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Ab Initio Interpretation of the Closed-Shell Intermolecular E···E Attraction in Dipnicogen $(H_2E{-}EH_2)_2$ and Dichalcogen $(HE{-}EH)_2$ Hydride Model Dimers

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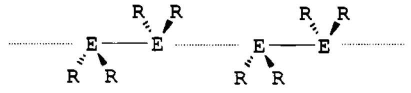
Quasirelativistic pseudopotential ab initio calculations at the second-order Moller−Plesset (MP2) level are reported on dimeric hydrides $(H_2E{-}EH_2)_2$ (E = As, Sb, Bi) and $(HE{-}EH)_2$ (E = Se, Te, Po), which serve as models for the nearly collinear chains found in the solid state for organyl-substituted molecules of this type. The intermolecular interaction is repulsive at the Hartree−Fock level but is attractive at the MP2 level. With sufficiently large basis sets, the E···E distances approach experimental ones in crystals containing $(R_nE{-}ER_n)_\infty$ chains with R = Me, $SiMe_3$, $SnMe_3$, etc. The calculated dimerization energies (MP2) lie in the range from 8 to 13 kJ mol^{-1}, increasing from right to left and from top to bottom in the periodic table.

Introduction

There is increasing evidence for E···E attraction between closed-shell systems containing heavier elements, E, even in cases where a Coulomb repulsion might be expected.[1−7] For oxidized or neutral closed-shell metal atoms, there are ab initio analyses for the cases Cu(I)···Cu(I),[8] Au(I)···Au(I),[9,10] Hg(0)···Hg(0),[11] or Tl(I)···Tl(I).[12] All these calculations suggest that correlation effects are essential; at the Hartree−Fock (HF) level, repulsive interactions are obtained instead. The extended Hückel theory (EHT) hybridization ideas[13] therefore only seem to be correct in the allegorical sense that the EHT contains correlation.[9]

It is important to carefully analyze the nature of the secondary bonding in closed-shell heavy-element compounds because so many different contributions may occur. The cation−cation attraction due to correlation[8−10,12] has already been addressed. Other recent examples are the strong, predicted Au−Xe bonds in $AuXe^+$ and $XeAuXe^+$ (about 0.9 eV per bond.[14a] In this case the long-range R^{-4} charge-polarizability interaction between Au^+ and Xe acquires strong covalent character near R_e. Another example is the formally ionic interaction between Tl^+ ($6s^2$) and $[Pt(CN)_4]^{2-}$ ($5d^8$) in $Tl_2[Pt(CN)_4]$ which has ionic, covalent,[14b] and correlation attractive parts and an intermolecular (crystal-field) lengthening of the Tl−Pt bond[14c] from the monomolecular value. We now extend the discussion to the E···E interactions where E is a pnicogen or chalcogen atom. Typical examples are the distibines and the dibismuthines[15−17]



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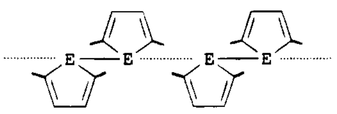
with R = Me, $SiMe_3$, $SnMe_3$, etc., or the heterocyclic systems



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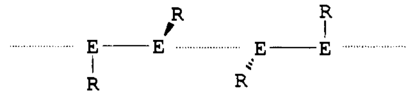
Many of them are thermochromic, as are several analogous dichalcogen systems[17] such as



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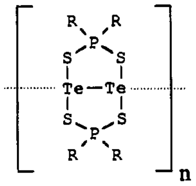
(R = Me, E = Se, Te).[17] Newton et al.[18] report the compound



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(1) (a) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972,** *15,* 1. (b) Alcock, N. W. *Bonding and Structure. Structural Principles in Inorganic and Organic Chemistry*; Ellis Horwood: New York, 1990; Chapter 7.5, "Secondary bonding".

(2) Glidewell, C. *Inorg. Chim. Acta* **1975**, *12*, 219.

(3) Jansen, M. *Angew. Chem.* **1987**, *99*, 1136; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098. Jones, P. J. *Gold Bull.* **1981**, *14*, 102, 159.

(4) Böttcher, P. *Angew. Chem.* **1988**, *100*, 781; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 759.

(5) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11.

(6) Krebs, B., Ed. *Unkonventionelle Wechselwirkungen in der Chemie metallischer Elemente*; VCH: Weinheim, 1992.

(7) Ansari, M. A.; McConnachie, J. M.; Ibers, J. A. *Acc. Chem. Res.* **1993**, *26*, 574.

(8) Kölmel, C.; Ahlrichs, R. *J. Phys. Chem.* **1990**, *94*, 5536. See also: ref 13.

(9) Pyykkö, P.; Zhao, Y.-F. *Angew. Chem.* **1991**, *103*, 622; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 604.

(10) Pyykkö, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133.

(11) Schwerdtfeger, P.; Li, J.; Pyykkö, P. *Theor. Chim. Acta* **1994**, *87*, 313.

(12) Schwerdtfeger, P. *Inorg. Chem.* **1991**, *30*, 1660.

(13) (a) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187. (b) Janiak, C.; Hoffmann, R., ref 6, p 45.

(14) (a) Pyykkö, P. *J. Am. Chem. Soc.* **1995**, *117*, 2067. (b) Ziegler, T.; Nagle, J. K.; Snijders, J. G.; Baerends, E. J. *J. Am. Chem. Soc.* **1989**, *111*, 5631. (c) Dolg, M.; Pyykkö, P.; Runeberg, N. To be published.

(15) Ashe, A. J., III. *Adv. Organomet. Chem.* **1990**, *30*, 77.

(16) Breunig, H. J.; Gülec, S., ref 6, p 218.

(17) Becker, G.; Mundt, O., ref 6, p 199.

(18) Newton, M. G.; King, R. B.; Haiduc, I.; Silvestru, A. *Inorg. Chem.* **1993**, *32*, 3795.

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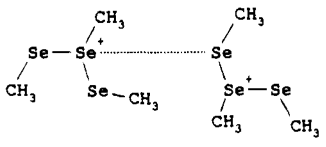
where the Te atoms are partially cationic. Laitinen et al.[19] observed small intermolecular distances between the trimethylselenonium cations in



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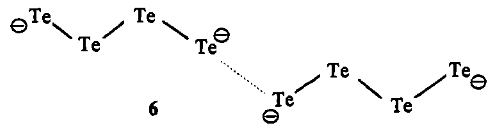
Note that the Se•••Se axis is parallel with the Se−Se axis of one monomer but nearly perpendicular to the adjacent Se−Se axis of the other.

In addition to interactions between neutral or cationic systems, tellurium exhibits interactions between negatively charged moieties[20,21] such as Te_4^{2-}.



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A large number of more complicated cases with short E•••E distances are known in transition metal complexes containing E_n^{2-} units or main group and transition metal solid state compounds including the elements P−Bi, Se, and Te.[4,7,22-24]

In the present work we investigate the origin and characteristics of the intermolecular E•••E interactions using neutral dipnicogen and dichalcogen hydride models, H_2E-EH_2 and HE−EH, respectively. The E−E•••E−E axis is taken as collinear; the real energy minima, however, are probably hydrogen bonded for such dimers, as in the related H_2S dimers.[25]

Computational Details

The Gaussian 92 package was used.[26] The six valence electron (VE) quasirelativistic (QR) pseudopotentials (PP) of the Stuttgart group were employed for the chalcogens and pnicogens.[27,28] During the calculations it became obvious that diffuse and polarization functions are necessary for a correct description of interaction energies and equilibrium distances. The optimized basis sets published with the PPs[27,28] were augmented successively by two diffuse s and p functions and three d and f functions, respectively (Table 2). The final calculations were done by using a (6s6p3d3f)/[4s4p3d3f] and a (5s3p)/[4s3p] basis for heavy elements and hydrogen,[29] respectively. Unless otherwise mentioned, the fixed HF-level intramolecular geometries (Table 3) were used in the dimer studies.

The interaction energies of the dimers $(H_2E-EH_2)_2$ and $(HE-EH)_2$ were obtained as

$$\Delta E = E_{\text{dimer}} - 2E_{\text{monomer}} = V(R)$$

All ΔEs are corrected for basis-set superposition errors (BSSE) using the full counterpoise method.[30] The dependence of $V(R)$ on the basis set was studied in detail for the case of the ditellane and dibismuthine dimers. As shown in Figure 1, even the addition of the last d and f function leads to a significant change in both interaction energies and equilibrium distances. Although it seems that a proper description of

Table 1. Selected Experimental E−E and E•••E Distances (pm), E−E•••E Angles (deg), and Their Ratio, Q^a

compound	E−E	E•••E	E−E•••E	Q	ref
Se_2Me_2	231	355	160	1.54	35c
Te_2Me_2	271	374	151	1.38	35c
$Te_2(C_6H_4OMe)_2$	271	357^b		1.32	40
As_2Me_4	243	370	179	1.52	35a,b
Sb_2Me_4	284	368	179	1.30	41
$(SbC_4H_2Me_2)_2$	284	363	174	1.27	42
$Sb_2(SiMe_3)_4$	287	399	166	1.39	43
$Bi_2Me_4{}^c$	312	358	178	1.15	35
$Bi_2(SiMe_3)_4$	304	380	169	1.25	44

[a] All structural parameters were derived from X-ray diffraction data. [b] Mean value. [c] Because of disorder or twinning, the derived values are doubtful.

Table 2. Basis Functions Successively Added to Those in Refs 27 and 28

element	functions
Se	s (0.046832, 0.017663); p (0.035013, 0.012020); d (0.60, 0.24, 0.10); f (0.77, 0.31, 0.12)
Te	s (0.04082, 0.017400); p (0.032942, 0.011199); d (0.17,[a] 0.057719,[a] 0.40,[b] 0.16,[b] 0.06[b]); f (0.11,[a] 0.58,[b] 0.23,[b] 0.09[b])
Po	s (0.034747, 0.012140); p (0.022201, 0.006817); d (0.324, 0.13, 0.05); f (0.57, 0.23, 0.09)
As	s (0.042342, 0.015991); p (0.029047, 0.010850); d (0.51, 0.20, 0.08); f (0.65, 0.26, 0.10)
Sb	s (0.039674, 0.014242); p (0.028951, 0.0098539); d (0.35, 0.14, 0.06); f (0.49, 0.20, 0.08)
Bi (quasirel)	s (0.040094, 0.015976); p (0.022662, 0.007397); d (0.27, 0.11, 0.04); f (0.50, 0.20, 0.08)
Bi (nonrel)	s (0.035789, 0.015104); p (0.024046, 0.008138); d (0.27, 0.11, 0.04); f (0.50, 0.20, 0.08)

[a] Used in [3s3p1d], [4s4p1d], [4s4p2d], and [4s4p2d1f]. [b] Used in [4s4p2d2f] and [4s4p3d3f].

Table 3. Optimized Structural Parameters of the Monomers E_2H_2 and E_2H_4

element	method	E−E	E−H	E−E−H	H−E−E−H
Se^a	HF	231.2	145.0	97.17	89.69
	MP2	232.5	145.9	96.27	90.89
	MP3	234.1	146.1	96.22	90.28
	MP4	234.6	146.5	96.23	90.32
Te^a	HF	271.3	163.7	95.94	89.70
	MP2	274.1	164.4	95.05	90.25
	MP3	275.8	164.7	94.98	90.21
	MP4	276.2	165.0	95.04	90.23
Po^b	HF	290.0	173.4	95.52	89.46
	MP2	291.0	174.0	94.79	89.58
	MP3	292.9	174.4	94.81	89.64
As^a	HF	244.1	150.6	93.91	86.33
	MP2	245.3	151.3	92.13	88.32
	MP3	246.7	151.5	92.16	88.39
	MP4	247.2	151.9	92.04	88.50
Sb^a	HF	282.4	169.2	92.91	86.82
	MP2	283.3	169.5	91.12	88.67
	MP3	284.9	169.8	91.11	88.83
	MP4	285.5	170.2	91.01	88.96
Bi^b	HF	302.0	181.0	91.63	88.10
	MP2	303.1	181.3	89.94	89.60
	MP3	305.0	181.8	90.08	89.66

[a] [4s4p1d] basis set as in Table 2. [b] [3s3p1d] basis set as in Table 2.

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(19) Laitinen, R.; Steudel, R.; Weiss, R. *J. Chem. Soc., Dalton Trans.* **1986**, 1095.
(20) Klinkhammer, K. W.; Böttcher, P. *Z. Naturforsch.* **1990**, *45b*, 141.
(21) Fenske, D.; Baum, G.; Wolkers, H.; Schreiner, B.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 489.
(22) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223.
(23) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993**, *93*, 1037.
(24) Haiduc, I.; King, R. B.; Newton, M. G. *Chem. Rev.* **1994**, *94*, 301.
(25) Voityuk, A. A.; Bliznyuk, A. A. *Theor. Chim. Acta* **1987**, *71*, 327.
(26) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision E.2*; Gaussian Inc.: Pittsburgh, PA, 1992.
(27) Igel-Mann, G.; Stoll, H.; Preuss, H. *Mol. Phys.* **1988**, *65*, 1321.
(28) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245.
(29) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.
(30) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

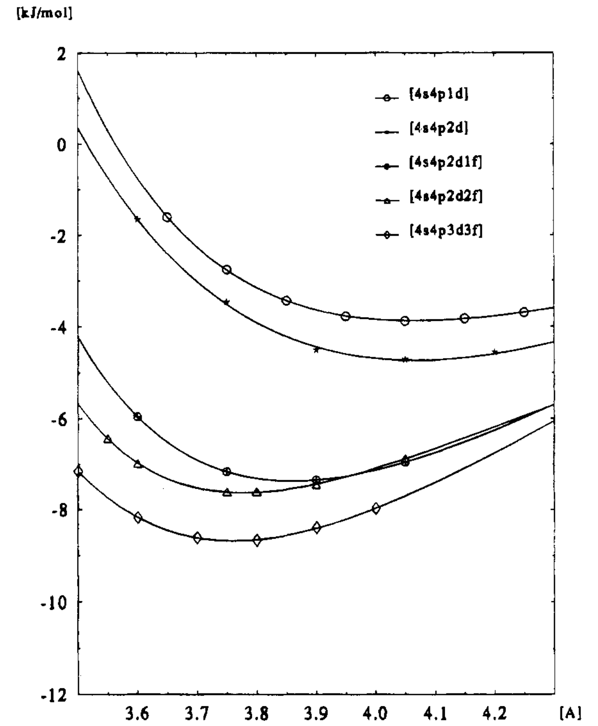


Figure 1. Basis-set dependence of the intermolecular interaction energy of the collinear $(H_2Te_2)_2$ dimers.

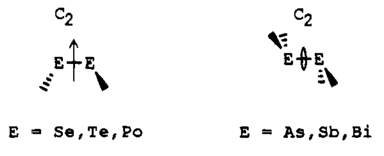
these quantities might require basis functions with even higher *l*-values, for technical reasons, this supposition could not be verified.

As a further technical test, the static polarizability of the monomeric H_2Te molecule was calculated using our largest [4s4p3d3f] basis set. The obtained value of 43.20 au is in excellent agreement with 43.28 and 43.40 au found by Sadlej[31] at the MP2 and MP4 levels (all-electron; HF-level relativistic corrections), respectively.

While the H_2Te α-tensor is nearly isotropic, we find the principal components for H_2Te_2 to be 115.19, 72.37, and 72.37 au, the large one lying along the Te−Te axis.

Results and Discussion

Monomers. Because of the lack of experimental and, at least partly, of theoretical data,[32] the geometries of the monomers E_2H_2 and E_2H_4 were calculated on the HF and MP*n* levels. [4s4p1d] basis sets were employed for the fourth- and fifth-row and [3s3p1d] basis sets for the sixth-row elements. The optimized geometries are given in Table 3. The assumed point symmetries were C_2 and C_{2h} for the dichalcogen and dipnicogen systems, respectively.



The resulting E−E bond lengths are somewhat larger than the experimental ones found in organyl derivatives (Table 1), particularly if correlation is taken into account. In Figure 2 the derived valence orbital schemes for H_2Se_2 and As_2H_4 are shown. The relative positions of the orbitals are representative for all three heavier dinuclear chalcogen and pnicogen hydrides. In the case of the dipnicogenanes E_2H_4, the HOMO can mainly be interpreted as the σ_p(E−E) bonding orbital whereas the two nearly degenerated HOMOs of the dichalcogenanes may be assigned to two combinations of the nonbonding p-orbitals on the chalcogen atoms. The LUMO in both cases is the σ_p^*(E−E) antibonding orbital.

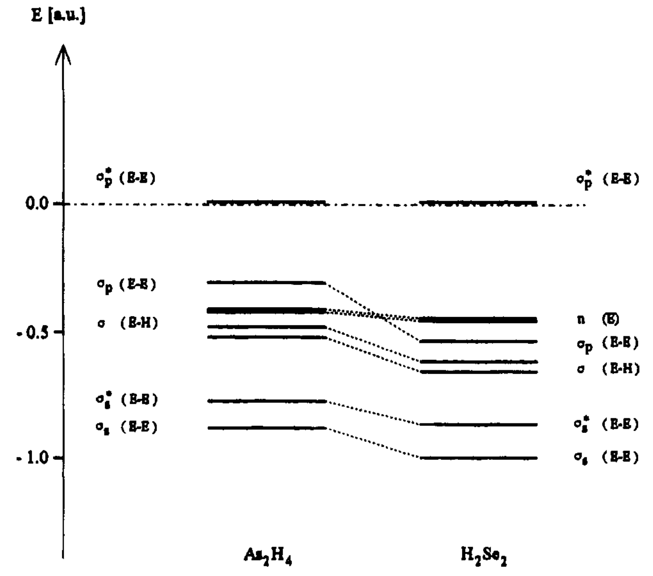


Figure 2. Orbital schemes deerived from HF calculation on As_2H_4 and H_2Se_2.

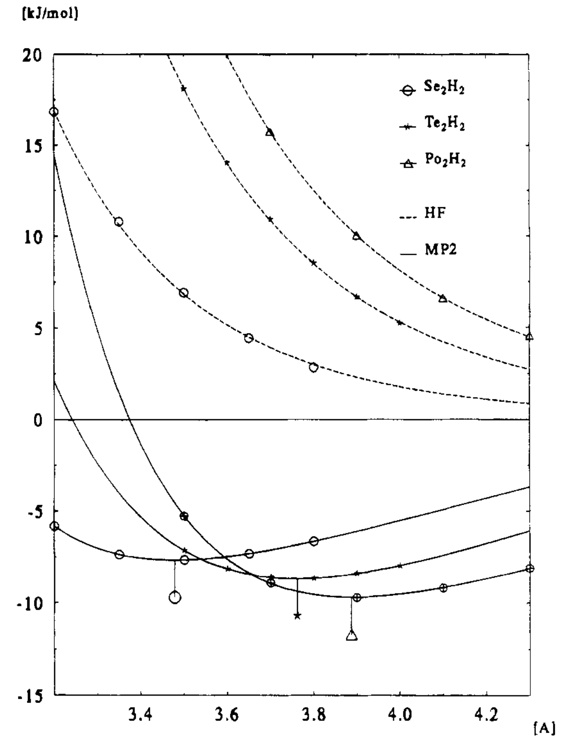


Figure 3. Dependence of the intermolecular interaction energy of the collinear $(HE{-}EH)_2$ dimers on the chalcogen E = Se, Te, Po. The vertical bars mark the calculated energy minima.

Dimers. (i) Correlation. The interaction energies at the HF level for the present collinear dimers are invariably repulsive; the attraction is not recovered before, at the MP2 level, correlation is taken into account (Figures 3 and 4). Earlier semiempirical models based on EHT also gave indications of intermolecular pnicogen bonding, both for dimers and for infinite-chain polymers.[33] If the real physics of the problem, however, consists of correlation effects, it is not evident how these are included in EHT.

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(31) Sadlej, A. J. *Theor. Chim. Acta* **1992**, *81*, 339.

(32) H_2Se_2 and H_2Te_2: Ewig, C. S.; Mei, E. H.; Van Wazer, J. R. *Mol. Phys.* **1980**, *40*, 241. Bi_2H_4: Lohr, L. L.; Ashe, A. J., III. *Organometallics* **1993**, *12*, 343.

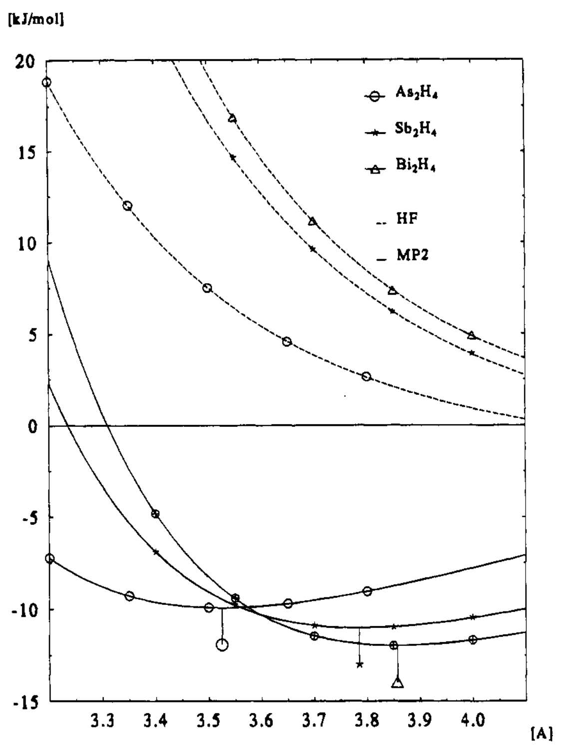

Figure 4. Dependence of the intermolecular interaction energy of the collinear $(H_2E-EH_2)_2$ dimers on the pnicogen E = As, Sb, Bi. The vertical bars mark the calculated energy minima.

Table 4. Calculated E−E Distances (pm), Interaction Energies $V(R_e)$ (kJ mol^{-1}), and Force Constants (N cm^{-1}) for the Best Basis Sets [4s4p3d3f] at the MP2 Level. Q is Defined as the Ratio $E-E_{intra}/E\cdots E_{inter}$

system	d(E−E)	d(E···E)	Q	$V(R_e)$	k
HSe−SeH	231.18	347.8	1.50	−7.68	0.0480
HTe−TeH	271.28	376.1	1.39	−8.68	0.0506
HTe−TeH[a]	271.28	377.9	1.39	−15.03	0.0772
HPo−PoH	289.9	388.7	1.34	−9.68	0.0532
$H_2As-AsH_2$	244.1	352.5	1.44	−9.92	0.0510
$H_2Sb-SbH_2$	282.4	378.5	1.34	−10.99	0.0514
$H_2Bi-BiH_2$	302.0	385.7	1.28	−11.96	0.0567
$H_2Bi-BiH_2$	312.0[b]	377.4	1.21	−13.44	0.0680
$H_2Bi-BiH_2$[c]	312.0[b]	400.0	1.28	−11.28	0.0432

[a] L-shaped dimer. [b] Distance observed in Bi_2Me_4.[17,35] [c] Nonrelativistic PP.

(ii) Dimerization Energies. The calculated intermolecular distances (R), dimerization energies (ΔE), and force constants (k) for the collinear dimers are given in Table 4. The corresponding potential energy [$V(R)$] curves are shown in Figures 3 and 4 for the dichalcogen and dipnicogen systems, respectively. The interaction energies and force constants increase on going down a column in both groups. On the same row, as for Sb and Te, the dipnicogen system possesses the bigger values. Ashe et al.[34] find an inter-ring Sb···Sb contact of 358 pm in substituted distibaferrocene but no As···As contact in the analogous diarsaferrocene, in agreement with this trend.

(iii) Distances. Some representative experimental E···E distances are tabulated in Table 1. It is easily seen that the calculated ones, for the present hydride dimer models, fall in the same range as the experimental ones. In particular, for the lighter members, As and Se, the theoretical R values tend to be shorter than the experimental ones. For the heavier elements, the opposite holds, perhaps due to a pronounced redistribution of inter- and intramolecular bonding. For strong intermolecular interactions, there is experimental evidence that the bonds in and between the molecules influence each other. In solid Me_4As_2[35a,b] and Me_2Te_2[35c] for instance, the intramolecular E−E bond is lengthened by about 2−3 pm, as compared with that of the gas phase.[36,37] In the crystal structure of Bi_2Me_4, one-dimensional chains were found. In these, very long intramolecular Bi−Bi distances of 312 pm (cf. Table 3) and comparatively short intermolecular distances of 355 pm alternate with each other. As a simple model for this kind of problem, a further calculation on collinear dimers of Bi_2H_4 was done where the fixed intramolecular Bi−Bi distance was lengthened from 302 pm to a value of 312 pm. In accordance with the experimental material, the lengthening of the intramolecular bond leads to a shortening of 7.5 pm in the adjacent intermolecular bond. Furthermore, the dimerization energy is raised by about 11% (Table 4, Figure 5). A real two-dimensional mapping of $V(R)$ against the quotient d_{intra}/d_{inter} and studies on intra/intermolecular cooperative effects in trimers or even bigger aggregates at a sufficiently high computational level are, at least at the moment, technically inaccessible, as are more realistic ligands, i.e., CH_3 instead of H.

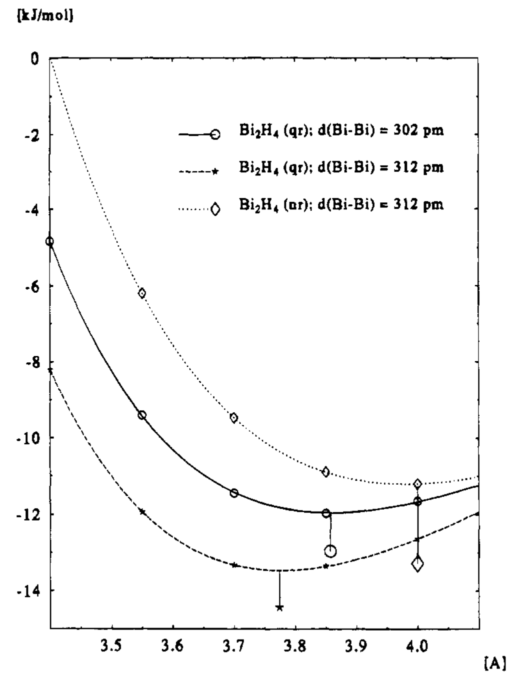

Figure 5. Influence of intramolecular Bi−Bi distance and relativity on the intermolecular interaction energy of the collinear $(H_2Bi-BiH_2)_2$ dimer.

(iv) Relativity. Effects of relativity were studied by calculations on the $H_2Bi-BiH_2$ dimer using appropriate nonrelativistic pseudopotentials[27] and a Bi−Bi distance of 312 pm. The results (Table 4, Figure 5) show that the interaction is enhanced by relativistic effects. The calculated interaction energy employing the nonrelativistic pseudopotentials is some 16% smaller, while the equilibrium distance is lengthened by about 23 pm.

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(33) Hughbanks, T.; Hoffmann, R.; Whangbo, M.-H.; Stewart, K. R.; Eisenstein, O.; Canadell, E. *J. Am. Chem. Soc.* **1982**, *104*, 3876. Canadell, E.; Shaik, S. S. *Inorg. Chem.* **1987**, *26*, 3797. Ashe, A. J., III; Kausch, C. M.; Eisenstein, O. *Organometallics* **1987**, *6*, 1185.

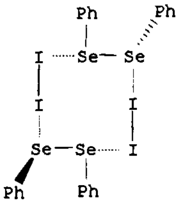
(34) Ashe, A. J., III; Kampf, J. W.; Pilotek, S.; Rousseau, R. *Organometallics* **1994**, *13*, 4067.

(35) (a) Ashe, A. J., III; Ludwig, E. G.; Oleksyszyn, J.; Huffman, J. C. *Organometallics* **1984**, *3*, 337. (b) Mundt, O.; Riffel, H.; Becker, G.; Simon, A. *Z. Naturforsch.* **1984**, *43b*, 952. (c) Becker, G.; Baumgarten, J.; Mundt, O.; Riffel, H.; Simon, A. To be published.

(36) Csaszar, A. G.; Hedberg, L.; Hedberg, K.; Ludwig, E. G.; Ashe, A. J., III. *Organometallics* **1986**, *5*, 2257.

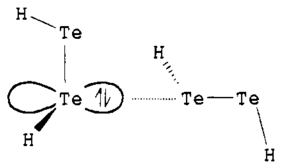
(37) Haaland, A.; Hammel, A.; Thomassen, H.; Volden, H. V. *Z. Naturforsch.* **1990**, *45b*, 1143.

(v) Influence of the E−E···E Orientation. As mentioned in the Introduction, in addition to the nearly linear chains, **1**−**4**, there are some examples with nearly 90° E−E···E angles, **5**−**6**. Related heteroatomic situations exist, such as the Se−Se···I−I links in the cyclic compound $[Ph_2Se_2{\cdot}I_2]_4$, **7**.[38]



7

We therefore looked at the interaction in a hypothetical L-shaped dimer of H_2Te_2, **8**.



Note that in this orientation the Te−Te bond of one molecule is lined up with a Te lone pair of the second. The resulting E···E distance of 377.9 pm is comparable with the one observed in the collinear case, but the interaction energy is nearly doubled (Table 4). Geometries of this type occur not only in the mixed halogen−chalcogen systems such as **7** but also, to a good approximation, in the solid halogens.[39] Although energetically favored, they are so far unknown in simple dichalcogenanes, perhaps for steric reasons.

Conclusions

(1) The "semibonding" E···E interaction between closed-shell molecules containing dipnicogen and dichalcogen moieties is attributed to correlation effects. At the Hartree−Fock level, no attraction is found. Thus it is completely analogous to the "metallophilic" [10] attraction between closed-shell metal ions. At long distances the R^{-6} "dispersion" or "van der Waals" forces are pure correlation effects. At the present, for the short E···E distances discussed in this article, no detailed analysis seems possible. For a qualitative discussion, however, such "van der Waals" forces now seem the likeliest simple picture for the E···E attraction. While the correlated ab initio methods include these effects, the density functional theories fail.[45] (2) The calculated E···E distances in the present dimer models are comparable to experimental ones. Although the interdependence of intra- and intermolecular E−E distances was demonstrated for the case of the dibismuthane dimer, cooperative effects, possibly operating in infinite chains, could not be studied so far. (3) The interaction energy increases down a column in the periodic table and toward the left along a row. (4) The strongest interaction consequently is the Bi···Bi one of some 13 kJ mol^{-1}. This is about half the value of the strongest "aurophilic" Au···Au interactions calculated at a similar level. (5) The relativistic enhancement of the interaction energies was estimated for the Bi···Bi case to be some 16%.

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Note Added in Proof: The intermolecular Sb···Sb force constants of Sb_2Me_4 and $Sb_2(SiMe_3)_4$ have been measured by Raman spectroscopy.[46] The results are 0.125 and 0.18 N cm^{-1}, respectively, as compared to 0.05 N cm^{-1} calculated here for an Sb_2H_4 dimer. Both cooperative effects, softer ligands[10] and basis-set effects may contribute to the difference.

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(38) Kubiniok, S.; du Mont, W.-W.; Pohl, S.; Saak, W. *Angew. Chem.* **1988**, *100*, 438; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 431. See also: du Mont, W.-W., ref 6, p 237.

(39) Greenwood, N. N.; Earnshaw, A. *Chemie der Elemente*; VCH: Weinheim, 1988; p 1038. Desiraju, G. R. *Crystal Engineering. The Design of Organic Solids*; Elsevier: Amsterdam, 1989; Chapter 6. Pedireddi, V. R.; Reddi, D. S.; Goud, B. S.; Craig, D. C.; Rae, A. D.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2353.

(40) Mundt, O.; Becker, G.; Rössler, M.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1983**, *506*, 42. Ludlow, S.; McCarthy, A. E. *J. Organomet. Chem.* **1981**, *219*, 169.

(41) Mundt, O.; Riffel, H.; Becker, G.; Simon, A. *Z. Naturforsch.* **1984**, *39b*, 317. See also: Ashe, A. J., III; Ludwig, E. G.; Huffman, J. C. *Organometallics* **1984**, *3*, 337.

(42) Ashe, A. J., III; Butler, W.; Diephouse, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 207.

(43) Becker, G.; Freudenblum, H.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1982**, *492*, 37.

(44) Mundt, O.; Becker, G.; Rössler, M.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1983**, *506*, 42.

(45) Kristyán, S.; Pulay, P. *Chem. Phys. Lett.* **1994**, *229*, 175.

(46) Bürger, H.; Eujen, R.; Becker, G.; Mundt, O.; Westerhausen, M.; Witthauer, C. *J. Mol. Struct.* **1983**, *98*, 265.