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May 21, 1996

Abstract

A theoretical investigation has been carried out on several group III-V (13-15) four-membered ring compounds which, if experimentally attainable, are potentially useful as precursors to nanocrystalline electronic and semiconductor materials. Four-membered ring compounds considered in this study have core structures of the form: $\overline{\text{MEM'E'}}$ and $\overline{\text{MEMX}}$ (M, M' = In, Ga, Al; E, E' = P, As; X = Cl, Br). Equilibrium geometries, binding energies, and bond energies were determined based on local density approximation (LDA) and gradient-corrected density-functional methods. Optimized ring geometries obtained with LDA agree closely with single crystal X-ray crystallographic structures of known compounds with the same four-membered ring cores. The following trends in bond energies are observed: M-Cl >> M-P > M-As >> M-Br (M = In, Ga, Al), and Al-Y > Ga-Y > In-Y (Y = P, As, Cl, Br). Although only one M-Br-containing mixed-bridge four-membered ring compound has been reported and no such Al-Cl-containing mixed-bridge species have yet been synthesized, our calculations suggest that compounds containing these two ring systems are stable.

Introduction

During the past decade, there has been considerable effort centered on the preparation of potential single-source precursors to various III-V (13-15) semiconductor and electronic materials. As a result, four-membered ring compounds containing cores of the form $\overline{\text{MEME}}$ (M = Al, Ga or In; E = P or As), 1-12, 14-15, 18 $\overline{\text{MEME}'}$ (M = Al, Ga, or In; E = As, E' = P),[19-21], $\overline{\text{MEMX}}$ (M = Ga or In; E = P or As; X = Cl) (M = Ga; E = As; X = Br)[4, 12-17] have been synthesized. Of particular interest are nanometer-size crystallites of semiconductor materials which have interesting properties as a result of quantum confinement effects not observed in bulk material[22-24]. Among such materials, III-V semiconductors are especially important because of their utility in high-speed digital circuits, microwave devices, and optoelectronics.[25,26] One avenue of synthesis for group III-V nanocrystals involves the thermal decomposition of suitable single-source precursors and, to this end, it has been recently demonstrated that the compounds $[X_2GaP(SiMe_3)_2]_2$ (X = Cl, Br, or I) undergo thermolysis at relatively low temperatures to yield nanocrystalline gallium phosphide (GaP)[5]. Consequently, there is considerable interest in understanding the structural and energetic properties of the various mentioned four-membered ring compounds in order to stimulate the synthesis and exploitation of new nanocrystalline materials.

Density-functional theory (DFT)[27-31] has been shown to be a a powerful theoretical tool for studying molecular structure and energetics, particularly for organotransition metal compounds.[32-33] Herein, we describe a theoretical investigation of III-V four-membered ring compounds using DFT. Optimized geometries, binding energies, and bond energies have been calculated in order to give insight into the structural features and bonding properties of these ring species.

Four-membered ring compounds containing several different ligands (R, R') have been synthesized and characterized by single crystal X-ray crystallography[1-21]. The four-membered ring compounds studied here are divided into two groups: compounds containing two pnicogens of the general form $R_2\overline{ME(R')_2M(R)_2E'(R')_2}$ (M = In,[1, 4, 10-12, 14-15, 18-19] Ga,[1-6, 11, 18, 20] Al,[1, 4, 7-9, 11, 21] E, E' =P, As) and compounds containing one halogen and one pnicogen of the general form $R_2\overline{ME(R')_2M(R)_2X}$ (M = In,[12, 14-15] Ga,[16-17] E= P, As; X = Cl, Br). In our theoretical investigation we consider the case of R, R' = H (Figs. 1 and 2). These model compounds are intended to capture the essential electronic bonding interactions of the four-membered ring core, and neglect mainly the steric effect of more bulky (and computationally demanding) ligands.

Computational Details

Density-functional calculations were performed using the Dmol software package.[35,36] Optimized geometries, vibrational frequencies, and zero-point energy corrections employed the Vosko-Wilk-Nussair local density approximation (LDA) to treat electron exchange and correlation effects. It is well known that LDA gives reasonable geometries although it generally overestimates binding energies.[30,33] Binding energies were calculated at the LDA optimized geometries using the gradient-corrected exchange functional of Becke[37] in conjunction with the Lee-Yang-Parr[38] correlation functional (BLYP). Vibrational frequencies were computed from force constant matrices calculated by mass-weighted finite differences of the energy gradients. It has been demonstrated that the gradient corrections typically have a minor influence on the calculated frequencies at a given reference geometry,[39,40] consequently, BLYP binding energies with LDA zero-point energy corrections were used to calculate M-H, E-H, and M-E bond

energies. A double numerical basis set with polarization functions was used in all calculations[36]. This basis set has been designed to give bond lengthes converged to the accuracy of 0.01 A.36 Mesh points for numerical integrations were chosen to give a precision of 10^{-5} a.u in computation of the matrix elements. Geometry optimizations were performed without symmetry constraints, and terminated when the norm of the gradient fell below 10^{-3} a.u..

Throughout this paper, we have ignored relativistic effects; this may affect our prediction of the bond lengths and bond energies for the In compounds to at most a few percent.41 For example, relativistic effect reduces the In-H bond length in InH3 from 1.762 A to 1.739 A.41

Results and Discussion

In the discussion of the relative binding energies of the various four-membered ring compounds, it is useful to make reference to *bond energies*. The bond energy *D(A-B)* describes the stabilization energy associated with formation of a single A-B bond. We define the binding energy of a molecule as the sum of bond energies[42]:

$$E_b \equiv E_{molecule} - E_{atoms} = -\sum_{\substack{bonds \\ A-B}} D(A-B) \qquad (1)$$

where E_b is binding energy and D(A-B) is the A-B bond energy. For related compounds, the bond energies for each bond type are expected to be similar. In this case a single set of transferable bond energies can be determined, and subsequently applied to new compounds to obtain approximate binding energies (via Eq. 1). In this way bond energies can be used as a predictive tool and provide qualitative insight into the energetics of bond formation for a host of related compounds. For a detailed discussion of bond energies refer to the work of Pauling[42].

(a) Geometric and energetic properties of dipnicogen four-membered ring compounds.

We have calculated optimized geometries and zero-point energy corrected binding energies for 18 ring compounds of the form $H_2\overline{ME(H)_2M'(H)_2E'(H)_2}$ (M, M' = In, Ga, Al; E, E' = P, As) (Fig.1). Binding energies of the optimized structures are listed in Table I.

Six of the 18 dipnicogen ring compounds are dimers (M = M', E = E'). The structures of several similar dimer compounds with the same (M, E) four-membered ring core, but with the hydrogen atoms replaced by bulky (R, R') ligands, have been determined by X-ray diffraction.[7-12, 14-17] A comparison of geometric parameters for the calculated and experimental structures is summarized in Table II. The structures obtained through optimization (in the absence of symmetry constraints) preserve the planarity and symmetry of the four-membered ring compounds observed experimentally.

The following trends in bond lengths and bond angles are observed (M = In, Ga, Al; E = As, P):

M-As > M-P, In-E > Al-E > Ga-E, M-E-M > E-M-E

An analysis of structural deviations between the calculated and experimental dimer compounds gives insight into the effects of different ligands. Almost all the calculated M-E bond lengths are shorter than the corresponding experimental values. The difference most likely arises from steric effects associated with the bulky R and R' ligands in the experimental compounds. A notable exception occurs when the R ligand is an electron-withdrawing group. For instance, the Ga-P bond length in the experimental $[Cl_2GaP(SiMe_3)_2]_2$ structure (2.379 Å),[6] is shorter than in the calculated $[H_2GaPH_2]_2$ structure (2.401 Å). In general, the calculated

M-E-M bond angles are larger than the corresponding experimental values, and conversely, the E-M-E bond angles are correspondingly smaller.

The other 12 calculated mixed-metal and mixed-pnicogen structures are similar to the dimeric structures (the largest deviation in M-E bond length from the corresponding dimeric value is less than 0.01 Å). The four-membered rings are all planar, and reveal the same geometrical trends described previously for the dimeric structures.

Bond energies were computed via Eq. 1 for the series of four-membered ring compounds from the binding energy data. In order for these energies to correspond to thermodynamic quantities, corrections to the binding energies are required to account for finite vibrational energy even at 0 K. These zero-point energy corrections are proportional to the normal mode vibrational frequencies (inversely proportional to the square root of the reduced mass) and hence most significant for chemical bonds involving hydrogen.

M-H and E-H bond energies were obtained directly from the binding energies of MH_3 and EH_3 compounds, respectively (Table III). These bond energies were subsequently applied to the four-membered ring compounds. The assumption of transferability of the M-H and E-H bond energies to the four-membered ring compounds is supported by the fact that the corresponding bond lengths are very similar for these structures (overall standard deviation 0.01Å, Table III).

Bond energies for M-E bonds in the four-membered ring compounds were computed in two ways by using two different data sets. The first data set consisted only of the six dimer compounds (the "minimal" set). These compounds have only three types of bonds: M-E bonds, and M-H and E-H bonds. The M-H and E-H bond energies were computed previously from the MH_3 and EH_3 compounds. Consequently, the bond energies (and bond lengths) for each M-E bond can be

determined directly and uniquely from the binding energy of the corresponding dimer. In this case, the sum of the bond energies is defined to be exactly the calculated binding energy. Alternately, a second data set consisting of all 18 mixed-bridge compounds (including the dimers) can be used to obtain bond energies and bond lengths (the "full" set). For this set, bond energies were obtained by a fitting procedure so as to best reproduce (in a least squares sense) the calculated binding energies of the compounds. Similarly, bond lengths were determined by simple averaging over all M-E bonds of the same type.

Comparison of bond lengths and energies obtained from the "minimal" and "full" sets provides an assessment of the assumption that these quantities are transferable. The M-E bond energies calculated from both sets are shown in Table IV along with the corresponding bond lengths. Binding energies predicted from the bond energies (Eq. 1) are in excellent agreement with the DFT calculated binding energies (the standard deviation using bond energies obtained from the minimal set and full set are 0.571 and 0.417 kcal/mol, respectively). The close agreement of the bond lengths and bond energies derived from the two sets strongly supports the assumption of transferability of these quantities, and the validity of the bond energy model (Eq. 1).

From Table IV, the following trends in bond energies are apparent:

M-As < M-P

In-E < Ga-E < Al-E

The bond energy trends are correlated with the bond length trends described earlier (large bond energies generally corresponding to shorter bond lengths; the exception being that Al-E bonds are predicted to be stronger than Ga-E bonds, although somewhat longer).

(b) Geometric and energetic properties of halogen-containing mixed-bridge four-membered ring compounds.

Optimized geometries and binding energies have been calculated for 12 halogen-containing mixed-bridge compounds of the form $H_2\overline{ME(H)_2M(H)_2X}$ (M = In, Ga, Al; E = P, As; X = Cl, Br) (Fig. 2). Binding energies without zero-point energy corrections are listed in Table V.

Halogen-containing mixed-bridge compounds with four-membered rings $\overline{InPInCl}$, $\overline{InAsInCl}$, $\overline{GaPGaCl}$, and $\overline{GaAsGaCl}$ with several bulky R and R' ligands have been synthesized and their structures determined by X-ray diffraction.[13-17] In some instances the four-membered ring cores are puckered (Table VI). In contrast, all the optimized geometries of compounds with R, R' = H result in planar ring structures, even though optimizations were performed using several puckered starting geometries.

The following trends in bond lengths and bond angles are observed (M = In, Ga, Al; E = As, P; X = Br, Cl):

In-X > Ga-X > Al-X , M-Br > M-Cl, In-E > Al-E > Ga-E, M-As > M-P, M-X-M > X-M-E, M-E-M > X-M-E

All the calculated M-E and M-X bond lengths are slightly shorter than the corresponding experimental values. The calculated M-E-M and M-X-M bond angles are larger than the corresponding experimental values, whereas the X-M-E bond angles are smaller. As stated previously for the dipnicogen-containing four-membered ring compounds, these differences are most likely attributed to steric effects of the bulky ligands in the experimental structures. Our results also indicate that Al-E bonds are longer than Ga-E bonds. This order of bond length agrees with the experimental observation. The experimental data (Table II) shows that Ga-E

bond is shorter than the Al-E bond when both have the same ligand, and the order can be reversed when they have different ligands.

The M-X bond energies were computed with Eq.1 from the binding energy data in conjunction with the M-E and M-H bond energy results presented in the previously section. The M-E bond lengths in the halogen-containing mixed-bridge compounds are similar to the M-E bond lengths in the dipnicogen-containing four-membered ring compounds, lending support to the assumption that the M-E bond energies will likewise be similar (transferable). As indicated in Table VI, the zero-point energy corrections are small for bonds involving two heavy atoms, and have an almost negligible affect on their relative values. Hence, zero-point energy corrections have not been included in the determination of the M-Br and M-Cl bond energies (Table VII).

From Table VII the following trends in bond energies are observed:

M-Cl > M-Br, Al-X> Ga-X > In-X

Our theoretical calculations indicate that for Cl or Br-containing mixed-bridge compounds, the Cl-containing compounds will be considerably more stable. The most stable compounds involve Al-Cl bonds (bond energy 285.6 kJ/mol). The least stable compounds are those containing In-Br bonds (bond energy 43.5 kJ/mol). Although several In-Cl and Ga-Cl containing mixed-bridge compounds have been reported,[13-17] attempts to synthesize Al-Cl containing mixed-bridge compounds have not been successful to date. The difficulty in synthesis of Al-Cl containing mixed-bridge compounds may be related to the unusual stability of the Al-Cl bonds which favor the reactants.[7] In addition, only one Br-containing mixed-bridge compound has been reported. Our calculations suggest that the M-Br bonds are weak compared to either the M-Cl or M-E bonds. Based on these data, we suggest that Br-containing mixed-bridge compounds have potential as precursors in the synthesis of III-V nanocrystals.

CONCLUSION

We have calculated equilibrium geometries, binding energies, and bond energies for several group III-V four-membered ring compounds used as precursors in the synthesis of semiconductor nanocrystals. Ring structures obtained using LDA density-functional methods agree well with structures of similar compounds determined by X-ray crystallography. The following trends are observed in the calculated bond energies: M-Br << M-As < M-P << M-Cl (M = I n, Ga, Al), and In-Y < Ga-Y < Al-Y [Y = E, X, where E = P, As (group V) and X = Cl, Br (halogen)]. The bond energies accurately reproduce the density-functional (gradient-corrected) binding energies, and are demonstrated to be transferable among the compounds studied. Consequently, the theoretical bond energy data reported here provides a tool to predict the stability of new four-membered ring compounds. From these data, we predict that Al-Cl containing mixed-bridge compounds are stable; hence synthesis from reactants rich in Al-Cl bonds may be energetically unfavorable. We further suggest that weakly bonded Br-containing mixed-bridge compounds may make attractive targets for synthetic precursors to nanocrystalline materials.

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Table I. Gradient-corrected density-functional binding energies (E_b) and zero-point corrected binding energies (E_b') for Dipnicogen-containing four-membered ring compounds

	E_b (kcal/mol)	E_b' (kcal/mol)
$H_2InP(H)_2In(H)_2PH_2$	-752.3	-715.6
$H_2InP(H)_2In(H)_2AsH_2$	-736.8	-701.5
$H_2InAs(H)_2In(H)_2AsH_2$	-721.3	-686.9
$H_2InP(H)_2Ga(H)_2PH_2$	-770.7	-732.6
$H_2InP(H)_2Ga(H)_2AsH_2$	-754.2	-717.5
$H_2InAs(H)_2Ga(H)_2AsH_2$	-737.7	-701.7
$H_2InP(H)_2Al(H)_2PH_2$	-776.6	-738.8
$H_2InP(H)_2Al(H)_2AsH_2$	-760.2	-723.3
$H_2InAs(H)_2Al(H)_2AsH_2$	-743.7	-708.5
$H_2GaP(H)_2Ga(H)_2PH_2$	-789.5	-750.2
$H_2GaP(H)_2Ga(H)_2AsH_2$	-772.1	-734.4
$H_2GaAs(H)_2Ga(H)_2AsH_2$	-751.9	-714.8
$H_2GaP(H)_2Al(H)_2PH_2$	-795.2	-755.9
$H_2GaP(H)_2Al(H)_2AsH_2$	-778.0	-740.0
$H_2GaAs(H)_2Al(H)_2AsH_2$	-760.6	-723.2
$H_2AlP(H)_2Al(H)_2PH_2$	-801.2	-763.5
$H_2AlP(H)_2Al(H)_2AsH_2$	-783.7	-745.4
$H_2AlAs(H)_2Al(H)_2AsH_2$	-766.6	-730.0

Table II. Calculated and experimental bond lengths and angles for dimeric compounds $R_2\overline{ME(R')_2M(R)_2E(R')_2}$

M	E	R	R'	M-E (Å)	M_1-E-M_2 (degree)	E_1-M-E_2 (degree)	R'-E-R' (degree)
In	P	H	H	2.618	99.1	80.9	97.9[a]
In	P	Me_3SiCH_2	Me_3Si	2.655	93.6	86.3	105.7[b, 14]
In	As	H	H	2.710	99.8	80.2	94.4[a]
In	As	Me_3SiCH_2	Me_3Si	2.727	94.6	85.6	105.4[b, 12]
Ga	P	H	H	2.401	97.6	82.4	98.5[a]
Ga	P	Cl	Me_3Si	2.379	86.4	93.6	112.1[b, 6]
Ga	As	H	H	2.503	100.7	79.2	95.7[a]
Ga	As	Me_3CCH_2	Me_3Si	2.584	95.1	85.0	102.3[b, 16]
Al	P	H	H	2.426	96.7	83.3	100.3[a]
Al	P	Et	Me_3Si	2.460	90.2	89.8	107.4[b, 8]
Al	As	H	H	2.514	97.3	82.7	97.8[a]
Al	As	Et	Me_3Si	2.539	91.0	89.0	101.6[b, 7]

[a]LDA optimized geometries

[b]Related X-ray crystal structures (having the same core four-membered ring, but different R and R' ligands). Geometrical parameters listed are: M-E bond length, M_1-E-M_2 angle, E_1-M-E_2 angle, and R'-E-R' angle. All calculated structures have D_{2h} symmetry. The numbers following b are the corresponding reference numbers

Table III. Bond energies and bond lengths for M-H and E-H bonds

bond type	bond energy [a] (kJ/mol)	bond length[b] (Å)	bond length[c] (Å)
In-H	247.1*(261.8)*	1.754	1.747
Ga-H	271.3*(285.8)*	1.563	1.556
Al-H	276.8*(291.9)*	1.596	1.597
P-H	339.2*(359.5)*	1.436	1.426
As-H	314.2*(336.0)*	1.535	1.519

[a] M-H and E-H bond energies with zero-point energy correction for MH_3 and EH_3 compounds are listed and those before correction are listed in parentheses

[b] M-H bond lengths in MH_3 and EH_3 compounds.

[c] Average M-H bond lengths in the calculated four-membered ring compounds

Table IV. Bond energies and bond lengths for M-E bonds

	bond energy[a] (kJ/mol)	bond energy[b] (kJ/mol)	bond length[c] (Å)	bond length[d] (Å)
In-P	162.0 *(165.5)*	162.2 *(165.6)*	2.624	2.618
In-As	157.4 *(156.8)*	157.2 *(156.7)*	2.707	2.710
Ga-P	174.5 *(180.8)*	174.2 *(180.5)*	2.404	2.401
Ga-As	163.3 *(165.8)*	162.2 *(164.7)*	2.496	2.503
Al-P	181.7 *(186.5)*	182.6 *(186.7)*	2.426	2.426
Al-As	172.4 *(174.1)*	172.6 *(174.0)*	2.517	2.514

[a]The M-E bond energies with zero-point energy correction are calculated from least square fitting, the bond energy without zero-point energy correction are listed in parentheses.
[b]The M-E bond energies with zero-point energy correction are calculated from six dimer compounds, the bond energies without zero-point energy correction are listed in parentheses.
[c]The M-E bond lengths are averaged over all 18 compounds.
[d]The M-E bond lengths are calculated from six dimeric compounds.

Table V. Gradient-corrected density-functional binding energies for twelve halogen-containing mixed-bridge compounds

	binding energy (kcal/mol)
$H_2InP(H)_2In(H)_2Cl$	-622.3
$H_2InAs(H)_2In(H)_2Cl$	-606.1
$H_2InP(H)_2In(H)_2Br$	-522.0
$H_2InAs(H)_2In(H)_2Br$	-506.1
$H_2GaP(H)_2Ga(H)_2Cl$	-657.2
$H_2GaAs(H)_2Ga(H)_2Cl$	-638.9
$H_2GaP(H)_2Ga(H)_2Br$	-556.7
$H_2GaAs(H)_2Ga(H)_2Br$	-537.5
$H_2AlP(H)_2Al(H)_2Cl$	-676.7
$H_2AlAs(H)_2Al(H)_2Cl$	-658.8
$H_2AlP(H)_2Al(H)_2Br$	-573.4
$H_2AlAs(H)_2Al(H)_2Br$	-555.4

Table VI. Calculated and experimental bond lengths and angles for mixed-bridge compounds $R_2\overline{ME(R')_2M(R)_2X}$

M	E	X	R	R'	M-E (Å)	M-X (Å)	M-X-M (degree)	M-E-M (degree)	X-M-E (degree)	torsion
In	P	Cl	H	H	2.589	2.579	97.8	96.9	82.6	0.0[a]
In	P	Cl	Me_3SiCH_2	Me_3Si	2.603	2.620	89.8	90.6	85.3	22.9[b, 14]
In	As	Cl	H	H	2.682	2.580	99.7	94.7	82.8	0.0[a]
In	As	Cl	Me_3SiCH_2	Me_3Si	2.677	2.619	99.7	94.7	82.8	0.0[b, 12]
Ga	P	Cl	H	H	2.372	2.376	94.1	94.3	85.8	0.0[a]
Ga	P	Cl	Ph	Me_3Si	2.389	2.414	89.4	90.4	89.8	6.4[b, 13]
Ga	As	Cl	H	H	2.465	2.376	96.6	92.1	85.6	0.0[a]
Ga	As	Cl	Me_3CCH_2	Me_3Si	2.528	2.422	94.4	89.8	88.0	pucker[b, 16]
Al	P	Cl	H	H	2.396	2.330	95.0	91.5	86.7	0.0[a]
Al	As	Cl	H	H	2.488	2.333	96.9	89.1	87.0	0.0[a]
In	P	Br	H	H	2.610	2.719	92.3	97.4	85.2	0.0[a]
In	As	Br	H	H	2.671	2.727	94.1	96.7	84.6	0.0[a]
Ga	P	Br	H	H	2.377	2.517	89.8	96.4	86.8	0.0[a]
Ga	As	Br	H	H	2.469	2.528	93.2	96.1	85.3	0.0[a]
Al	P	Br	H	H	2.403	2.448	89.4	93.5	88.5	0.0[a]
Al	As	Br	H	H	2.481	2.488	91.8	92.1	88.0	0.0[a]

[a]Calculated LDA optimized geometries

[b]Related X-ray crystal structures having the same core four-membered ring, but different R and R' ligands. Geometrical parameters listed are: M-E bond length, M-X bond length, M-X-M angle, M-E-M angle, X-M-E angle, and endocyclic torsion angle. The numbers following b are the corresponding reference numbers.

Table VII. Bond energies and bond lengths for M-X bonds

	bond energy (kJ/mol)	bond length (Å)
In-Cl	253.2	2.579
Ga-Cl	263.3	2.376
Al-Cl	285.6	2.331
In-Br	43.5	2.723
Ga-Br	53.1	2.522
Al-Br	69.3	2.488

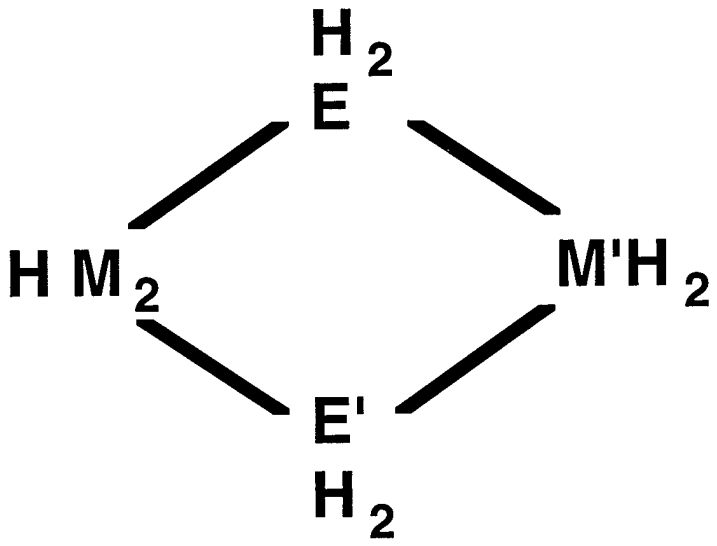

Fig. 1 Structures of $H_2\overline{ME(H)_2M'(H)_2E'}(H)_2$ (M, M' = In, Ga, Al; E, E' = P, As)

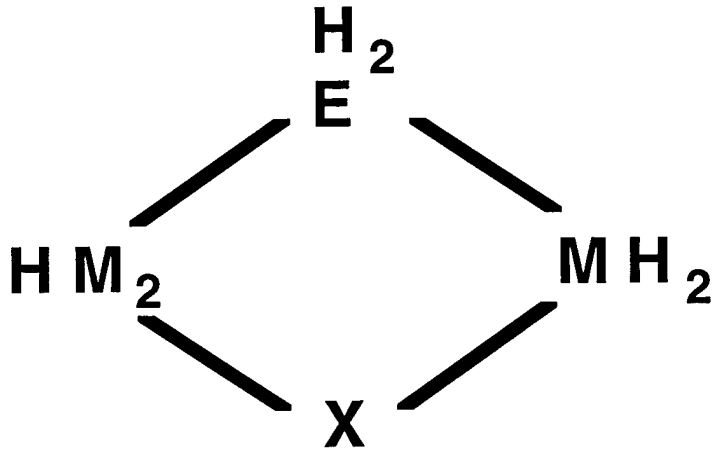

Fig. 2 Structure of $H_2\overline{ME(H)_2M(H)_2X}$ (M = In, Ga, Al; E = P, As; X = Cl, Br)

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