

# Unusual Structures of the Parent Molecules Diarsene, Distibene, and Dibismuthene. Toward Their Observation

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## Abstract

There is considerable interest, from both experimental and theoretical perspectives, in molecules incorporating multiple bonds between main group elements. Herein, we not only consider the parent molecules  $\text{HE}=\text{EH}$  ( $\text{E} = \text{As}, \text{Sb}, \text{Bi}$ ), but also a number of their isomers. For each  $\text{E}_2\text{H}_2$  molecule, a number of different structures were optimized with four different DFT methods. Final structures were determined with the coupled cluster method CCSD(T) using large basis sets, namely cc-pVQZ-PP, incorporating relativistic pseudopotentials. All feasible dissociation pathways are examined. For all three  $\text{E}_2\text{H}_2$  molecules the *trans* isomer lies lowest in energy, with the *cis* isomer higher by 2.7 (As), 2.1 (Sb), and 1.8 (Bi) kcal/mol, respectively. However, both *cis* and *trans* structures should be observable, as large barriers (27.7, 20.5, and 17.7 kcal/mol) separate them. For both the *cis* and *trans* structures, in the infrared the strong E-H stretching frequencies should also be observable. Only the *cis* structures have dipole moments (0.62, 0.01, and 0.83 debye, respectively), and their observation by microwave spectroscopy would be stunning. Also considered were the higher energy vinylidene-like, pyramidal, monobridged, and linear structures. We conclude that molecules such as  $\text{HSb}=\text{SbH}-\text{Fe}(\text{CO})_4$ ,  $\text{HBi}=\text{BiH}-\text{Fe}(\text{CO})_4$ , and related systems, should be feasible synthetic targets.

## Introduction

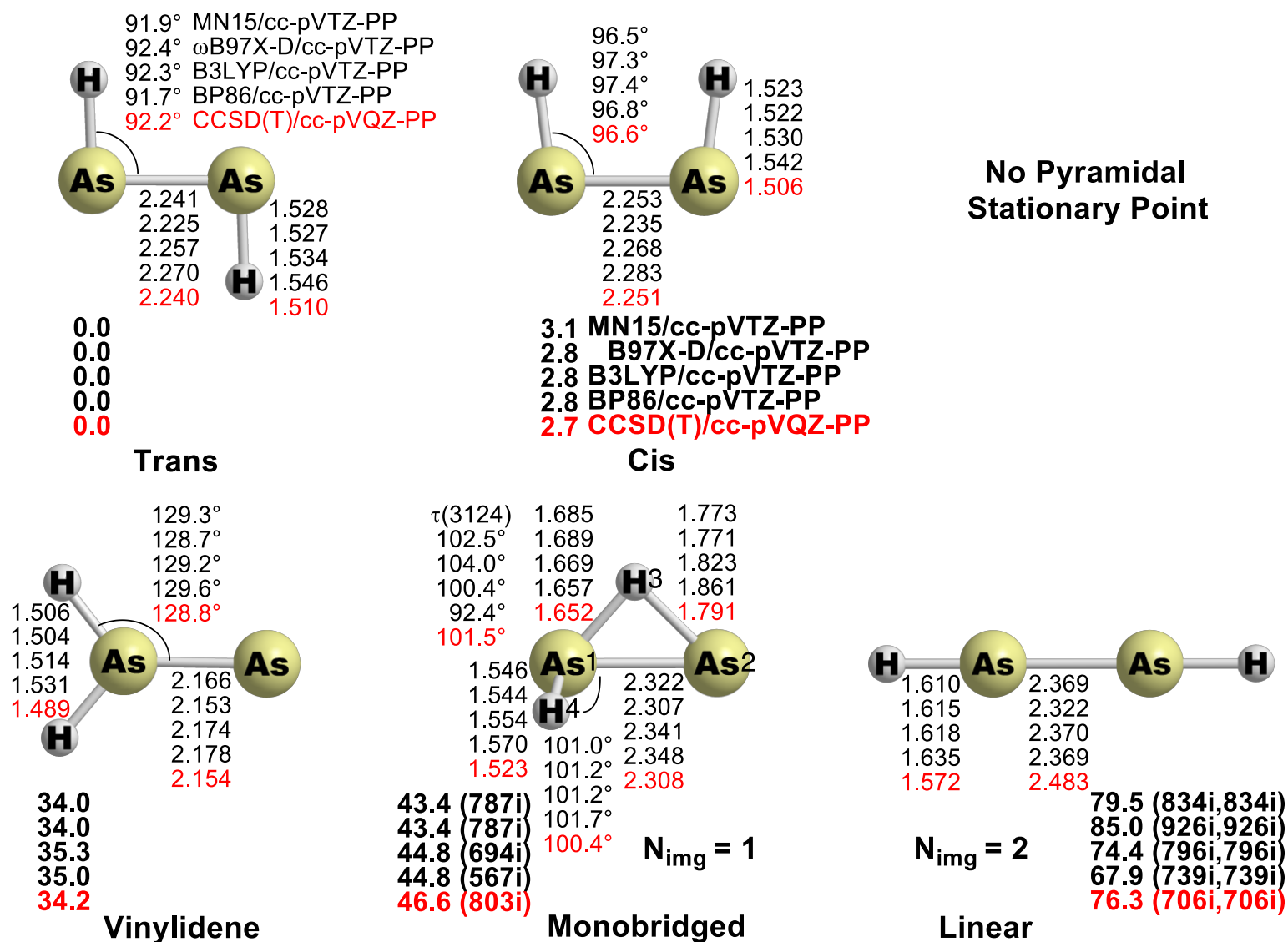
Main group inorganic chemistry has undergone a renaissance over the past quarter century.<sup>[1]</sup> Much of this progress has been driven by molecules containing multiple bonding between main group elements, particularly boron, silicon, and phosphorus.<sup>[1a-1c,2]</sup> Among the most relevant molecules to this submitted work<sup>[3]</sup> are diarsenes, distibenes, and dibismuthenes. All these known  $E_2R_2$  species ( $E = As, Sb, Bi$ ) are substituted compounds. The parent  $HAs=AsH$ ,  $HSb=SbH$ , and  $HBi=BiH$  molecules have not been examined in the gas phase. The literature reveals only two compounds containing arsenic-arsenic double bonds. To this end, Scheer<sup>[4]</sup> synthesized a remarkable compound wherein the parent diarsenes  $HAs=AsH$  serves as a side-on bound ligand in an  $Fe(CO)_4$  iron carbonyl complex. The second compound, prepared by Ghadwal,<sup>[5]</sup> concerns radical cations and dications of divinylldiarsene. In the present study we computationally investigate the parent diarsene ( $HAsAsH$ ) and the parent distibene ( $HSbSbH$ ) and the parent dibismuthene ( $HBiBiH$ ), along with some interesting isomers. Lastly, we suggest options for experimental observation.

We note the foundational theoretical study of Trinquier<sup>[6]</sup> three decades ago: a valuable consideration of the *trans* bent and vinylidene-like structures of all three molecules. In addition, Schoeller,<sup>[7]</sup> studied the *trans-cis* rotation of all three molecules. In a more recent study, Su<sup>[8]</sup> considered several isomers of  $As_2H_2$ . To be prudent, we employed four distinct approaches<sup>[9]</sup> for preliminary structural predictions and energetic considerations. In all DFT computations reported herein we utilized the correlation consistent cc-pVTZ-PP basis sets of Peterson.<sup>[10]</sup> Final structures and energetics were found with the high level CCSD(T)/cc-pVQZ-PP method.

## Results and Discussion

**a. Diarsene:** Our DFT predictions for the  $\text{As}_2\text{H}_2$  systems are summarized in Figure 1 and Table 1. All these results were obtained with the cc-pVTZ-PP basis set. Analogous vibrational results are found in Table 2. Since the  $\text{HAs=AsH}$  double bond structure has already been observed in the laboratory, we were not surprised to find that it lies lowest among  $\text{As}_2\text{H}_2$  isomers. Consequently, only the CCSD(T) relative energies are noted in our work. The *trans*  $\text{As}_2\text{H}_2$  structure is predicted to lie 2.7 kcal/mol below the *cis* structure, which is also a minimum. In the experimental  $\text{As}_2\text{H}_2\text{--Fe(CO)}_4$  structure<sup>[4]</sup> the  $\text{As}_2\text{H}_2$  moiety is also *trans* bent. The *trans* structure lies much lower (34.2 kcal/mol) than the vinylidene structure, also a minimum. The monobridged structure lies at 46.6 kcal/mol above the *trans* global minimum. The monobridged structure is seen to be a transition state connecting the vinylidene-like structure of  $\text{As}_2\text{H}_2$  to the *trans* minimum. The barrier height with respect to the vinylidene minimum is 12.4 kcal/mol. Thus, the vinylidene structure maybe observable, possibly in a carefully designed low-temperature experiment. Finally, the linear  $D_{\infty h}$  structure has two imaginary vibrational frequencies and lies 76.3 kcal/mol above that of the *trans* isomer.

Our final structures and energetics (noted above) are shown in Figure 1. These predictions were made with the CCSD(T) method<sup>[11]</sup> and the larger cc-pVQZ-PP basis sets of Peterson.<sup>[10]</sup> For the E (As, Sb, Bi) atoms, we utilized Peterson's correlation consistent cc-pVQZ-PP basis sets, in which the MCDHF (multiconfiguration Dirac-Hartree-Fock adjusted) small-core relativistic pseudopotentials (PP) were included. With the pseudopotential, 10 core electrons ( $1s^2 2s^2 2p^6$ ) for the As atoms are embodied in the effective core, with 28 core electrons ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ ) for the Sb atom, and 60 core electrons ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14}$ ) for the Bi atom. In the CCSD(T) studies, the 3s3p-like MOs are frozen for the As atom, the 4s4p-like MOs are frozen for the Sb atom, and the 5s5p-like MOs are frozen for the Bi atom.



**Figure 1.** Geometries and energetics for five As<sub>2</sub>H<sub>2</sub> stationary points. Bond distances are in Å and energies in kcal/mol.

**Table 1.** Relative energies (in kcal/mol), E-E bond distances (in Å), E-E stretching harmonic frequencies ( $\nu_{(E-E)}$ , in  $\text{cm}^{-1}$ ), E-E Wiberg bond indices ( $\text{WBI}_{(E-E)}$ ), and E atom natural charges ( $q_E$ ) from natural bond orbital (NBO) analyses for  $\text{H}_2\text{E}_2$  (E = As, Sb, Bi) structures. The relative energies, geometries and vibrational frequencies are achieved with the CCSD(T)/cc-pVQZ-PP method.

Molecule	Structure	Relative Energy	E-E	$\nu_{(E-E)}$	$\text{WBI}_{(E-E)}^a$	$q_E^a$
$\text{As}_2\text{H}_2$	<b>Trans</b>	0.0	2.240	348	2.03	0.08/0.08
	<b>Cis</b>	2.7	2.251	339	2.01	0.07/0.07
	<b>Staggered<sup>b</sup></b>	27.7	2.399	265	1.08	0.08/0.08
	<b>Vinylidene</b>	34.2	2.154	381	1.99	0.13/-0.08
	<b>Monobridged</b>	46.6	2.308	310	1.38	0.25/-0.10
	<b>Linear</b>	76.3	2.483	148	2.35	0.18/0.18
$\text{Sb}_2\text{H}_2$	<b>Trans</b>	0.0	2.629	226	2.02	0.15/0.15
	<b>Cis</b>	2.1	2.642	221	2.00	0.13/0.13
	<b>Staggered<sup>b</sup></b>	20.5	2.802	178	1.05	0.16/0.16
	<b>Pyramidal</b>	33.8	2.642	(299, 50) <sup>c</sup>	1.50	0.16/0.02
	<b>Vinylidene</b>	33.5	2.534	247	1.93	0.24/-0.06
	<b>Monobridged</b>	37.7	2.694	206	1.33	0.37/-0.05
$\text{Bi}_2\text{H}_2$	<b>Trans</b>	0.0	2.780	158	2.02	0.16/0.16
	<b>Cis</b>	1.8	2.794	154	2.01	0.14/0.14
	<b>Staggered<sup>b</sup></b>	17.7	2.964	126	1.04	0.16/0.16
	<b>Pyramidal</b>	34.5	2.912	126	1.15	0.15/0.07
	<b>Vinylidene</b>	41.8	2.695	164	1.76	0.20/-0.03
	<b>Monobridged</b>	34.4	2.856	144	1.29	0.37/-0.03
	<b>Linear</b>	49.7	2.952	100	2.26	0.24/0.24

<sup>a</sup> The WBIs and  $q_E$  values are obtained with MN15 method. The atomic charges ( $q_E$ ) before the slash are for the E atom bearing more H atoms.

<sup>b</sup> All staggered results refer to the lowest triplet electronic state, since these electronic structures cannot be realistically described by closed-shell schemes with spin-restricted wavefunctions.

<sup>c</sup> The Sb-Sb stretching and the rocking internal coordinates are mixed in these two vibrational frequencies.

**Table 2.** Vibrational frequencies and infrared intensities for *trans* and *cis* HE=EH structures (E = As, Sb, Bi) predicted by different theoretical methods.

	<i>trans</i>	<i>cis</i>
MN15/cc-pVTZ-PP		
HAs=AsH	363(0), 574(13), 684(3), 843(0), 2154(0), 2172(251)	354(1), 619(0), 650(8), 730(26), 2174(17), 2200(193)
HSb=SbH	241(0), 442(17), 552(12), 669(0), 1959(0), 1974(353)	236(0), 506(0), 506(5), 577(32), 1974(16), 1993(282)
HBi=BiH	170(0), 376(20), 499(18), 591(0), 1795(0), 1812(467)	167(0), 449(0), 469(0), 517(28), 1829(22), 1848(367)
$\omega$ B97XD/cc-pVTZ-PP		
HAs=AsH	372(0), 581(10), 689(2), 846(0), 2161(0), 2178(222)	364(1), 629(0), 658(8), 736(20), 2174(15), 2199(176)
HSb=SbH	248(0), 447(15), 561(9), 670(0), 1959(0), 1973(342)	244(0), 511(0), 526(7), 604(30), 1991(18), 2010(277)
HBi=BiH	173(0), 411(18), 518(17), 611(0), 1774(0), 1791(501)	170(0), 459(1), 468(0), 534(28), 1837(26), 1857(401)
B3LYP/cc-pVTZ-PP		
HAs=AsH	345(0), 578(9), 667(2), 833(0), 2106(0), 2124(221)	336(1), 608(0), 637(6), 723(21), 2119(13), 2144(176)
HSb=SbH	228(0), 444(15), 528(10), 657(0), 1890(0), 1903(326)	223(0), 484(0), 497(4), 574(30), 1903(14), 1921(267)
HBi=BiH	160(0), 384(19), 477(18), 581(0), 1763(0), 1778(443)	157(0), 441(0), 444(0), 516(28), 1782(20), 1800(355)
BP86/cc-pVTZ-PP		
HAs=AsH	333(0), 552(8), 645(2), 805(0), 2048(0), 2066(198)	324(1), 587(0), 613(5), 688(20), 2061(10), 2086(158)
HSb=SbH	221(0), 424(14), 511(9), 633(0), 1840(0), 1854(286)	216(0), 467(0), 480(3), 546(27), 1854(10), 1872(235)
HBi=BiH	156(0), 367(19), 462(16), 559(0), 1723(0), 1738(376)	153(0), 428(0), 428(0), 491(25), 1744(15), 1760(302)
CCSD(T)/cc-pVQZ-PP		
HAs=AsH	348(0), 588(9), 669(1), 846(0), 2189(0), 2205(175)	339(1), 606(0), 651(8), 736(19), 2200(11), 2223(141)
HSb=SbH	226(0), 444(14), 525(6), 660(0), 1995(0), 2008(258)	221(0), 478(0), 501(6), 579(29), 2005(11), 2021(213)
HBi=BiH	158(0), 385(16), 473(12), 587(0), 1860(0), 1875(363)	154(0), 436(0), 451(1), 519(26), 1878(10), 1894(299)

After the *trans* global minimum, the energies of the final CCSD(T) other stationary points are *cis* (2.7), vinylidene-like (34.2), monobridged (46.6), and  $D_{\infty h}$  linear (76.3 kcal/mol). Our coupled cluster energies are in broad agreement with the DFT predictions, except that for the linear structure there is an unacceptably large range in the DFT energies from 67.9 (BP86) to 85.0 kcal/mol ( $\omega$ B97X-D). The “better” DFT methods in this respect are MN15 and B3LYP. Notably, BP86 provides the worst agreement with the coupled cluster predictions.

Table 1 shows the vinylidene-like structure to have the shortest As-As distance, 2.154 Å [CCSD(T)]. This is followed by the *trans* (2.240 Å) and *cis* (2.251 Å) As-As distances. With respect to *trans*, the monobridged transition state distance is 0.068 Å longer, and that for the linear structure 0.243 Å longer. A simple interpretation of these As-As distance would be that the vinylidene structure has the strongest double bond. In this context, let us consider the CCSD(T) As-As stretching vibrational frequencies are 348 (*trans*), 339 (*cis*), 381 (vinylidene-like), 310 (monobridged), and 148  $\text{cm}^{-1}$  (linear). Thus both the As-As bond distance and As-As stretching vibrational frequency agree that the vinylidene-like structure (34 kcal above the *trans*) has a slightly stronger As=As double bond.

It is informative to consider the predicted NBO As-As bond orders.<sup>[12]</sup> These are 2.03 (*trans*), 2.01 (*cis*), 1.99 (vinylidene-like), 1.38 (monobridged), and 2.35 (linear). The first three structures clearly display conventional double bonds. The monobridged transition state does not have significant double bond character ( $\text{WBI} = 1.38$ ). Perhaps the most surprising result is the WBI for the high-lying (76 kcal/mol above *trans*) linear structure is the largest 2.35. Notably, the notion of highest bond order yielding the lowest energy is violated in this instance.

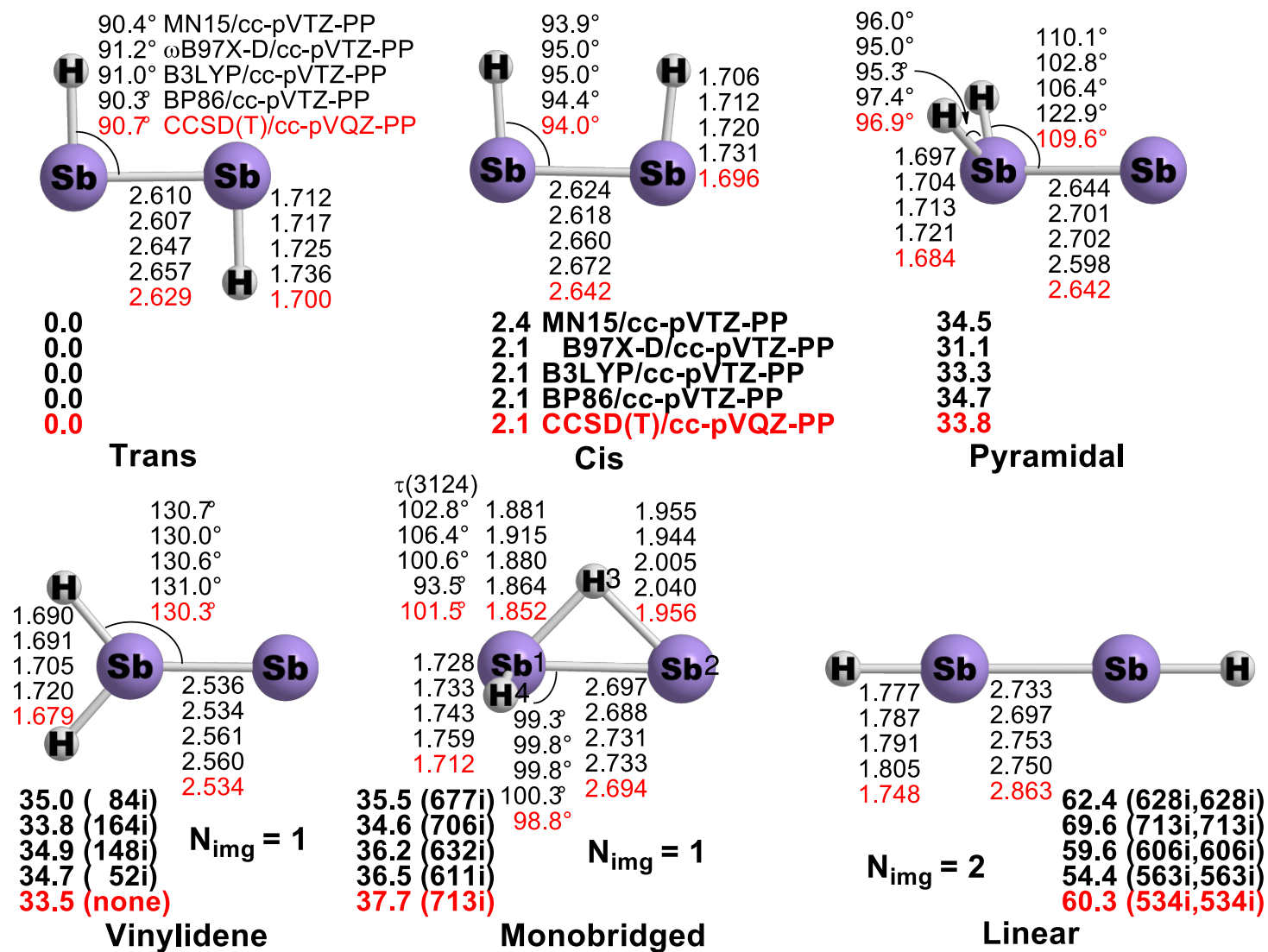
The NBO charges on the arsenic atoms should also provide some insight into the nature of the difference  $\text{As}_2\text{H}_2$  stationary points. We note that the Pauling electronegativities of H (2.20) and As (2.18) are comparable within the bounds of such simple estimates. By the same scale, the electronegativities of Sb and Bi are 2.05 and 2.02, respectively. The NBO charges in Table 1 indicate that the AsAs (except the monobridged structures) bonds are all double bonds. The near

neutrality of the atoms would seem to discourage any significant ionic bonding. The largest charge for any of our structures is 0.18 for the linear  $\text{HAsAsH}$ . Almost all the structures have positive charges on both arsenic atoms. The only exception is the -0.08 charge on the terminal As of the vinylidene-like structure. Recall that this structure also has the shortest As=As bond distance, namely 2.154 Å.

We note that our computed *trans*  $\text{HAs=AsH}$  (2.240 Å) distance is considerably shorter than that reported for  $(\text{HAs=AsH})\text{-Fe(CO)}_4$  (2.368 Å). We conclude that the As=As bond is weakened by complexation with  $\text{Fe(CO)}_4$ . We also note that the As=As bond distance (2.224 Å) in the “uncomplexed” diarsene, reported by Cowley,<sup>[3a]</sup> is in much closer agreement with the parent diarsene (2.240 Å). Indeed, the uncomplexed As=As distances reported by Power<sup>[3c]</sup> (2.224, 2.244, and 2.276 Å) are all in good agreement with the parent diarsene.

**b. Distibene:** The theoretical predictions for the  $\text{Sb}_2\text{H}_2$  structures are reported in Figure 2 and Table 1. The CCSD(T) cc-pVQZ-PP  $\text{Sb}_2\text{H}_2$  *trans-cis* energy difference is reduced to 2.1 kcal/mol, compared to 2.7 kcal/mol for  $\text{As}_2\text{H}_2$ . One new feature for antimony is the existence of a pyramidal equilibrium geometry predicted by the DFT methods, lying 33.8 kcal/mol above the *trans* global minimum, and the vinylidene structure is a transition state, which connects (with a tiny barrier) the two mirror image structures of the pyramid. However, we observe that the potential energy associated with this inversion is virtually flat, especially with the MN15 and BP86 methods, with the energy difference less than 0.5 kcal/mol. Furthermore, with the CCSD(T) method, the vinylidene structure is predicted to be a local minimum, lying 0.3 kcal/mol below the pyramidal structure. The monobridged structure is a transition state from the shallow pyramidal minimum to the *trans* global minimum. This antimony monobridged structure (37.7 kcal/mol) lies 8.9 kcal/mol lower than that (46.6 kcal/mol) for  $\text{As}_2\text{H}_2$ . The Sb linear  $\text{D}_{\infty\text{h}}$  structure (like As with two imaginary vibrational frequencies) is predicted to lie at 60.3 kcal/mol, as opposed to 76.3 kcal/mol for the analogous  $\text{As}_2\text{H}_2$  system.



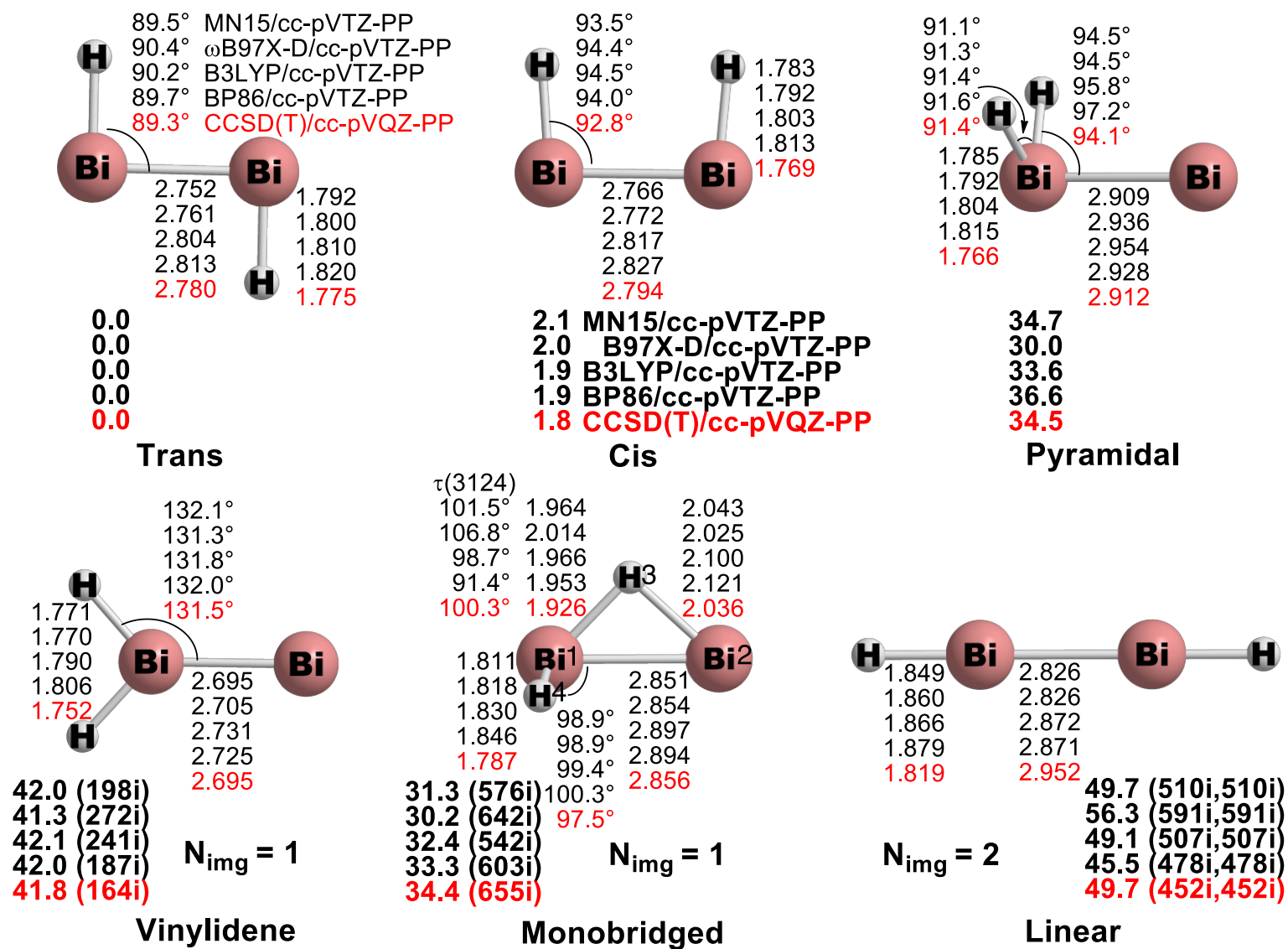


**Figure 2.** Geometries and energetics for six  $\text{Sb}_2\text{H}_2$  stationary points. Bond distances are in Å and energies in kcal/mol.

Even though the vinylidene-like  $\text{Sb}_2\text{H}_2$  structure is a transition state, it still (like  $\text{As}_2\text{H}_2$ ) has the shortest Sb-Sb bond distance (2.534 Å). This is 0.095 Å less than predicted for the *trans* global minimum. In contrast, the constrained  $\text{D}_{\infty\text{h}}$  linear structure again (compared to arsenic) has the longest Sb-Sb distance (2.863 Å). Also like  $\text{As}_2\text{H}_2$  the linear structure has the largest Wiberg bond order, 2.31. The monobridged structure has an Sb-Sb bond order of 1.33 and a low Sb-Sb stretching frequency, namely 206  $\text{cm}^{-1}$ . The highest Sb-Sb vibrational frequency (247  $\text{cm}^{-1}$ ) is that for the vinylidene-like structure, consistent with its short Sb-Sb bond distance.

Recently reported experimental Sb=Sb bond distances by Tokitoh<sup>[3h]</sup> (2.668 Å), Schulz<sup>[3i]</sup> (2.643, 2.646, 2.648 Å), and Coles<sup>[3j]</sup> (2.665, 2.662 Å) all agree satisfactorily with our cc-pVQZ-PP CCSD(T) prediction for the parent *trans*  $\text{HSb}=\text{SbH}$ .

**c. Dibismuthene:** For  $\text{Bi}_2\text{H}_2$ , (Figure 3 and Table 1) the *trans* and *cis* structures differ in energy by only 1.8 kcal/mol. Furthermore, their bond order values (2.02 and 2.01) closely approaches that of the conventional double bond value (2.00). The pyramidal  $\text{Bi}_2\text{H}_2$  structure is predicted to lie 34.5 kcal above the *trans* global minimum, an energy difference only 0.7 kcal/mol above the analogous antimony result. However, we note that the bond order for the  $\text{Bi}_2\text{H}_2$  pyramid isomer (1.15) is much less than that for  $\text{Sb}_2\text{H}_2$  (1.50). Consistent with this, the Bi-Bi pyramid stretching frequency (126  $\text{cm}^{-1}$ ) is much lower than that for  $\text{Sb}_2\text{H}_2$ . Also the vinylidene-like structure is a transition state. The constrained  $\text{D}_{\infty\text{h}}$  linear structure has a degenerate imaginary vibrational frequency, corresponding to motions toward the *trans* and *cis* equilibria. The energy of this constrained linear structure for  $\text{Bi}_2\text{H}_2$  is significantly lower, 49.7 kcal/mol, compared to 60.3 for  $\text{Sb}_2\text{H}_2$  and 76.3 kcal/mol for  $\text{As}_2\text{H}_2$ .

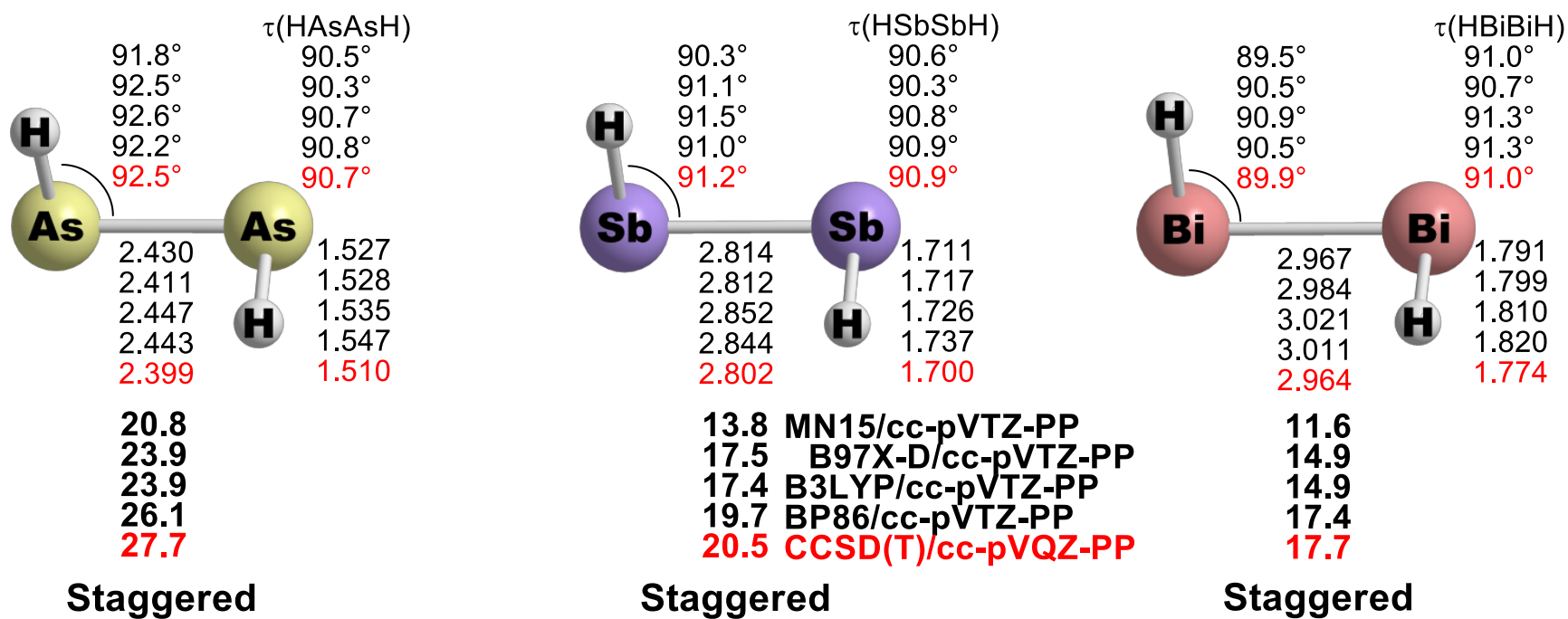


**Figure 3.** Geometries and energetics for six  $\text{Bi}_2\text{H}_2$  stationary points. Bond distances are in Å and energies in kcal/mol.

Our cc-pVQZ-PP CCSD(T) prediction of the Bi=Bi *trans* distance is 2.780 Å, in reasonable agreement with the original Tokitoh<sup>[3b]</sup> crystal structure 2.821 Å for the first dibismuthene synthesized. A second dibismuthene, again synthesized by Tokitoh's group,<sup>[3h]</sup> gave a distance of 2.854 Å. The possibility that the huge R groups may be somewhat increasing the Bi=Bi distances in their RBi=BiR crystal structures is plausible.

**d. Staggered Structures:** Regarding the staggered structures we report only triplet electronic state structures. Like the well-known case of twisted ethylene, the staggered E<sub>2</sub>H<sub>2</sub> triplet states lie below the analogous singlet states. Consequently, the triplet energies of staggered E<sub>2</sub>H<sub>2</sub> molecules are effective lower bounds to the true singlet energies. The structures of these transition states are seen in Figure 4. Table 1 reveals that these barriers are substantial, namely 27.7 (As<sub>2</sub>H<sub>2</sub>), 20.5 (Sb<sub>2</sub>H<sub>2</sub>), and 17.7 (Bi<sub>2</sub>H<sub>2</sub>) kcal/mol. With barriers of this magnitude, both *trans* and *cis* structures should be viable, perhaps first observed by matrix isolation IR spectroscopy. In contrast, the *cis* isomers, having dipole moments, may be observable with microwave spectroscopy.

The staggered triplet states have much longer E-E distances than either the *trans* or *cis* structures. Of course this is due to the loss of the E-E  $\pi$  bond for the staggered structure. Increases in E-E bond distance going from *trans* to staggered are (2.399 – 2.240) = 0.159 Å (As<sub>2</sub>H<sub>2</sub>); (2.802 – 2.629) = 0.173 Å (Sb<sub>2</sub>H<sub>2</sub>); and (2.964 – 2.780) = 0.184 Å (Bi<sub>2</sub>H<sub>2</sub>). In an analogous manner the shifts in E-E stretching vibrational frequencies are (348 – 265) = 83 cm<sup>-1</sup> (As<sub>2</sub>H<sub>2</sub>); (226 – 178) = 48 cm<sup>-1</sup> (Sb<sub>2</sub>H<sub>2</sub>); and (158 – 126) = 32 cm<sup>-1</sup> (Bi<sub>2</sub>H<sub>2</sub>). Finally, at these rotational transition states, the E-E bond orders (compared to the global minimum *trans* structure) are reduced by (2.03 – 1.08) As<sub>2</sub>H<sub>2</sub>; (2.02 – 1.05) Sb<sub>2</sub>H<sub>2</sub>; and (2.02 – 1.04) Bi<sub>2</sub>H<sub>2</sub>. Intuitively, these results confirm that rotation causes the *trans* or *cis* double bonds to evolve into single bonds. However, these staggered transition states show little change in the NBO charges of the E atoms compared to those for either the *trans* or the *cis* structures.



**Figure 4.** Staggered  $\text{E}_2\text{H}_2$  structures at their triplet equilibrium geometries. Bond distances are in Å and energies in kcal/mol.

**e. Some Comparisons with Other  $E_2H_2$  Molecules:** We now compare the present results with some reported earlier for other  $E_2H_2$  molecules. The excitement in this field was fueled by the bold prediction nearly four decades ago by Lishka and Köhler<sup>[13]</sup> that the global minimum of  $Si_2H_2$  was a butterfly structure. This prediction was experimentally confirmed less than a decade later using microwave spectroscopy.<sup>[14]</sup> Importantly, we find no evidence here for a butterfly structure for  $As_2H_2$  or  $Sb_2H_2$  or  $Bi_2H_2$ . The butterfly  $Si_2H_2$  prediction was followed by the even more remarkable prediction of a monobridged equilibrium geometry.<sup>[15]</sup> This result was also confirmed experimentally by the microwave spectroscopy.<sup>[16]</sup> Similar mono-bridged equilibrium geometries have been predicted<sup>[17]</sup> for  $Ge_2H_2$ ,  $Sn_2H_2$ , and  $Pb_2H_2$ . The difference with  $As_2H_2$ ,  $Sb_2H_2$ , and  $Bi_2H_2$  is that for the latter three the monobridged transition states lie 34-47 kcal/mol above the *trans* minima; for  $Si_2H_2$  and  $Ge_2H_2$  the monobridged equilibria lie only about 8 kcal/mol above the global minimum.

Moreover, monobridged equilibrium structures are not restricted to  $Si_2H_2$ ,  $Ge_2H_2$ ,  $Sn_2H_2$ , and  $Pb_2H_2$ .  $Al_2H_2$  has a monobridged equilibrium geometry at 9 kcal/mol above its global minimum.<sup>[18]</sup> In 1997 it was shown<sup>[19]</sup> from theoretical vibrational frequencies and infrared intensities that four years earlier Chertihin and Andrews<sup>[20]</sup> had unknowingly observed this  $Al_2H_2$  monobridged structure. Chertihin did not consider the monobridged structure in the analysis of their  $Al_2H_2$  IR spectra. Similarly  $Ga_2H_2$  is predicted<sup>[21]</sup> to have a monobridged equilibrium, again about 8 kcal/mol above its global minimum, in this case a planar dibridged structure. The 2002 matrix isolation observations of Himmel, Manceron, Downs, and Pullumbi<sup>[22]</sup> discuss the monobridged structure, but they do not identify it experimentally.

The vinylidene-like  $EEH_2$  structures are also rather different energetically from those predicted and found experimentally<sup>[23]</sup> for  $Si_2H_2$ ,  $Ge_2H_2$ ,  $Al_2H_2$ , and  $Ga_2H_2$ . In the latter molecules the vinylidene-like structures are all minima and lie with 10 kcal/mol of the respected global minima. For our systems (Table 1) the vinylidene-like structure lies more than 30 kcal/mol above the *trans* global minima. Of the arsenic, antimony, and bismuth  $E_2H_2$  vinylidene-like structures, those for  $AsAsH_2$  and  $SbSbH_2$  are minima, while that for  $BiBiH_2$  is a transition state.

**f. Observation in the Infrared?** Table 3 and 4 report CCSD(T) predictions of the harmonic vibrational frequencies of *trans* and *cis*  $As_2H_2$ ,  $Sb_2H_2$ , and  $Bi_2H_2$ . It is clear that all three molecules are most likely to be identified by the E-H stretching frequencies. In that sense the IR spectra of these molecules may be rather simple. The *trans*  $\omega(E-H \text{ asym})$  features lie 18, 13, and  $19 \text{ cm}^{-1}$ , respectively, below the IR strongest *cis*  $\omega(E-H \text{ sym})$  frequencies. For each of the three molecules, the *trans* IR intensity is a bit larger than the *cis*.

**g. Dissociation Energies:** Table 5 shows some relevant dissociation energies for our  $E_2H_2$  systems. Compared to CCSD(T) the MN15 dissociation energies are usually reasonable, the largest difference being 9.0 kcal/mol ( $HAsAsH \text{ trans} \rightarrow As + AsH_2$ ). Among the different dissociation limits, only those going to  $E_2 + H_2$  are competitive. Most notably *trans*  $HBiBiH$  is predicted to lie 4.1 kcal/mol *below* separated  $Bi_2 + H_2$ . However, the barriers between *trans*  $E_2H_2$  and  $E_2 + H$  should be substantial. Thus, nothing in Table 5 rules out the viability of  $As_2H_2$ ,  $Sb_2H_2$ , or  $Bi_2H_2$ .

**Table 3.** Vibrational frequency assignments for *trans* HE=EH structures (E = As, Sb, Bi) predicted by the CCSD(T)/cc-pVQZ-PP method.

	symmetry	HAs=AsH	HSb=SbH	HBi=BiH
E-H stretching (asym.)	b <sub>u</sub>	2205(175)	2008(258)	1875(363)
E-H stretching (sym.)	a <sub>g</sub>	2189(0)	1995(0)	1860(0)
H-E-H bending (sym.)	a <sub>g</sub>	846(0)	660(0)	587(0)
H-E-E-H torsion	a <sub>u</sub>	669(1)	525(6)	473(12)
H-E-E bending (asym.)	b <sub>u</sub>	588(9)	444(14)	385(16)
E-E stretching	a <sub>g</sub>	348(0)	226(0)	158(0)

**Table 4.** Vibrational frequency assignments for *cis* HE=EH structures (E = As, Sb, Bi) predicted by the CCSD(T)/cc-pVQZ-PP method.

	symmetry	HAs=AsH	HSb=SbH	HBi=BiH
E-H stretching (sym.)	a <sub>1</sub>	2223(141)	2021(213)	1894(299)
E-H stretching (asym.)	b <sub>2</sub>	2200(11)	2005(11)	1878(10)
H-E-H bending (asym.)	b <sub>2</sub>	736(19)	579(29)	519(26)
H-E-H bending (sym.)	a <sub>1</sub>	651(8)	501(6)	451(1)
H-E-As-H torsion	a <sub>2</sub>	606(0)	478(0)	436(0)
E-E stretching	a <sub>1</sub>	339(1)	221(0)	154(0)

**Table 5.** Dissociation Energies (in kcal/mol) for *trans* structures predicted by both MN15/cc-pVTZ-PP and CCSD(T)/cc-pVQZ-PP methods.

	MN15	CCSD(T)
HAsAsH ( <i>trans</i> ) → As <sub>2</sub> + H <sub>2</sub>	6.5	5.5
HSbSbH ( <i>trans</i> ) → Sb <sub>2</sub> + H <sub>2</sub>	1.6	2.1
HBiBiH ( <i>trans</i> ) → Bi <sub>2</sub> + H <sub>2</sub>	-4.5	-4.1
HAsAsH ( <i>trans</i> ) → 2 AsH	130.4	124.7
HSbSbH ( <i>trans</i> ) → 2 SbH	110.5	105.7
HBiBiH ( <i>trans</i> ) → 2 BiH	101.4	98.2
HAsAsH ( <i>trans</i> ) → As + AsH <sub>2</sub>	55.3	64.3
HSbSbH ( <i>trans</i> ) → Sb + SbH <sub>2</sub>	44.4	52.2
HBiBiH ( <i>trans</i> ) → Bi + BiH <sub>2</sub>	41.2	45.9

\* The As, Sb, Bi atoms are at their quartet states.



**h. Observation by Microwave Spectroscopy:** The *trans* structures of the  $E_2H_2$  molecules will not be readily observed by microwave spectroscopy, as each has no permanent dipole moment. However, as seen in Table 6, the *cis* structures have dipole moments, namely 0.62 ( $As_2H_2$ ), 0.01 ( $Sb_2H_2$ ), and 0.83 ( $Bi_2H_2$ ) Debye. The small *cis*  $Sb_2H_2$  dipole moments suggests that it will be difficult to observe in the microwave. The DFT dipole moments do not agree well with the above CCSD(T) results. However, all DFT methods concur that the largest *cis* dipole moment is that of  $Bi_2H_2$ . The very small dipole moment (0.01 debye) of  $Sb_2H_2$  is only understandable when we appreciate the *signs* of the dipole moments. In fact the polarity of *cis*  $As_2H_2$  is  $As^-H^+$ , while that of  $Bi_2H_2$  is  $Bi^+-H^-$ . In the intermediate case  $Sb_2H_2$ , the dipole moment is close to zero. By this particular measure the “charges” on Sb and H in *cis*  $Sb_2H_2$  are virtually identical.

## Conclusions

Herein we report high level theoretical studies of five stationary points for  $As_2H_2$  and six stationary points for the valence isoelectronic  $Sb_2H_2$  and  $Bi_2H_2$ . In Scheer’s<sup>[4]</sup> crystal structure the As-As bond distance is reported to be 2.368 Å, compared to 2.240 Å here for the parent. We conclude that in Scheer’s compound the As=As double bond is slightly weakened (i.e., elongated) compared to the parent. The attachment of  $Fe(CO)_4$  to the  $HAs=AsH$  somewhat weakens the latter’s  $\pi$ -bond. The analogous molecules  $(HSb=SbH)-Fe(CO)_4$  and  $(HBi=BiH)-Fe(CO)_4$  or related structures should be amenable to synthesis. Moreover, we predict that both the *trans* and *cis* structures of  $AsH_2$ ,  $Sb_2H_2$ , and  $Bi_2H_2$  should be observable in the gas phase, due to the substantial barriers separating them and large infrared intensities of the E–H stretching fundamentals. Even more spectacular would be the observation by microwave spectroscopy of the *cis* structures, which (unlike the *trans*) have nonzero dipole moments.

**Table 6.** Dipole moments ( $\mu$ , in Debye) and Rotational Constants (A, B, and C, in GHz) for *cis* structures of HE=EH predicted with five theoretical methods.

	Rotational Constants (A, B, and C, in GHz)	Dipole Moments ( $ \mu $ , in Debye)
MN15/cc-pVTZ-PP		
<i>Cis</i> HAs=AsH	111.02, 2.61, 2.55	0.297
<i>Cis</i> HSb=SbH	87.26, 1.20, 1.19	0.368
<i>Cis</i> HBi=BiH	79.50, 0.63, 0.62	1.233
$\omega$ B97X-D/cc-pVTZ-PP		
<i>Cis</i> HAs=AsH	111.44, 2.65, 2.59	0.532
<i>Cis</i> HSb=SbH	86.95, 1.21, 1.19	0.126
<i>Cis</i> HBi=BiH	78.94, 0.63, 0.62	1.081
B3LYP/cc-pVTZ-PP		
<i>Cis</i> HAs=AsH	110.44, 2.58, 2.52	0.388
<i>Cis</i> HSb=SbH	86.10, 1.17, 1.15	0.287
<i>Cis</i> HBi=BiH	78.00, 0.61, 0.60	1.192
BP86/cc-pVTZ-PP		
<i>Cis</i> HAs=AsH	108.47, 2.54, 2.48	0.368
<i>Cis</i> HSb=SbH	84.90, 1.16, 1.14	0.282
<i>Cis</i> HBi=BiH	77.06, 0.60, 0.60	1.150
CCSD(T)/cc-pVQZ-PP		
<i>Cis</i> HAs=AsH	113.53, 2.62, 2.56	0.615 (0.726) <sup>a</sup>
<i>Cis</i> HSb=SbH	88.31, 1.19, 1.17	0.009 (0.070) <sup>a</sup>
<i>Cis</i> HBi=BiH	80.72, 0.62, 0.61	0.832 (0.888) <sup>a</sup>

<sup>a</sup>In parentheses are the dipole moment based on the H-F wavefunctions.

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