NH[20] and approach 90° as the M atom becomes heavier. This is because the heavier atoms have a lower tendency to form hybrid orbitals and maintain the $(ns)^2(np)^3$ valence electron configuration even in compounds, known in terms of the so-called 'inert ns electron pair effect' originating from relativistic effects.[27] The tendency is not especially unfavourable in forming double bonds in **3** and **4**, as shown in Fig. 2. This contrasts with the fact that the Sn and Pb atoms with $(ns)^2(np)^2$ must hybridize to form double bonds in distannenes and diplumbenes.

Table 2 summarizes the energies of the isomerizations *via* 1,2-H shift (*trans*-HM=MH → H_2MM) calculated on the HF/DZ(d,p) optimized geometries using Møller–Plesset perturbation (MP) theory up to full fourth order (MP4).[28] The calculated sizeable barriers show that **3** and **4** are kinetically stable to isomerization, as are **1** and **2**. At the MP4/DZ(d,p)//HF/DZ(d,p) level, **3** and **4** are 35.1 and 36.7 kcal mol^{-1} more stable than the 1,2-H shifted isomers, H_2SbSb and H_2BiBi, respectively; these energy differences favouring double bonded forms are rather larger than those of 27.3 and 34.1 kcal mol^{-1} for **1** and **2**. In addition, H_2SbSb isomerizes to **3** with a small barrier of 4.5 kcal mol^{-1}, while H_2BiBi collapses to **4** almost with no barrier at the MP level. These also contrast with the relative energies of H_2SnSnH_2 *vs.* H_3SnSnH and H_2PbPbH_2 *vs.* H_3PbPbH, 1,2 shifted isomers being increasingly favoured in group 14 upon going to the heavier systems.[15]

The additions of H_2 to **3** and **4**, giving $H_2Sb–SbH_2$ and $H_2Bi–BiH_2$, were 4.6 kcal mol^{-1} (exothermic) and 3.0 kcal mol^{-1} (endothermic) at the MP4/DZ(d,p)//HF(d,p) level, respectively. At the same level, the H_2 additions to **1** and **2** were 24.5 and 16.6 kcal mol^{-1} (exothermic), respectively.[‡]

[†] At the same level of theory, the rotational barriers in **1** and **2** were 31.2 and 23.4 kcal mol^{-1} ($\Delta G^{\ddagger}$ = 29.4 and 22.0 kcal mol^{-1} at room temperature), respectively.

[‡] For comparison, the H_2 additions to P_2 were 4.2 kcal mol^{-1} (exothermic) while those to As_2, Sb_2 and Bi_2 were 0.2, 7.9 and 14.7 kcal mol^{-1} (endothermic) at the MP4/DZ(d,p)//HF/DZ(d,p) level, respectively.

In conclusion, the heavier Sb and Bi atoms in group 15 can form double bonded compounds,§ as do the lighter P and As atoms. As the frontier orbital energy levels in Fig. 3 show,¶ however, steric protection by bulky substituents may be essential for the stable isolation. Details of the kinetic stability of **3** and **4** will be reported elsewhere.||

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§ We have also found that the Sb and Bi analogues of benzene and cyclobutadiene correspond to energy minima, unlike the Sn and Pb analogues,[29] and may present interesting targets for the syntheses of conjugated π systems of aromaticity or antiaromaticity.

¶ The high π orbitals (compared with the lone-pair n orbitals) in **3** and **4** prefer π to n coordination. This is consistent with the fact that π bonded complexes of the η^2 type have always been observed for distibenes.[6–9]

|| The dimerizations of **3** and **4**, giving cyclic $(SbH)_4$ and $(BiH)_4$ compounds, were 38.0 and 35.9 kcal mol^{-1} (exothermic) while those of **1** and **2** were 28.9 and 37.5 kcal mol^{-1} (exothermic) at the MP4/DZ(d,p)//HF/DZ(d,p) level, respectively.