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X–X Direct Bonds versus Bridged Structures in Group 13 X_2H_2 Potential Energy Surfaces

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Abstract: The singlet potential energy surfaces for all group 13 X_2H_2 systems have been explored through ab initio SCF + CI calculations. Effective core potentials including relativistic effects for the heaviest atoms of the series were used. Geometries of the various isomers were determined at the Hartree–Fock level and confirmed to be minima by vibrational analysis. In all cases but boron, the global minimum is found to be the D_{2h} di-H-bridged structure. For boron, the H—X═X—H linear form is found to be the global minimum, the $^1\Delta_g$ state being 14.7 kcal/mol above the $^3\Sigma^-_g$ state. For all other atoms, this linear form is only a transition state, and a trans-bent isomer appears as a minimum on the surfaces for Al, Ga, and In. However, our analysis reveals two other low-lying minima, namely, the asymmetric X–XH_2 isomer and the C_s mono-H-bridged structure. A simple rule for the occurrence of trans-bent isomers is derived from a MO model treating σ—π mixing. In HX═XH, a trans-bent distortion occurs when the singlet–triplet energy separation of the XH fragments is larger than half of the bond energy in the linear $^1\Delta_g$ state. Qualitative rules concerning the existence of the bridged structures are also established.

Introduction

There has recently been considerable interest for group 13 hydride molecules. Successful syntheses of digallane(6)[1] and mixed borogallane(6)[2] have strongly stimulated theoretical studies on these molecules and the corresponding diborane-like X_2H_6 compounds. Up to now, ab initio studies have been reported on the equilibrium structures and binding energies of B_2H_6,[3–5] Al_2H_6,[4–7] Ga_2H_6,[4–8] $AlBH_6$, $AlGaH_6$, and $BGaH_6$.[9,10] All these XH_3 dimers are characterized by a μ-hydrido bridging structure. An analysis of the correlated wave function in terms of orthogonal valence-bond determinants applied by Trinquier et al.[11] to the double bridge of B_2H_6 indicates that the B–H_b (b stands for bridging) interactions are by far the most prominent.

A second type of group 13 hydrides of theoretical interest is formed by the tetrahydrides X_2H_4 with 10 valence electrons. The prototype B_2H_4 designated as diborane(4) can be expected to exhibit two structural possibilities, a classical form H_2B–BH_2 (D_{2d} or D_{2h}) with a boron–boron bond, and other nonclassical structures with hydrogen bridges. Various theoretical calculations[12,13] have shown that the competition is energetically in favor of the D_{2d} classical structure. However, the situation appears to be more complicated for the heavier analogues of diborane(4). Dialane(4)[14] and digallane(4)[15] have been shown to prefer a tridentate salt-like structure of C_{3v} symmetry.[16] Studies of the mixed gallium hydrides $BGaH_4$ and $AlGaH_4$[17] have led to the same global minimum. These structures can be described in terms of ionic interactions between a X^+ cation and a tetrahedral XH_4^- anion.

By comparison, very little is known about the dimers of the low-valent borene-like XH species. Diborene (B_2H_2) is the boron analogue of acetylene. It has two electrons less than acetylene, and the π orbitals are occupied by only two electrons. So, diborene may be considered as the model of an unsaturated bond between two boron atoms. However, this molecule is found to have a linear triplet ground state,[18] and there is no experimental evidence for B–B double bonding. On other hand, a dibridged structure is found to be the most stable structure of the dihydride of aluminum, Al_2H_2, by Baird[19] both using MNDO and ab initio methods. The case of the heaviest analogue Tl_2H_2 is even more confusing. The question of the formation of a genuine thallium–thallium bond was first examined by Janiak and Hoffmann[20] through extended-Hückel calculations. They concluded that a strong Tl–Tl bond may be obtained upon trans-bending of the hydrogens at an angle of about 75°. Very recently, this result was invalidated by Schwerdtfeger[21] by means of ab initio calculations taking into account relativistic and electron correlation effects. His findings are in favor of a very weak Tl–Tl bonding interaction in the trans-bent structure due to correlation effects. Moreover, this author has shown that a symmetric Tl_2H_2 rhombus with a nonbonded Tl–Tl situation exists as a second deeper minimum on the potential energy surface (PES). Experimentally, only halo derivatives such as thallous fluoride, Tl_2F_2,[22] or derivatives with more bulky ligands such as pentabenzylcyclopentadienylindium[23] and -thallium[24] have been extensively studied. The solid-state structure of the latter is a trans-

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bent dimer,[25] while the former is a planar rhombus with alternating Tl and F atoms.

In this paper, we present a theoretical study of the X_2H_2 potential surfaces, with X varying from boron to thallium. Our goal was to obtain more insight in the bonding character of their various isomers, and to provide structural and energetic data. After an exploration of the singlet PES, we will try to propose a simple rule for the existence of a direct X–X bond, be it linear or trans-bent. Finally, the bridged structures are discussed and rationalized.

Computational Methods

Restricted Hartree–Fock (RHF) and unrestricted Hartree–Fock (UHF) calculations were performed with the PSHONDO algorithm[26] which is derived from the standard HONDO program[27] by introducing the pseudopotentials of Durand and Barthelat.[28] For gallium, indium, and thallium, we used effective core potentials, taking into account mean relativistic effects through mass–velocity and Darwin term corrections.[29] Valence basis sets of contracted Gaussian functions are of double-zeta plus polarization (DZP) quality. The exponents for the d polarization functions are taken at 0.60, 0.28, 0.16, 0.11, and 0.08 for B, Al, Ga, In, and Tl, respectively. The exponent for the p functions on hydrogen is taken at 0.9. Molecular structures on the potential energy surfaces (PES) were located by using self-consistent-field (SCF) gradient techniques. The convergence threshold for the gradient components was fixed at 10^{-4}. The triplet states of the XH monomers and dimers are optimized using the UHF version of the program package. In all cases, the mean value $\langle S^2 \rangle$ remains within 1% of $S(S+1)$. Stationary points were characterized as minima or transition states by determining the harmonic vibrational frequencies by using a numerical derivation of the analytical first derivatives (single-point differencing formula).

Valence-shell configuration interaction (CI) calculations were performed for the SCF-optimized structures with the CIPSI algorithm.[30] According to this procedure, a variational zeroth-order wave function is built up from an iterative selection of the most important determinants. The remaining determinants are treated through a second-order Möller–Plesset perturbation. In the final step, we included in the variational subspace all determinants that contribute to the first-order perturbed wave function by a coefficient larger than or equal to 0.015. For the Ga-containing closed-shell species as a typical example, the subspaces which are variationally treated include about 100 determinants while the number of determinants involved in the perturbation ranges from 3×10^5 to 10^6.

Mono- and Dihydrides of Group 13

In order to obtain comparable results for the energetics of the dimers, monomers XH are studied by using the same basis set of double-ζ plus polarization quality. Two electronic states were investigated, namely, the $^1\Sigma^+$ ground state and the $^3\Pi$ first excited state. The SCF predicted bond lengths and harmonic vibrational frequencies together with the singlet–triplet energy gap (ΔE_{ST}) are reported in Table I. Although larger basis sets would be needed to better describe the monomers, we obtain an overall good agreement with the available experimental data.[31] The geometries and frequencies are also in agreement with other calculated ones at the same level of theory for the ground state of the lighter monohydrides BH and AlH by Pople et al.[32] For GaH, results obtained by Bock et al.[33] and Balasubramanian[34] at higher levels of computation are also included in Table I for comparison. Note that, owing to the importance of electron correlation effects, $TlH(^3\Pi)$ is found to be unbound at the SCF level. Therefore, the singlet–triplet energy separation of TlH must be determined after CI optimizations of the two states. For the singlet state, our CI-calculated bond length (1.93 Å) is comparable to those recently optimized by Balasubramanian and Tao[35] (1.95 Å) and Schwerdtfeger[21] (1.91 Å).

Table I. Equilibrium Bond Distances (in Å), Harmonic Vibrational Frequencies (in cm^{-1}), and Singlet-Triplet Energy Separation ΔE_{ST} (in kcal mol^{-1}) for Group 13 Monohydrides[a]

	$^1\Sigma^+$		$^3\Pi$	ΔE_{ST}	
	X–H	freq	X-H	SCF	CI
BH	1.227	2532	1.189	9.7	27.7
	1.225[b]	2513[b]			
	(1.232)	(2367)	(1.201)		
AlH	1.651	1738	1.584	28.0	42.7
	1.652[b]	1771[b]			
	(1.648)	(1683)	(1.609)		(34.3)[c]
GaH	1.677	1605	1.589	36.8	46.6
	1.689[d]		1.602[d]		50.7[d]
	1.662[e]	1612[e]	1.603[e]		48.2[e]
	(1.663)	(1604)	(1.601)[f]		(49.9)[f]
					(49.6)[g]
InH	1.849	1535	1.769	36.1	47.0
	(1.838)	(1476)	(1.766)[f]		(48.6)[c,f]
					(46.5)[g]
TlH	1.899	1383			
	1.928[h]		3.357[h]		51.9[h]
	(1.870)	(1391)			(50.7)[g]

[a] Numbers in parentheses refer to experimental values (ref 31). [b] Reference 32. [c] Estimated value. [d] Reference 33. Bond lengths are $RHF(^1\Sigma^+)$ or $UHF(^3\Pi)$ optimized values and ΔE_{ST} is a MP4 (SDTQ) value. [e] Reference 34. Values obtained using the CASSCF/SOCI method. [f] Averaged over the 0^+, 0^-, 1, 2 spin–orbit components of the $^3\Pi$ state. [g] Energy separation between the $^1\Sigma^+{}_{0^+}$ ground state and the $^3\Pi_{0^+}$ state. [h] CI-optimized values taking into account all relativistic effects except spin–orbit coupling (this work).

Table II. SCF-Optimized Geometries[a] for $XH_2(^2A_1)$

	X–H	HXH
BH_2	1.194	127.1
	1.185[b]	126.5[b]
AlH_2	1.590	118.7
	1.595[b]	118.0[b]
GaH_2	1.580	119.7
	1.600[c]	119.4[c]
	1.610[d]	120.4[d]
InH_2	1.755	119.0
	1.802[e]	118.9[e]
TlH_2	1.760	121.7
	1.869[e]	121.1[e]

[a] Bond lengths in angstroms and bond angles in degrees. [b] Reference 32. [c] Reference 33. [d] Reference 34. Values obtained from more sophisticated CASSCF calculations. [e] Reference 35. Values obtained from more sophisticated CASSCF calculations.

We also examined the geometries of the dihydrides XH_2 in their $^2A_1$ ground state at the SCF level. The optimized geometries are compared with other calculations in Table II. The X–H bond lengths in XH_2 are found to be shorter than their values in XH, and the bond angles are close to the typical value of 120°. These results suggest a sp^2 hybridization of the X atom in all the dihydrides.

Spin–orbit effects are not included in our quasi-relativistic calculations. They could be important for the heaviest compounds such as TlH or TlH_2.[36] In fact, the $^3\Pi$ state of TlH[37] is strongly

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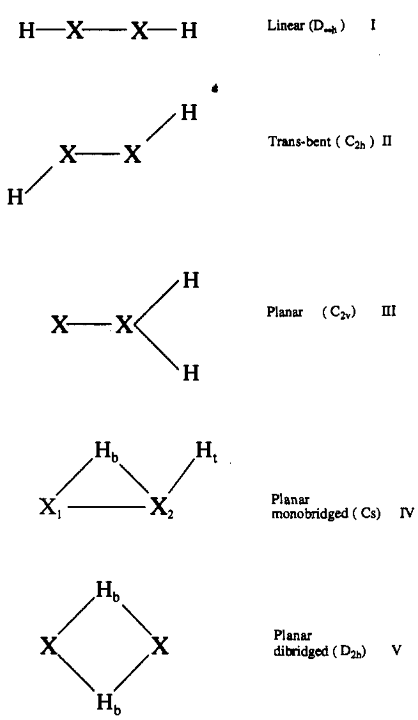


Figure 1. Valence isomers of X_2H_2 investigated in this study.

contaminated by spin–orbit coupling with the $^1\Sigma^+$ state. However, it is obvious from the energy difference between the $^1\Sigma^+{}_{0^+}$ and $^3\Pi_{0^+}$ experimental states reported in Table I that ΔE_{ST} is not significantly altered. Moreover, Balasubramanian and Tao[35] have shown that the spin–orbit coupling has no significant effect on the equilibrium geometries, for instance, 0.01 Å on the TlH bond length and 1° on the HTlH bond angle for $TlH_2(^2A_1)$. So we hope that spin–orbit coupling cannot strongly alter our description of the singlet Tl_2H_2 potential surface.

Results and Discussion

The various X_2H_2 isomers are depicted in Figure 1. The SCF-optimized geometries are given in Table III. Harmonic vibrational frequencies and relative energies predicted by this work are collected in Tables IV–IX, respectively.

For comparison, we determined, still at the SCF level, the optimized geometries of the eclipsed (D_{2h}) and staggered (D_{2d}) forms of H_2X–XH_2. These molecules can be considered as representative of a system containing a X–X single bond. Our results are compared with previous SCF calculations in Table X. In all cases, a hyperconjugation effect stabilizes the D_{2d} form with respect to the D_{2h}. This relative stabilization which appears to be more important for H_2B–BH_2 is also responsible of a characteristic shortening of the XX bond length upon twisting the planar conformation into the D_{2d} conformer.

A. Stationary Points on the X_2H_2 Potential Energy Surfaces. (1) Isomers without Hydrogen Bridge. We first consider the diborene-like molecules in $D_{\infty h}$ symmetry. These linear (I) structures have a valence electron configuration given by $1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 1\pi_u{}^2$, which leads to a $^3\Sigma_g{}^-$ triplet state and two singlet states, $^1\Delta_g$ and $^1\Sigma_g{}^+$. For all the series, the lowest state is found to be the triplet state, at both SCF and CI levels. However, a vibrational frequency analysis indicates that these structures are not local minima on the triplet potential energy surfaces, except for HB═BH (see Table IV).

The SCF-calculated X═X bond lengths can be compared with their corresponding values in H_2X—$XH_2(D_{2d})$ taken as references for single X—X bonds. We obtain a relative shortening of 10–12% indicating some double-bond character of the X═X bond. However, the open-shell nature of this $^3\Sigma_g{}^-$ state with two unpaired π electrons confers a status of nonclassical multiple bond on this XX link.

Table III. SCF-Calculated Geometries for the Stationary Points of the X_2H_2 Potential Energy Surfaces[a]

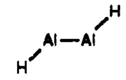
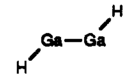
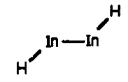
isomers	states	parameters	B	Al	Ga	In	Tl
HX═XH linear	$^1\Sigma^+{}_g$	X═X	1.533	2.336	2.258	2.545	2.494
		X—H	1.177	1.561	1.532	1.702	1.677
	$^1\Delta_g$	X═X	1.524	2.319	2.241	2.529	2.480
		X—H	1.177	1.562	1.533	1.703	1.678
	$^3\Sigma^-{}_g$	X═X	1.509	2.295	2.218	2.510	2.462
		X—H	1.179	1.564	1.536	1.707	1.681
HX═XH trans bent	^1A_g	X═X		2.737	2.951	3.329	
		X—H		1.615	1.642	1.820	
		HXX		120.1	116.6	116.7	
	^3B_g	X═X		2.406	2.341	2.668	2.696
		X—H		1.578	1.562	1.741	1.756
		HXX		146.5	146.1	144.7	144.0
X—XH$_2$	$^1A_1$	X—X	1.767	2.786	2.763	3.084	3.087
		X—H	1.201	1.600	1.594	1.770	1.787
		HXH	117.6	113.3	111.9	110.4	108.1
X(μ-H)XH[b]	$^1A'$	X_1—X_2		2.655	2.823	3.164	
		X_1—H_b		1.881	1.826	1.984	
		X_2—H_b		1.827	2.028	2.203	
		X_2—H_t		1.601	1.622	1.799	
		$X_1H_bX_2$		91.0	94.1	98.0	
		$H_bX_2H_t$		103.2	97.6	97.4	
X(μ-H)$_2$X	^1A_g	X···X	1.999	2.940	3.059	3.367	3.518
		X—H_b	1.371	1.823	1.897	2.067	2.173
		XH_bX	93.6	107.5	107.4	109.1	108.1

[a] Interatomic distances in angstroms and bond angles in degrees. [b] See Figure 1 for the definition of the geometrical parameters.

Table IV. Harmonic Vibrational Frequencies (cm^{-1}) for the $^3\Sigma^-{}_g$ States of the Linear Forms

H—B═B—H		H—Al═Al—H		H—Ga═Ga—H		H—In═In—H		H—Tl═Tl—H	
π_g	523	π_g	450i	π_g	476i	π_g	500i	π_g	597i
π_u	657	π_u	415	σ_g	344	σ_g	238	σ_g	183
σ_g	1335	σ_g	536	π_u	450	π_u	397	π_u	432
σ_u	2887	σ_u	2033	σ_u	2050	σ_u	1911	σ_u	1912
σ_g	2931	σ_g	2044	σ_g	2067	σ_g	1931	σ_g	1951

Table V. Harmonic Vibrational Frequencies (cm^{-1}) for the ^1A_g States of the Trans-Bent Forms

					
a_g	210	a_g	60	a_g	45
a_u	293	b_u	147	b_u	81
b_u	340	a_u	309	a_u	274
a_g	533	a_g	503	a_g	367
a_g	1856	a_g	1695	a_g	1590
b_u	1856	b_u	1705	b_u	1605

The situation is similar on the singlet PES where the lowest state in energy, i.e., the $^1\Delta_g$ state, is a saddle point, except for the case of boron. Only the ethylene-like $^1\Sigma_g{}^+$ state appears to be a local minimum in all cases.

The imaginary frequency for the $^3\Sigma_g{}^-$ and $^1\Delta_g$ states of the linear forms HX═XH (X = Al, Ga, In, Tl) corresponds to the π_g vibration. This suggests the possible existence of a trans-bent (II) form of C_{2h} symmetry. Such a structure corresponding to a valence electron configuration given by $1a_g{}^2 1b_u{}^2 2a_g{}^2 2b_u{}^2 (^1A_g)$ is found to be a local minimum only in the case of Al, Ga, and In (see Table V). A criterion predicting the existence of this trans-bent distortion for the X═X bond will be discussed later. From now on, it can be noted that a trans-bent structure does not exist as a minimum for Tl_2H_2 at the HF level.

As concerns the search for a ^3B_g trans-bent triplet form, frequency analysis from the SCF-optimized C_{2h} geometries reveals one imaginary frequency, except for Ga_2H_2. A nonplanar

Table VI. Harmonic Vibrational Frequencies (cm^{-1}) for the H_2X–X Forms

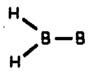
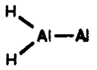
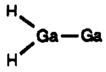
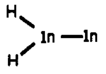
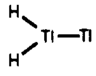
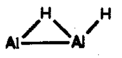
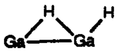
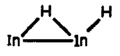
									
b_1	550	a_1	303	a_1	180	a_1	126	a_1	92
a_1	816	b_1	334	b_1	280	b_1	250	b_1	222
b_2	864	b_2	532	b_2	471	b_2	436	b_2	436
a_1	1261	a_1	844	a_1	835	a_1	724	a_1	714
a_1	2681	b_1	1916	b_1	1851	b_1	1732	b_1	1610
b_1	2747	a_1	1918	a_1	1864	a_1	1749	a_1	1623

Table VII. Harmonic Vibrational Frequencies (cm^{-1}) for the Mono-H-Bridged Forms

					
a′	251	a′	90	a′	68
a″	269	a″	248	a″	228
a′	438	a′	440	a′	384
a′	991	a′	704	a′	688
a′	1236	a′	1206	a′	1161
a′	1901	a′	1753	a′	1648

geometry of C_2 symmetry is then optimized. However, the Hartree–Fock triplet surface is very flat with respect to a variation of the HXXH dihedral angle. In that case, it is well-known that the inclusion of correlation effects may change the nature of a SCF stationary point. A geometry optimization at the CI level shows that the planar C_{2h} geometry is a local minimum on the triplet potential energy surface for Al_2H_2, Ga_2H_2, and In_2H_2.

Another isomer containing a X–X bond between two X atoms with different valence coordination numbers may be investigated. To form the XXH_2 structure, the $^2A_1$ state of the XH_2 species may combine with a ^2P X atom. The resulting molecule has one XX single bond and one remaining lone pair of s character located on the X atom. This (III) structure of C_{2v} symmetry is found to be a local minimum on the singlet PES in all cases (see Table VI).

(2) Bridged Structures. Two types of bridged structures may be located on the singlet PES depending on whether one or two H atoms are involved in the building of the cycle. The singly bridged (IV) structure is found to have a planar C_s geometry with a $^1A'$ electronic ground state. This stationary point is a local minimum on the singlet PES for Al_2H_2, Ga_2H_2, and In_2H_2 (see Table VII). Attempts to reach such a local minimum failed for the lightest analogue B(μ-H)BH and the heaviest analogue Tl(μ-H)TlH of the series. The X–X bonds in the monobridged structures are found to be shorter than that in the trans-bent (II) forms but longer than the typical single bond calculated in H_2X—XH_2(D_{2d}). The two X—H bond lengths of the X_1—H_b—X_2 bridges are longer than that in the XH($^1\Sigma^+$) monomers by 13.9% and 10.7% for Al_2H_2, 8.9% and 20.9% for Ga_2H_2, and 7.3% and 19.1% for In_2H_2. These lengthenings are characteristic of those generally encountered in the XHX three-center two-electron bridges. Note that in Al_1–H_b–Al_2, the Al_1–H_b bond is longer than the Al_2–H_b one, while it is the reverse for Ga and In where the longer bond is X_2—H_b. On the other hand, the X_2—H_t bond lengths are quite comparable to those in the XH($^1\Sigma^+$) monomers. They are only shorter by about 3%. All these structural parameters are consistent with other singly hydrogen bridges observed in the possible isomers of dialane(4) and digallane(4) by Lammertsma et al.[14,15]

The doubly bridged (V) structure with a planar D_{2h} geometry has a ^1A_g electronic ground state arising from the configuration $1a_g^2 1b_{1u}^2 1b_{3u}^2 2a_g^2$. Vibrational frequency analyses (see Table VIII) show that this stationary point is a minimum on all of singlet PES investigated. All di-H-bridged structures have X–X separations longer than normal X—X single bonds in X_2H_4(D_{2d}) systems (from 12% in Al_2H_2 to 27% in Tl_2H_2). This indicates that there is no direct bonding between the X atoms. Moreover, the bridging X–H distances are longer than that observed in the XH($^1\Sigma^+$) monomers by 11.7% for B_2H_2, 10.4% for Al_2H_2, 13.1% for Ga_2H_2, 11.8% for In_2H_2, and 14.4% for Tl_2H_2. This significant lengthening can be closely connected with a similar observation in the cycles of diborane(6) and its heavier analogues (i.e., a XH bond lengthening of 11.6% in B_2H_6, 10.1% in Al_2H_6, and 12.8% in Ga_2H_6 with respect to the XH_3 monomers[4]). Therefore, as suggested by these geometrical parameters, the same bonding picture of three-center two-electron XH_bX bridges can be applied to the doubly hydrogen-bridged structures of X_2H_6 and X_2H_2 (see Section E).

B. Energetics and Shapes of the PES. The relative energies for the X_2H_2 isomers are reported in Table IX, at both SCF and CI levels. Since the inclusion of correlation effects does not change the energy ordering, we shall only consider the CI energy values for the following discussion.

As in group 14,[38] these results evidence the contrasting behavior of a first-row atom and the heavier elements of the same group. Indeed, while the B_2H_2 singlet PES exhibits a $^1\Delta_g$ linear ground state, the dibridged structure (V) is found to be the global minimum for all the other X_2H_2 singlet PES. On the B_2H_2 surface, the dibridged (V) appears to be a high-lying minimum at 64.8 kcal/mol. Two other local minima, the $^1\Sigma_g^+$ linear (I) and the asymmetric structure (III), are lower in energy, at 8.7 and 17.6 kcal/mol, respectively.

On the Al_2H_2 singlet PES, the three lowest minima are the dibridged (V), the asymmetric H_2Al—Al form (III), and the monobridged (IV) form. The dibridged form is preferred over H_2Al—Al by 10.9 kcal/mol at the CI level. Note that the CI stabilizes this form with respect to H_2Al—Al which is found to be only 0.3 kcal/mol higher at the SCF level. The monobridged structure (IV) is only 4.8 kcal/mol less stable than the H_2Al–Al structure (III). The $^1\Delta_g$ linear form (I) is no longer a minimum. A distortion from linearity occurs and a new local minimum with the trans-bent structure (II) lies at 19.2 kcal/mol. A similar distortion takes place on the Al_2H_2 triplet PES. A ^3B_g trans-bent structure becomes the lowest state. Our findings concerning these singlet- and triplet-state distortions are in qualitatively good agreement with a previous work of Baird.[19]

For the Ga_2H_2 and In_2H_2 surfaces, a similar energy ordering is obtained. When going from Al to In, the energy differences between the four lowest singlet minima increase, and the dibridged (V) appears as more and more preferred over the H_2X–X structure (III). The same tendency is obtained for the Tl_2H_2 singlet PES. The only peculiarity on this surface is that the monobridged (IV) and the trans-bent (II) do not exist as stable compounds with respect to two TlH monomers, at the SCF level. As previously pointed out by Schwerdtfeger,[21] only a CI optimization taking accurately into account the correlation effects allows one to get a very weak Tl–Tl interaction between two TlH in a trans-bent structure.

From all these considerations, we can try to picture parts of the singlet PES linking some of the stationary points. Starting from the H_2X–X structure, two pathways corresponding to H migrations can be imagined to reach its degenerate isomer X–XH_2.

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(38) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130.

Table VIII. Harmonic Vibrational Frequencies (cm^{-1}) for the Di-H-Bridged Forms

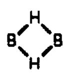
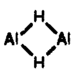
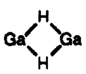
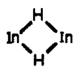
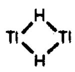
									
b_{2u}	564	a_g	330	a_g	189	a_g	142	a_g	96
a_g	618	b_{2u}	476	b_{2u}	442	b_{2u}	400	b_{2u}	364
b_{3u}	1275	b_{1u}	1017	b_{2g}	810	b_{2g}	827	b_{2g}	572
b_{2g}	1443	b_{2g}	1083	b_{1u}	900	b_{1u}	842	b_{1u}	732
b_{1u}	1750	b_{3u}	1287	b_{3u}	1092	b_{3u}	1074	b_{3u}	908
a_g	2161	a_g	1454	a_g	1309	a_g	1214	a_g	1036

Table IX. Relative Energies (in kcal/mol)

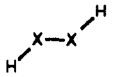
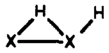
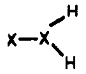
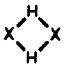
		B_2H_2		Al_2H_2		Ga_2H_2		In_2H_2		Tl_2H_2	
	state	SCF	CI	SCF	CI	SCF	CI	SCF	CI	SCF	CI
2XH	$^1\Sigma^+$	108.1	97.5	21.3	29.5	15.4	23.1	19.4	27.0	15.0	18.8
H—X═X—H	$^3\Sigma^-_g$	0.0	0.0	11.8	29.1	23.3	36.9	34.0	44.3	56.6	62.1
	$^1\Delta_g$	21.5	14.7	29.0	40.2	41.2	48.2	50.0	54.0	72.2	72.4
	$^1\Sigma^+_g$	40.2	23.4	43.2	46.4	55.7	55.5	63.6	61.2	85.4	79.7
	^1A_g			13.7	19.2	13.0	20.2	17.6	24.0		
	^3B_g			9.4	26.5	18.9	33.2	27.7	38.7	46.5	52.1
	$^1A'$			8.7	15.7	9.5	15.4	12.6	17.4		
	$^1A_1$	42.6	32.3	0.3	10.9	3.5	12.0	10.2	17.1	17.8	22.7
	^1A_g	108.9	79.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

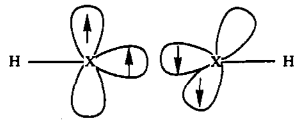
Table X. SCF-Optimized Geometries[a] and Energy Differences ΔE[b] for the Eclipsed (D_{2h}) and Staggered (D_{2d}) Forms of $H_2X–XH_2$

symmetry	parameters	B	Al	Ga	In	Tl
D_{2h}	X–X	1.754	2.632	2.555	2.860	2.815
		1.762[c]	2.628[d]	2.542[e]		
	X–H	1.202	1.589	1.575	1.748	1.743
		1.196[c]	1.593[d]	1.602[e]		
	HXH	116.3	116.1	116.4	115.9	116.5
		116.5[c]	115.8[d]	115.4[e]		
D_{2d}	X–X	1.678	2.615	2.530	2.838	2.775
		1.684[c]	2.613[d]	2.517[e]		
	X–H	1.204	1.589	1.575	1.747	1.742
		1.196[c]	1.594[d]	1.602[e]		
	HXH	116.5	116.2	116.3	115.9	116.1
		116.8[c]	116.0[d]	115.5[e]		
	ΔE	10.6	1.3	1.9	1.4	2.2
		10.9[c]	1.5[d]	2.2[e]		

[a] Bond lengths in angstroms, bond angles in degrees, and relative energies in kcal/mol. [b] $\Delta E = E(D_{2h}) - E(D_{2d})$. [c] Reference 12. [d] Reference 14. [e] Reference 15.

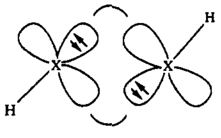
The first one is a nonsymmetrical pathway with the linear $^1\Delta_g$ form as intermediate (see the upper part of Figure 2), while the second one is a concerted pathway with the dibridged structure as intermediate (lower part of Figure 2). The energy shapes along these two pathways are schematized in Figures 3 and 4, using the CI relative energies of Table IX. The transition states connecting two minima have not been optimized in this study and the barrier heights are arbitrary. Nevertheless, these figures clearly illustrate that when going down the group 13 column, the dibridged structure (V) appears to be more and more favored while the linear (I) or trans-bent (II) are more and more disfavored. It can be noted that the same holds for the X_2H_4 isomers of group 14 when going from carbon to lead.[39]

C. Dissociation into Two XH. The linear form (I) can be considered as the product of the combination of two XH molecules in their $^3\Pi$ states.



So, the energy benefit due to the coupling of two triplet XH fragments into a linear structure is a possible measure of the ($\sigma + \pi$) X═X bond energy. The corresponding CI values for all linear states are listed in Table XI. As expected, the strongest binding energies occur for the case of boron, and the others are slowly decreasing from aluminum to thallium. They can be compared with the X–X single bond energies obtained from the energy differences between $H_2X–XH_2(D_{2d})$ and the two $XH_2(^2A_1)$ fragments, also reported in Table XI. For aluminum and the heavier atoms, the energy increase due to the formation of a double bond is about half the value obtained for boron. This is characteristic of a relative instability of X–X p–π bonds for all atoms of group 13 other than boron atom.

By contrast, the dissociation product of the trans-bent ^1A_g structure is a pair of $^1\Sigma^+$ XH molecules, according to the scheme



The n_σ lone pair of one XH species delocalizes into the p_π empty orbital of its partner. As one may expect from the very long XX equilibrium distances, the binding energies relative to $2\,XH(^1\Sigma^+)$ are small, 10.3 kcal/mol for Al_2H_2 and only 3 kcal/mol for Ga_2H_2 and In_2H_2. Although two lone pairs are involved into the formation of the XX bond, this type of interaction between two singlet XH remains very weak in the case of Ga and In. Note that for Tl_2H_2 trans-bent, Schwerdtfeger[21] found a dissociation energy of the same order of magnitude (3.3 kcal/mol) after CI geometry optimizations. In that case, Tl_2H_2 trans-bent may most likely be considered as an intermolecular complex $(TlH)_2$.

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(39) Trinquier, G. J. Am. Chem. Soc. **1991**, 113, 144.

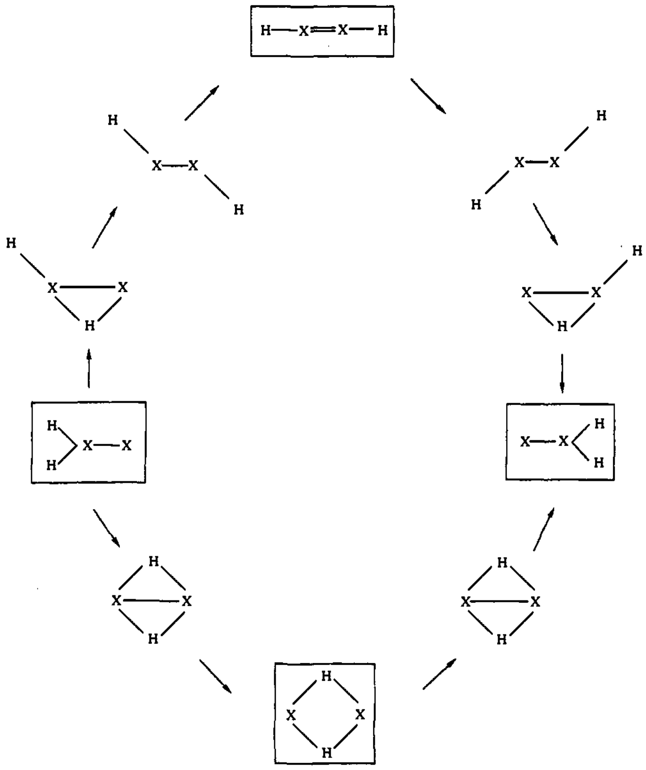
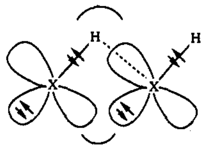


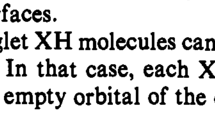
Figure 2. Connection of various stationary points.

However, two singlet XH molecules may interact in another way. Firstly, they can be arranged in a parallel manner, so that one XH electron pair can delocalized into the p_π empty orbital of its partner while this one uses its n_σ lone pair to contract a XX bond, according to the following scheme



The two singlet XH fragments are then bound through a three-center two-electron bridge $X_1H_bX_2$ and a dative bond $n_\sigma(X_2) \rightarrow p_\pi(X_1)$. Although taking into account this double interaction, the binding energy relative to two $XH(^1\Sigma^+)$ remains small, only a little greater than that observed in the trans-bent structure (II) for Al_2H_2 (13.8 kcal/mol) and below 10 kcal/mol for Ga_2H_2 and In_2H_2 (7.7 and 9.6 kcal/mol, respectively). Recall that this atomic arrangement which gives rise to the mono-H-bridged structure (IV) is found to be a local minimum only on the Al_2H_2, Ga_2H_2, and In_2H_2 singlet surfaces.

Lastly, the two singlet XH molecules can be brought together from top to bottom. In that case, each XH electron pair can delocalize into the p_π empty orbital of the other, leading to the formation of two three-center two-electron bonds.



The di-H-bridged structure (V) obtained is the most stable form of dimeric XH, except for BH. The binding energies relative to two $XH(^1\Sigma^+)$ range from 18 kcal/mol to 29.5 kcal/mol in the following order: B_2H_2, 18.0 kcal/mol; Tl_2H_2, 18.8 kcal/mol; Ga_2H_2, 23.1 kcal/mol; In_2H_2, 27.0 kcal/mol; Al_2H_2, 29.5 kcal/mol. It can be shown in Figure 5 that these values are strongly dependent on the electronegativity of the X atom defined by Allen[40] as the average one-electron energy of the valence electrons.

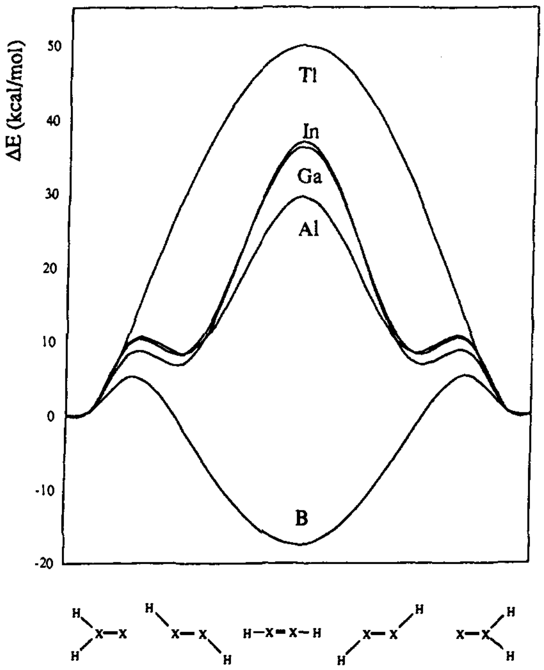


Figure 3. Schematic cross sections of the singlet potential surfaces, along the pathway described in the upper part of Figure 2. The common zero energy corresponds to the XXH_2 isomers. Energy barriers are arbitrary.

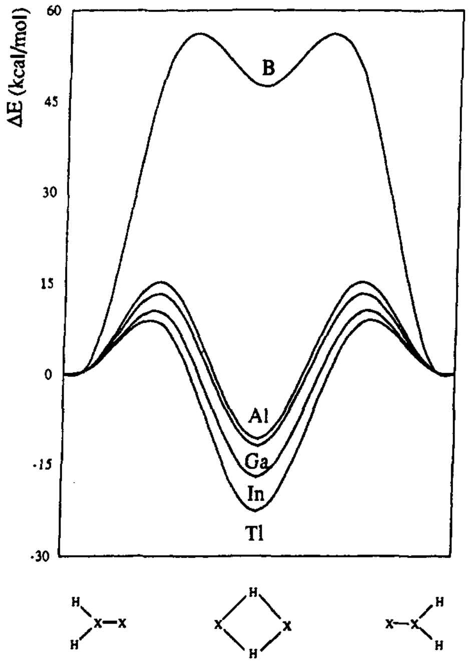


Figure 4. Schematic cross sections of the singlet potential surfaces, along the pathway described in the lower part of Figure 2. The XXH_2 isomers are the zero energy common to all surfaces. Energy barriers are arbitrary.

D. Occurrence of Trans-Bending. A condition for the existence of the trans-bent form may be derived from a simple molecular orbital model. A similar derivation leading to the condition of occurrence of trans-bent distortions at homopolar double bonds in group 14 has been recently achieved by Malrieu and Trinquier.[41] As already mentioned by these authors, when a molecule containing a $(\sigma + \pi)$ double bond enters a trans-bent distortion, two opposite facts take place, i.e. a destabilizing effect due to the

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(40) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.
(41) Malrieu, J. P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916.

Table XI. X–X Bond Dissociation Energies[a] (in kcal/mol)

system	B	Al	Ga	In	Tl
linear HX=XH/2XH($^3\Pi$)					
$^3\Sigma^-_g$	153	86	79	77	61
$^1\Delta_g$	138	75	68	67	50
$^1\Sigma^+_g$	130	69	61	60	43
H_2X—$XH_2(^1A_1)$/2 $XH_2(^2A_1)$	99	58	52	47	39
X—$XH_2(^1A_1)$/X(^2P) + $XH_2(^2A_1)$	62	39	34	32	30
trans-bent HX=XH(^1A_g)/2XH($^1\Sigma^+$)		10	3	3	

[a] These values are obtained from CI calculations.

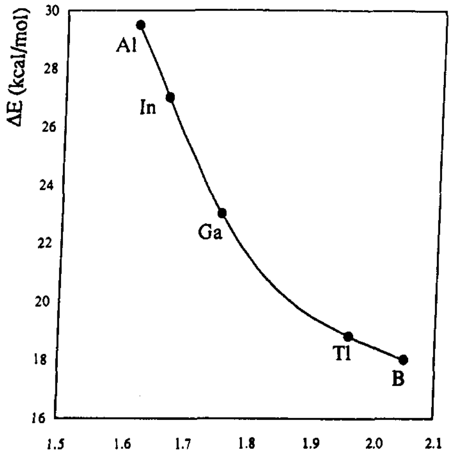


Figure 5. Variation of the binding energy relative to 2 XH($^1\Sigma^+$) with the electronegativity of X in the di-H-bridged structures.

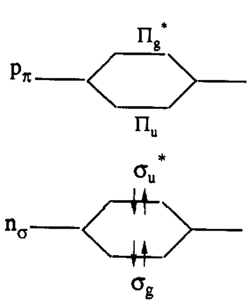
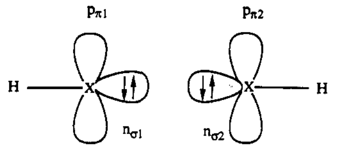


Figure 6. MO diagram of the linear interaction of two singlet XH monomers.

weakening of the σ and π bonds and a stabilizing effect through a σ—π mixing. The stability of the trans-bent form depends on a delicate balance between these two effects.

Let us call ϵ_n and ϵ_p the energies of the n_σ and p_π orbitals of each XH singlet species. The starting point is defined by the linear approach of two singlet monomers



This interaction gives two σ MO's and two π MO's according to the diagram of Figure 6. The reference electronic configuration $\sigma_g{}^2\sigma_u{}^{*2}\pi_u\pi_g{}^*$ is obtained so that the total energy is equal to zero.

The orbital energies associated with the four MO's can be approximated as

$$\epsilon_{\sigma_g} = \epsilon_n + F_\sigma \qquad \epsilon_{\sigma_u^*} = \epsilon_n - F_\sigma$$

$$\epsilon_{\pi_u} = \epsilon_p + F_\pi \qquad \epsilon_{\pi_g^*} = \epsilon_p - F_\pi \tag{1}$$

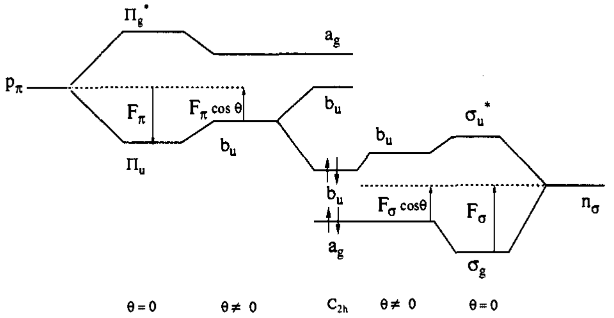


Figure 7. Schematic MO diagrams showing the π—σ* interaction leading to the trans-bent distortion of the HX–XH molecule.

where F_σ and F_π are the off-diagonal matrix elements of the monoelectronic Fock operator. ($F_\sigma = \langle n_{\sigma 1}|F|n_{\sigma 2}\rangle$ and $F_\pi = \langle p_{\pi 1}|F|p_{\pi 2}\rangle$.) The energy differences $\Delta_{\pi\sigma^*}$ and $\Delta_{\sigma\pi^*}$ are defined as positive quantities by

$$\Delta_{\pi\sigma^*} = \epsilon_{\pi_u} - \epsilon_{\sigma_u^*} \qquad \Delta_{\sigma\pi^*} = \epsilon_{\pi_g^*} - \epsilon_{\sigma_g} \tag{2}$$

As a consequence of the $\sigma_g\sigma_u{}^*\pi_u\pi_g{}^*$ ordering, the $\sigma_u{}^*$ and π_u levels are always much closer in energy than the σ_g and $\pi_g{}^*$ levels. The main mixing will therefore occur between $\sigma_u{}^*$ and π_u, and the mixing between σ_g and $\pi_g{}^*$ will be neglected. $\Delta_{\pi\sigma^*}$ can be written as

$$\Delta_{\pi\sigma^*} = (\epsilon_p - \epsilon_n) + (F_\sigma + F_\pi) \tag{3}$$

In our monoelectronic scheme, $(\epsilon_p - \epsilon_n)$ may be roughly approximated by the singlet–triplet energy separation ΔE_{ST}. On the other hand, a reasonable estimate of the $(F_\sigma + F_\pi)$ sum may be obtained by considering that, in the linear $^1\Delta_g$ state, the (σ + π) bond energy can be expressed as

$$E_{\Delta_g} = -2(F_\sigma + F_\pi) \tag{4}$$

This bond energy which is a positive number is listed in Table IX. The energy level separation (3) now becomes

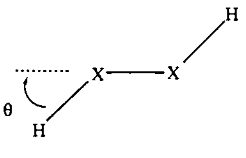
$$\Delta_{\pi\sigma^*} = \Delta E_{ST} - {}^1/{}_2 E_{\Delta_g} \tag{5}$$

The initial condition $\Delta_{\pi\sigma^*} > 0$ leads to

$$\Delta E_{ST} > {}^1/{}_2 E_{\Delta_g} \tag{6}$$

If (6) is not fulfilled, then the initial ordering becomes $\sigma_g\pi_u\sigma_u{}^*\pi_g{}^*$ and we have two electrons in the π_u orbital, leading to a linear (σ + π) interaction between the two XH monomers. In fact, this is the case of BH for which any trans-bent distortion has never been found for the dimeric species.

Assuming that condition 6 is satisfied, let us now introduce a bending angle θ defined by



The θ dependence of F_σ and F_π can be taken as a simple cosine law

$$F_\sigma(\theta) = F_\sigma \cos\theta \qquad F_\pi(\theta) = F_\pi \cos\theta \tag{7}$$

These quantities and the resulting MO diagram are depicted on Figure 7. Equation 5 becomes a function of θ

$$\Delta_{\pi\sigma^*}(\theta) = \Delta E_{ST} - {}^1/{}_2 E_{\Delta_g} \cos\theta \tag{8}$$

If we consider the π–σ* interaction as a perturbation, the corresponding second-order energy may be written as

Table XII. Comparison of Values of Some Characteristic Quantities[a] of the Trans-Bent Structure Obtained Using our Perturbative MO Model with ab Initio Calculated Values

	bending angle			energy gain			force constant		
	model[b]			model[b]			model[b]		
	SCF	CI	ab initio	SCF	CI	ab initio	SCF	CI	ab initio
HAl–AlH	55	54	59.9	14	22	10.3	0.2	0.3	0.14
HGa–GaH	68	64	63.4	9	15	2.9	0.1	0.2	0.08
HIn–InH	71	65	63.3	7	14	2.9	0.1	0.2	0.12
HTl–TlH[c]		75			6			0.1	

[a] Bending angle in deg, energy in kcal/mol, and force constant in mdyn Å/rad². [b] SCF or CI means values obtained by using in eq 12, 14, 17 of the model, SCF or CI values for ΔE_{ST} and E_{Δ_g}, respectively. [c] Only a CI value is available for ΔE_{ST} in the case of TlH (see Table I).

$$E^{(2)} = -2\langle\pi|F|\sigma^*\rangle^2/\Delta_{\pi\sigma^*}(\theta) \qquad (9)$$

The matrix element $\langle\pi|F|\sigma^*\rangle$ can be evaluated from the previously defined F_σ and F_π assuming a sine law for its θ dependence

$$\langle\pi|F|\sigma^*\rangle = {}^1/_2(F_\sigma + F_\pi)\sin\theta \qquad (10)$$

that is to say

$$\langle\pi|F|\sigma^*\rangle = -{}^1/_4 E_{\Delta_g}\sin\theta \qquad (11)$$

by using eq 4. Since the zero-order energy $E^{(0)}$ is zero, we obtain the total energy E as a function of θ

$$E = E^{(0)} + E^{(2)} = -\frac{1}{4}\frac{E_{\Delta_g}{}^2\sin^2\theta}{2\Delta E_{ST} - E_{\Delta_g}\cos\theta} \qquad (12)$$

The stationary points on the θ-dependent potential energy surface are given by the condition $dE/d\theta = 0$. Let us calculate the first and second derivatives of E with respect to θ:

$$\frac{dE}{d\theta} = -\frac{1}{4}\frac{E_{\Delta_g}{}^2\sin\theta(4\Delta E_{ST}\cos\theta - E_{\Delta_g}\cos^2\theta - E_{\Delta_g})}{(2\Delta E_{ST} - E_{\Delta_g}\cos\theta)^2} \qquad (13)$$

$$d_1 = 2\sin\theta\sin 2\theta + 3\cos\theta\cos 2\theta + \cos^3\theta$$

$$d_2 = \cos^2\theta - 4\sin^2\theta + 2\sin^4\theta - 3\cos^4\theta$$

$$\frac{d^2E}{d\theta^2} = \frac{2E_{\Delta_g}{}^3\Delta E_{ST}d_1 - 8E_{\Delta_g}{}^2\Delta E_{ST}{}^2\cos 2\theta + E_{\Delta_g}^4 d_2}{4(2\Delta E_{ST} - E_{\Delta_g}\cos\theta)^3} \qquad (14)$$

Two values of the bending angle θ are possible. The first solution corresponds to $\theta = 0$. This is the linear form which is always a stationary point. However, this point is not a local minimum since, for $\theta = 0$, the second derivative of E is negative as long as $2\Delta E_{ST} > E_{\Delta_g}$. Indeed, (14) takes the following value

$$\left(\frac{d^2E}{d\theta^2}\right)_0 = -\frac{E_{\Delta_g}^2}{2(2\Delta E_{ST} - E_{\Delta_g})} \qquad (15)$$

The other solution is given by the equation

$$E_{\Delta_g}\cos^2\theta - 4\Delta E_{ST}\cos\theta + E_{\Delta_g} = 0 \qquad (16)$$

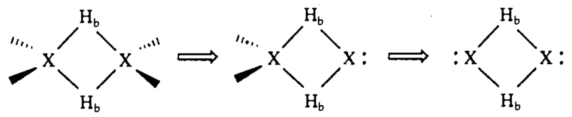
Only one root of this equation is compatible with the previously established condition (6)

$$\cos\theta = \frac{2\Delta E_{ST} - \sqrt{4\Delta E_{ST}{}^2 - E_{\Delta_g}{}^2}}{E_{\Delta_g}} \qquad (17)$$

For the corresponding value of θ, the force constant deduced from eq 14 is positive and the trans-bent form is a local minimum.

The bending angle, energy gain due to the trans-bent distortion, and force constant evaluated for AlH, GaH, InH, and TlH monomers are listed and compared with ab initio values in Table XII. These results demonstrate the overall efficiency of our model to correctly reproduce the tendency to trans-bending for heavier analogues of diborene. Despite the crude approximations used, we are able to explain the weakness of this trans-bent bond especially for Ga_2H_2 and In_2H_2. As expected, the energy gain calculated from the perturbative expression (12) is always overestimated (by about 5 kcal/mol or 12 kcal/mol depending on whether SCF or CI values are used for ΔE_{ST} and E_{Δ_g}). The criterion for trans-bent structure (6) does not prohibit the existence of this dimeric species for TlH. However, it can be noted that TlH presents the greatest value for ΔE_{ST} (51.9 kcal/mol; see Table I) and the smallest value for E_{Δ_g} (50.2 kcal/mol), so that the energy difference $\Delta_{\pi\sigma^*}$ becomes too important to allow a stabilization of the dimer by a trans-bending distortion.[42] Indeed in that case, the energy gain obtained from CI values of ΔE_{ST} and E_{Δ_g} is only of 6 kcal/mol which is well smaller than the additional 12 kcal/mol usually obtained for the other XH molecules. This is coherent with the previous result of Schwerdtfeger[21] concerning Tl_2H_2 trans-bent.

E. Structures of the Bridged Forms. As in diborane and its heavier analogues, the bonding in the dibridged structures is governed by a three-center two-electron scheme. In all cases, there is an excess of electrons on the bridge hydrogens. Mulliken population analyses indicate that hydrogens bear negative charges ranging from −0.08 e (boron) to −0.34 e (thallium). The outcome is a highly ionix $X^+ - H^- - X^+$ bond, at least for the heavier atoms of the series. For instance, for In and Tl, the building of the planar ring leads to a stabilization due to a strong enhancement of the XH bond polarity. This is not the case for the corresponding boron compound, probably due to the smallest electropositivity of boron. The electrostatic consideration are also responsible for the shapes of these planar cycles. They are rhombuses with the XX axis as the long diagonal. Indeed, the excess of electron in H regions induces obtuse angles on H (see Table III). The geometrical parameters of all the possible four-membered rings belonging to $H_2X(\mu\text{-}H)_2XH_2$, $H_2X(\mu\text{-}H)_2X$, and $X(\mu\text{-}H)_2X$ are compared in Table XIII for X = B, Al, and Ga. It is of interest to note that, when going from X_2H_6 to X_2H_2, there are a lengthening of the XX distance and an opening of the XH_bX angle, which suggests an increase of electron density near the bridge hydrogens. As shown in the following scheme,



when two terminal H atoms are replaced by a lone pair, the electron attractor character of X decreases from X_2H_6 to X_2H_2. The intermediate case of $X_2H_4(C_{2v})$ exhibits two different XH_b bonds. One of them is very close in length to the corresponding XH_b bond in X_2H_6 and the other to the corresponding XH_b bond

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(42) It is interesting to note that the influence of spin—orbit coupling should not change this fact. Indeed, E_{Δ_g} is assumed to be lowered by spin–orbit coupling due to a destablization of HTl═TlH($^1\Delta_g$) with respect to two TlH($^3\Pi$) as happens for the ground state of Tl_2 with respect to two Tl atoms.[36c] On the other hand, ΔE_{ST} is not significantly affected by spin—orbit coupling (see Table I).

Table XIII. Comparison of SCF-Optimized Geometries for Some Dibridged Structures[a]

molecules	r(XX)	$r(XH_b)$	XH_bX	H_bXH_b	ref
B_2H_6 (D_{2h})	1.797	1.331	84.9	95.1	4
B_2H_4 (C_{2v})	1.880	1.290		95.0	16[b]
B_2H_2 (D_{2h})	1.999	1.371	93.6	86.4	this work
Al_2H_6 (D_{2h})	2.616	1.732	98.1	81.9	4
Al_2H_4 (C_{2v})	2.805	1.723	102.5	81.3	14
		1.872		73.7	
Al_2H_2 (D_{2h})	2.940	1.823	107.5	72.5	this work
Ga_2H_6 (D_{2h})	2.654	1.774	96.8	83.2	4
Ga_2H_4 (C_{2v})	2.847	1.750	100.3	84.9	15
		1.954		74.4	
Ga_2H_2 (D_{2h})	3.059	1.897	107.4	72.6	this work

[a] Bond lengths in angstroms and bond angles in degrees. [b] Incomplete results.

in X_2H_2. While X_2H_6 and X_2H_2 bridge structures are the dimeric forms of XH_3 and :XH, respectively, the doubly H-bridged structure of X_2H_4 appears as composed of :XH complexed to XH_3.

While only a few $H_2X(\mu\text{-}H)_2XH_2$ have been experimentally isolated, all the previously discussed dibridged forms are expected to be amenable to experiment since they are found to be local minima on the singlet PES's. In order to predict the existence of such dibridged structures obtained by cycloaddition of two X–H bonds, one has to consider the parent fragments. When the spin multiplicity of the ground state of each fragment allows that it possesses at least one vacant MO, the building of a double bridge is encountered as a minimum on the PES. This qualitative rule follows from the concept of three-center two-electron bond. Obviously, the rule works well for the XH and XH_3 fragments of group 13, which are known to have a singlet ground state allowing one p_π orbital to be empty. It can easily be shown that it also applies to all main groups. For instance, let us consider the YH monomer in group 14. Since YH is known to have a doublet ground state, the previous rule allows one to predict the existence of dibridged structures as minima on the singlet Y_2H_2 hypersurfaces. In fact, Binkley[43] has located a dibridged structure which appears to be a local minimum on the C_2H_2 PES, while a C_{2v} dibridged form has been found to be the global minimum on the Si_2H_2[44] and Ge_2H_2[45] PES. Similarly, if we consider the group 14 YH_2 monomers, the results for the Y_2H_4 systems[38] are the following: in all cases but carbon, a trans-dibridged structure is found to be a local (in the cases of Si and Ge) or global (in the cases of Sn and Pb) minimum. These results can be easily rationalized using the previous rule since it is well-known that all YH_2 except methylene have singlet ground states with an empty p_π MO. As expected, for all group 14 YH_3 monomers, the existence of dibridged structures on the Y_2H_6 PES is forbidden by this rule.

A similar qualitative rule of occurrence for singly bridged structures has recently been suggested by Treboux and Trinquier.[46] They stated that the building of the three-center two-electron X_1—H—X_2 bridge can occur only if an antagonistic electron migration can happen, for instance, through a $X_2 \rightarrow X_1$ dative bond, to counterpoise the initial charge migration from X_1–H toward X_2. This is clearly the case for the mono-H-bridged structures (IV) of group 13.

Conclusion

The problem of the group 13 X_2H_2 singlet PES may be summarized as follows. For boron, the most stable form is the linear structure in its $^1\Delta_g$ state. Only two other minima exist, corresponding to the :X–XH_2 form and the doubly bridged form which is found to be very high in energy. Going down to heavier atoms, the linear form no longer exists as minimum, but it becomes trans-bent distorted (except for Tl_2H_2, where this structure is predicted to be nonexistent at the SCF level). Moreover, for Al_2H_2, Ga_2H_2, and In_2H_2, a fourth type of minimum appears, corresponding to the singly bridged structure with an X–X bond. For Tl_2H_2, the reluctance of thallium in :TlH to further engage its lone pair reduces the number of minima; only the :X—XH_2 and the doubly bridged structures remain. Beyond boron, the preference for doubly bridged structures becomes more and more pronounced. For Al_2H_2, Ga_2H_2, and In_2H_2, three other atomic arrangements are possible within 25 kcal/mol above the doubly bridged isomer, while only one remains, namely, the :X—XH_2 form, for Tl_2H_2. Finally, it may be underlined that, with respect to the possible atomic arrangements on the X_2H_2 singlet PES, boron and thallium appear as the most singular among the group 13 elements.

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