

Use of ELF and AIM Parameter Ratios for Bond Order Characterization of Two-, Three-, and Four-Coordinate Gallium Hydrides

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ABSTRACT: Calculations at the B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) level involving the electron localization function (ELF) and atoms-in-molecules (AIM) methods have been carried out for two-, three-, and four-coordinate gallium hydrides present in Na and Li salts and as the isolated dianionic species, for some isoelectronic germanium compounds, and for several neutral gallium hydrides. Using the ratio of delocalization indices and bond basin populations referenced to reasonable standards, formal bond orders are derived. While chemically expected bond orders are found in most cases, the situation in the $[\text{HGaGaH}]^{2-}$ species appears to lie intermediate between bonds of order 2 and 3, and that for neutral trans-bent HGaGaH is found to be best described as a bond of order 1. In these cases the larger bond order predicted by ELF bond basin populations evidently results from overlap of the bond basin into the lone pair (nonbonding) region of the molecule. © 2003 Wiley Periodicals, Inc. *Heteroatom Chem* 14:175–185, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10120

What's in a name? That which we call a rose by
any other word would smell as sweet.

Juliet, Act 2, Scene 1,
in *Romeo and Juliet* by William Shakespeare

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INTRODUCTION

The idea of the order of a chemical bond is a useful qualitative concept in discussing a molecule's electronic structure. It can be quantitatively *defined* in a variety of ways, but, because it is not a physical observable, different definitions can and often do lead to different results. While similar levels of theory usually lead to very similar results for observables such as the structure or energy or electron density, this is, unfortunately, not the case for bond orders. This clearly calls for caution in discussing this useful concept and often leads to controversy. Such is the case for the gallium–gallium bond in two-coordinate gallium where some arguments have been put forth for considering the bond to be triple and others for taking it to be a double bond. A rose by any other word, indeed! And while some may consider such discussions to not be useful, they do help us refine our ideas, both qualitative and quantitative, concerning the chemical bond.

The synthesis and crystal structure of $\text{Na}_2[\text{Mes}_2\text{C}_6\text{H}_3-\text{Ga}\equiv\text{Ga}-\text{C}_6\text{H}_3\text{Mes}_2]$ where Mes is 2,4,6-i- $\text{Pr}_3\text{C}_6\text{H}_2$ led Su et al. [1] in 1997 to declare the first experimental confirmation of a group 13 metal engaging in triple bond formation: “*the first Ga≡Ga gallyne.*” Their declaration was based on the two-coordinate nature of the gallium atoms and the rather short Ga–Ga bond distance of 2.319(3) Å. The carbons bonded directly to gallium form a planar trans-bent geometry with the bridging sodium atoms above and below this plane at the Ga–Ga bond midpoint. This type of trans-bent geometry

for two-coordinate metals in the fourth row of the periodic table has been rationalized on the basis that upon separation these species prefer a low-spin configuration. Accordingly, species such as HSi or HGa^- (shown below in Scheme 1 as either left- or right-hand species) can approach each other in the manner indicated so that one π bond and two bent dative bonds are formed. While structures with gallium-bridging hydrogens are generally lower in energy than the trans-bent form for gallium [2] or silicon [3,4], a bulky substituent such as that used by Su et al. would preclude such structures on steric grounds and favor the trans-bent form. The orbital diagram in Scheme 1 suggests the formation of three bonds for HSiSiH or $[\text{HGaGaH}]^{2-}$ and this is where differences of opinion arise as to the bond order of such species.

Klinkhammer [5] argues from a natural bond order (NBO) point of view that there is one σ bond, one "ordinary" π bond, and one "slipped" π bond in $[\text{HGaGaH}]^{2-}$ (gallyne) arising from the gallium lone pairs of the HGa^- fragment extending into the bonding region between the gallium atoms. He contends that this point of view is equivalent to the one- π -two-dative bonds picture and that a triple bond exists in gallyne. The slipped π NBO bond he shows does extend into both the bonding and lone pair regions of the system, which is the source of much of the controversy.

Cotton, Cowley, and Feng [6] carried out density functional calculations on a variety of multiply bonded species including $\text{Na}_2[\text{Ga}_2(\text{C}_6\text{H}_5)_2]$ and conclude that there is one σ and one π bond, and one lone pair orbital on each gallium, so that the bond is double and not triple. In their analysis the centroids of the lone pair orbitals clearly point away from the Ga—Ga bonding region. They point out the very interesting fact that while the Ga—Ga distance in the phenyl derivative is 2.46 Å, making the substituent group larger and more bulky such as $\text{C}_6\text{H}_5(\text{C}_6\text{H}_5)_2$ in which a total of four phenyl groups have been added to the compound reduces this distance to 2.36 Å, close to that observed in the study of Su et al. [1].

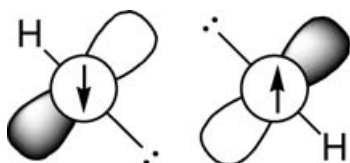
Xie et al. [2] use large basis sets in a density functional theory approach to give a rather thorough characterization of both neutral and dianionic

methyl- and hydrogen-substituted digallium compounds. They characterize their results in terms of Scheme 1 above and, using a localized molecular orbital approach, conclude that aside from a π bond, the other two localized orbitals involved in bonding are "obviously dative bonding orbitals (not lone pairs)." Their orbitals clearly point into the bonding region as the dative bond picture in Scheme 1 would predict. Xie et al. suggest that triple bonds do not have to be linear and that "the nature of a chemical bond is determined primarily by the electronic structure, not by the molecular geometry."

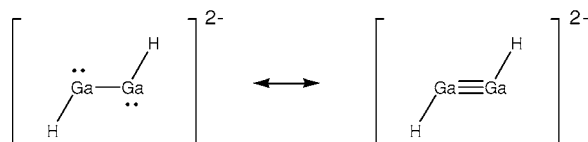
Allen, Fink, and Power [7] studied the *trans*- $\text{Li}_2\text{MeGaGaMe}$ species and concluded from a study of the canonical molecular orbitals that the Ga—Ga bond order was somewhat less than 2.00 because of the antibonding character of one of the molecular orbitals. They speak of the HOMO for this system as representing gallium lone pairs. For the isoelectronic *trans*- MeGeGeMe molecule they state that the species is doubly bonded.

Grützmacher and Fässler [8] provide a thorough review of the bonding studies of unsaturated main group elements and display topographical diagrams in the electron localization function (ELF) approach [9–16] for $[\text{HGaGaH}]^{2-}$ which lead them to state that "clearly this compound has a triple bond." However, they do go on to comment that the tilted torus exhibited can be interpreted in terms of resonance contributions from the two species shown in Scheme 2, which would lead one to interpret the bond order as perhaps something approaching 2.00 if equal contributions were made by each species. Unfortunately, without quantitative data the proportions of mixing cannot be determined. Nor do these authors present basin populations.

Molina et al. [17] used the delocalization index of Fredra, Austin, and Bader [18] in the atoms-in-molecules (AIM) approach [19] to study this problem at the Hartree–Fock 6-311++G(d,p) level. Finding a delocalization index of 1.74 for the optimized $[\text{HGaGaH}]^{2-}$ structure and 2.07 at the experimentally observed Ga—Ga bond distance (with the other parameters optimized), they conclude that the bond is double in nature, especially since they consider the Hartree–Fock approach to represent an upper



SCHEME 1



SCHEME 2

limit to the number of shared pairs between AIM atomic basins. They also present graphics for the ELF basins and interpret them as arising from two Ga–H bonds, one Ga–Ga π bond, and two regions that they describe as belonging to the gallium lone pairs. No quantitative data regarding the ELF basin populations were given.

The problem arises, then, that different *orbital* approaches used to characterize the two-coordinate gallium–gallium bond lead to different interpretations. The quantitative delocalization index appears to suggest a double bond, while no quantitative data is given for the ELF approach. Orbital approaches can lead to quite different pictures such as the classic example of OPH_3 . Gordon and coworkers [20–22] used energy localized orbitals to picture the situation about OP as one PO σ bond and three equivalent oxygen orbitals characterized primarily as lone pairs polarized toward phosphorus and staggered with respect to the PH bonds. But at the same time they [20] and others [23,24] when using the Boys localization scheme [25,26] derive a single lone pair orbital on oxygen pointing away from the H_3P group and three bent or banana bonds strongly polarized toward oxygen.

Recently we suggested that while bonding parameters involved in ELF basin populations and AIM delocalization indices may not in an absolute sense reflect our simple ideas of bond orders, ratios of these parameters referenced to a suitable standard may be a more viable measure of the bonding situation [27]. We applied this to all two-heavy-atom hydrides of the first and second row elements and found that a division into classes of clearly defined formal bond order was clear for the AIM delocalization index and apparent though less clear for the ELF bond basin populations. This approach had been successfully used earlier [4] in the characterization of the bonds in the various Si_2H_2 isomers and led to the characterization of the Si–Si bond in trans-bent HSiSiH as triple. In the present paper we apply this method to the gallium hydrides in two-, three-, and four-coordinate situations for both neutral Na and Li salts and the isolated dianionic species. Our results suggest that the bond order in the $[\text{HGaGaH}]^{2-}$ moiety is intermediate between a bond of order 2.00 and 3.00.

THEORETICAL BACKGROUND

The two approaches used here to characterize the nature of the bonding interactions are the *delocalization index* of Fradera, Austen, and Bader [18] based on the electron pair density in the AIM approach [19], and ELF isosurfaces and *bond basin populations* from

the ELF approach of Becke and Edgecombe [9] as extensively developed by Savin and Silvi and coworkers [10–16]. In the AIM approach atomic basins are derived from the scalar field of the electron density, $\rho(\vec{r})$, that ELF basins arise from a potential (see below) that is based on strong physical arguments regarding the Fermi hole [28,29] and the corresponding tendency of electron pairs to occupy different regions of space.

The Electron Localization Function

ELF is a robust descriptor of chemical bonding based on topological analyses of local quantum mechanical functions related to the Pauli exclusion principle. For a closed shell single determinantal wavefunction built from Hartree–Fock or Kohn–Sham orbitals, φ_i , the ELF function of position $\eta = \eta(\vec{r})$ is defined as

$$\eta = \frac{1}{1 + (D/D_h)^2} \quad (1)$$

where

$$\begin{aligned} D &= \frac{1}{2} \sum_{j=1}^N |\nabla \varphi_j|^2 - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho} \\ D_h &= \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3} \\ \rho &= \sum_{j=1}^N |\varphi_j|^2 \end{aligned} \quad (2)$$

and where the scaling factor is chosen to be the homogeneous electron gas kinetic energy density of a system of the same electron density. D is the local Pauli kinetic energy density, the excess kinetic energy electrons have (because of the Pauli exclusion principle) compared to a system of bosons of the same density [12]. The ELF function can be viewed as a local measure of the Pauli repulsion between electrons because of the exclusion principle and allows one to define regions of space that are associated with different electron pairs in a molecule or solid.

Using the vector field of the gradient of the electron localization function, the topology of the ELF function can be used to define basins within which one or more electron pairs are to be found [11–13,16]. Gradient paths end within each subsystem at what are called *attractors*. The region of 3-D space traversed by all gradient paths that terminate at a given attractor defines the *basin* of the attractor. ELF basins are labeled as either core or valence basins. Core basins contain a nucleus while valence basins do not; hydrogen basins are taken as exceptions since, although they contain a proton, they represent

a shared pair interaction. A valence basin is characterized by its number of connections to core basins, referred to as its synaptic order. Basins are connected if they are bounded by part of a common surface.

The population of a basin Ω_i , N_i is given by integrating the total electron density, $\rho(\vec{r})$, over the basin volume.

$$N_i = \int_{\Omega_i} \rho(\vec{r}) d\vec{r} \quad (3)$$

The ELF basin populations are particularly important in that they tend to reflect delocalization effects and, in the case of bond basins, the bond order.

The Delocalization Index

Bader's AIM approach [19] is based on the electron density, $\rho(\vec{r})$, a key observable in a molecule's description. The gradient field of the electron density defines atomic basins which can be integrated over to obtain AIM atomic basin electron populations. The delocalization index [18] is defined in terms of the electron pair density as it relates to the AIM atomic basins. The (spinless) electron pair density [28,29], $P_2(\vec{r}_1, \vec{r}_2)$, is the diagonal part of the reduced second-order density matrix and is normalized as

$$\int d\vec{r}_1 \int d\vec{r}_2 P_2(\vec{r}_1, \vec{r}_2) = \int d\vec{r}_1 (N-1)\rho(\vec{r}_1) = N(N-1) \quad (4)$$

where $\rho(\vec{r}_1)$ is the electron number density and N the total number of electrons. It proves convenient to define the pair density in terms of a quantity explicitly referencing the antisymmetric character of electron wavefunctions,

$$P_2(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2)[1 + f(\vec{r}_1, \vec{r}_2)] \quad (5)$$

so that

$$\frac{P_2(\vec{r}_1, \vec{r}_2)}{\rho(\vec{r}_2)} - \rho(\vec{r}_1) = \rho(\vec{r}_1)f(\vec{r}_1, \vec{r}_2) \quad (6)$$

The quantity on the left is the *conditional probability* of finding an electron at \vec{r}_1 given that there is one at \vec{r}_2 , minus the number density at \vec{r}_1 , $\rho(\vec{r}_1)$, where integration for the number density is over the coordinates of all electrons. This quantity (either side of Eq. (6)) is the *Fermi hole* [28,29] associated with the reference electron at \vec{r}_2 .

If we integrate the pair density over two AIM basins, Ω_i and Ω_j , we obtain by definition the quantity N_{ij} , the interbasin pair number, and using Eq. (5)

can write [19,30,31]

$$\begin{aligned} N_{ij} &= \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2 P_2(\vec{r}_1, \vec{r}_2) \\ &= \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2 \rho(\vec{r}_1)\rho(\vec{r}_2)[1 + f(\vec{r}_1, \vec{r}_2)] \\ &= N_i N_j + \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2 \rho(\vec{r}_1)\rho(\vec{r}_2)f(\vec{r}_1, \vec{r}_2) \\ &= N_i N_j - F_{ij} \end{aligned} \quad (7)$$

where N_i and N_j are the basin populations (electron numbers) and where here, in contrast to Fradera et al. [18], we have explicitly introduced the negative sign in the definition of F_{ij} because it is generally positive.

It is the sum of the off-diagonal terms, $F_{ij} + F_{ji} = 2F_{ij} \equiv \delta_{ij}$, in the AIM approach that Fradera, Austen, and Bader [18] define as the *delocalization index* and use as a quantitative measure of electron pair sharing between basins Ω_i and Ω_j ; they also denote F_{ii} as the *atomic localization index*.

Details of the Calculations

The structures employed here used optimized geometries found in the B3LYP approach [32,33] with a 6-311+G(d,p) basis using Gaussian 98 [34]. Our models for the neutral compounds involving Na and Li are of C_{2h} symmetry and, as pointed out by Xie et al. [2], are actually transition states where the metal ions want to move so as to lower the symmetry to C_s . Geometries for the other species were obtained at both energy minima and transition state geometries and are so identified in the tables. We have not exhaustively searched for all minima and transition states but have focused only on those species relevant to the major question posed of the nature of the two-coordinate Ga—Ga bond.

The AIM and ELF calculations were carried out employing the TopMod Package of Noury and co-workers [35], also in the B3LYP/6-311+G(d,p) approach. Step sizes of 0.1 au and box sizes that extended 5.0 au from the outermost atomic coordinates in each direction were used for the neutral species (the Na and Li salts, and the neutral gallium and germanium hydrides). Because of the diffuse character of the dianionic species, step sizes of 0.2 au and large boxes extending 15.0 au from the outermost atomic coordinates in each direction had to be employed. The numerical uncertainty of the ELF basin populations calculated with a step size of 0.2 au is expected to be of the order of 0.05.

RESULTS AND DISCUSSION

The value of the AIM picture is that it is well defined in terms of the electron density, an observable of particular importance. And while it does not allow for what we would consider to be bonding regions separate from the AIM atoms, the delocalization index permits the calculation of what Frederica et al. [18] refer to as the number of electron pairs shared by two AIM atoms. At the same time, these authors are quick to point out that generally this cannot be looked at as a bond order because of polarization effects.

The ELF picture's great attraction is its representation of core, bonding, and lone pair regions (basins) from which one can derive (by integration of the electron density over the basin) basin electron populations. The graphical representation of these basins and their electron populations generally matches up remarkably well with the chemist's idea of atomic cores, bonds, and lone pairs *when the basins tend to occupy regions of space that can be relatively unambiguously interpreted as atomic cores, bond basins, or lone pairs*. A problem arises, however, when basins occupy regions encompassing both bonding and lone pair character.

The approach we take here is to look at ratios of AIM delocalization indices and ELF basin populations relative to that situation where we generally would accept a particular bond order. Our working premise is that, if polarization effects are kept relatively constant, the *ratios* of delocalization indices and bond populations appropriately referenced should provide insight into the nature of the formal bond order involved. We propose a principle of local electronic similarity whereby the formal bond order is derived from a comparison of the same two (heavy) atoms in differing states of bond multiplicity. For example, in our prior work [4] on H_2NCH_3 , HNCH_2 (planar), and HCN (linear) δ_{CN} values of 0.99, 1.77, and 2.57 were found, in the ratio of 1.12:(2.0):2.90 taking HNCH_2 to define a double bond; the corresponding CN bond basin populations were 1.63, 2.91, and 4.37, respectively, in the ratio of 1.12:(2.0):3.00.

In certain cases the standard may be a transition state when the bonding is particularly transparent. In our work here we find discrepancies between the AIM and ELF results in certain cases where the ELF basin bond order is significantly larger than that defined by the associated delocalization index. In these cases (*vide infra*) we shall propose that the ELF populations represent a combination of bonding and lone pair populations.

The problem is illustrated by examining Fig. 1 which shows the $\eta = 0.5$ isosurfaces for the trans-bent (C_{2h}) minimum energy form of $[\text{HGaGaH}]^{2-}$.

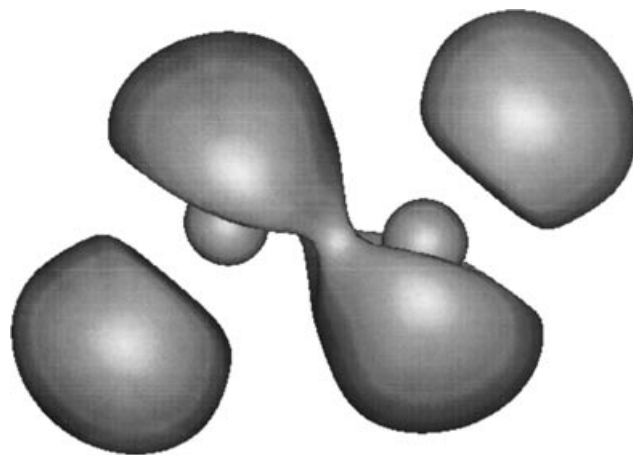


FIGURE 1 ELF isosurfaces ($\eta = 0.50$) for trans-bent $[\text{HGaGaH}]^{2-}$ exhibiting the “slipped” multiple bond basin viewed from the side. The other basins are those for hydrogen (the larger ones) and the core basins for gallium (smaller ones).

One is looking down on the plane of the molecule where the gallium core and hydrogen basins are readily noted. Does the remaining basin extend into the Ga–Ga bonding region? Yes, but it is also present in those regions where Ga lone pairs are expected. Our approach here will allow us to better answer the question of the nature of this ELF basin and how it relates to the Ga–Ga bond order in this molecule.

Na and Li Salts and the Dianions

In our discussion here we shall abbreviate the $[\text{HGaGaH}]^{2-}$, $[\text{H}_2\text{GaGaH}_2]^{2-}$, and $[\text{H}_3\text{GaGaH}_3]^{2-}$ species as h2, h4, and h6, respectively. Geometrical data for these two-, three-, and four-coordinated digallium species are given in Table 1, with the site symmetries of the gallium hydride portion of the molecule presented in Table 2. Table 1 shows that the Ga–Na distances are in the neighborhood of the experimental distance (2.855 Å) found in the work of Su et al. [1] although the h2 compound's distance for the sodium case is a good 0.1 Å longer. Ga–Li distances are noticeably reduced (0.33 Å on average) corresponding to the decreased ionic radius of the smaller lithium ion. Ga–Ga distances for the h2 and h4 species are remarkably similar, which is suggestive of similar bonding in the h2 and h4 species. However, as Xie et al. [2] have pointed out, it is the electronic structure rather than bond lengths which, in their opinion, determines bond multiplicities. We note the very short distance in the linear h2 dianion, a transition state some 21.2 kcal/mol above the C_{2h} (trans-bent) form; the Ga–H distance is also greatly shortened in this species.

TABLE 1 Distances (Å) Between Gallium and the Bridging Metal Atom ($R_{\text{Ga-metal}}$), Between the Two Gallium Atoms (R_{GaGa}), and the Hydrogen–Gallium Bond (R_{HGa}) for the Species Involving $[\text{HGaGaH}]^{2-}$ (h2), $[\text{H}_2\text{GaGaH}_2]^{2-}$ (h4), and $[\text{H}_3\text{GaGaH}_3]^{2-}$ (h6) in the Na and Li Salts and in the Isolated Dianionic Species

| | h2 | h4 | h6 |
|-----------------------|--------------------|-------|--|
| $R_{\text{Ga-metal}}$ | | | |
| Na salt | 2.965 | 2.783 | 2.818 |
| Li salt | 2.672 | 2.427 | 2.485 |
| R_{GaGa} | | | |
| Na salt | 2.442 | 2.434 | 2.588 |
| Li salt | 2.398 | 2.422 | 2.592 |
| Dianion | 2.481 | 2.422 | 2.671 |
| | 2.216 ^a | | |
| R_{HGa} | | | |
| Na salt | 1.624 | 1.642 | 1.601, ^b 1.645 ^c |
| Li salt | 1.616 | 1.630 | 1.588, ^b 1.643 ^c |
| Dianion | 1.650 | 1.602 | 1.637 |
| | 1.549 ^a | | |

^aLinear $[\text{HGaGaH}]^{2-}$ transition state.

^bThe two hydrogens in the plane normal to the Na–Na line.

^cThe four hydrogens not in the plane normal to the Na–Na line.

Table 2 shows that the h2 and h4 species generally exhibit trans-bent geometries with the exception of the h4 dianion which is found to have a planar minimum (D_{2h}) in our studies. Xie et al. [2] found the planar form to be a transition state in their work.

Before we examine the bonding involved between the gallium atoms, we need to characterize the Na and Li salts relative to the dianionic species. ELF core populations for the metal atoms indicate virtually complete transfer of one electron each (a charge of +0.97) from each metal atom to the gallium hydride portion of the salt. The same is shown by the AIM atom populations, a transfer on the average of 0.85 electrons. We do note that in the case of $\text{Na}_2[\text{H}_2\text{GaGaH}_2]$ sodium has an AIM atomic charge of only +0.77, the smallest positive charge of all the metal species studied here. With the exception of the $\text{Na}_2[\text{H}_2\text{GaGaH}_2]$ and $\text{Li}_2[\text{H}_2\text{GaGaH}_2]$ cases, all the delocalization indices involving the metal atoms are less than 0.08; in $\text{Na}_2[\text{H}_2\text{GaGaH}_2]$ the value of δ_{NaGa} is 0.25 and in $\text{Li}_2[\text{H}_2\text{GaGaH}_2]$ δ_{LiGa} is equal to

TABLE 2 Point Group Site Symmetry for the Gallium Hydride Portion of the Species Involving $[\text{HGaGaH}]^{2-}$ (h2), $[\text{H}_2\text{GaGaH}_2]^{2-}$ 2 (h4), and $[\text{H}_3\text{GaGaH}_3]^{2-}$ (h6) in the Na and Li Salts and in the Isolated Dianionic Species

| | Na salt | Li salt | Dianion |
|----|-----------------------|-----------------------|-----------------------|
| h2 | C_{2h} (trans-bent) | C_{2h} (trans-bent) | C_{2h} (trans-bent) |
| h4 | C_{2h} (trans-bent) | C_{2h} (trans-bent) | D_{2h} (planar) |
| h6 | C_{2h} | C_{2h} | D_{3d} |

0.14. The small values of the delocalization indices involving the metal atoms is consistent with an ionic model such as $(\text{Na}^+)_2[\text{H}_2\text{GaGaH}_2]^{2-}$ but the figures mentioned above for the h2 cases involving Na and Li indicate some small degree of electron pair sharing. As we note later, this is consistent with the somewhat unusual ELF isosurface picture found for these species.

Figure 2 contains the $\eta = 0.70$ isosurfaces for the planar $[\text{H}_2\text{GaGaH}_2]^{2-}$ dianion (Fig. 2a) and the neutral $\text{Na}_2[\text{H}_2\text{GaGaH}_2]$ salt (Fig. 2b). The planar dianion should be characteristic of a double bond and, indeed, exhibits twin basins above and below the molecular plane midway between the gallium atoms, as ELF often characterizes the bent or banana bond description of double bonds. In Fig. 2b one is looking almost down the line which would connect the Na core basins; the hydrogens and gallium core basins are apparent, and the Ga–Ga bonding basins definitely lean in toward the bonding region between the gallium atoms. Qualitatively we would consider this to represent double bonding. Table 3 contains the absolute basin populations and delocalization indices in part A, and in part B are given the ratios of these parameters relative to the $[\text{H}_2\text{GaGaH}_2]^{2-}$ dianion as our reference of bond order 2.00. An examination of part B of this table clearly suggests that all the h4 species are double in nature and the h6 species single as regards the Ga–Ga bond. We have also included in this table the results for the linear $[\text{HGaGaH}]^{2-}$ transition state dianion which, because of the disposition of its orbitals, we would consider to represent a triple bond.

The key question, of course, is what about the h2 cases? Figure 3a and b show two views of $\text{Na}_2[\text{HGaGaH}]$; Fig. 3a looks nearly down a line connecting the two Na atoms while b is a view in the HGaGaH molecular plane. The ELF isosurfaces here are notably different from those in the $[\text{HGaGaH}]^{2-}$ dianion shown in Fig. 1. Aside from the obvious core and hydrogen basins, the remaining ELF surfaces show more of an extension into the Ga–Ga bonding region and at the same time an elongation toward the polarizing Na atoms. This elongation is apparently what is reflected in the δ_{NaGa} value of 0.25. It appears qualitatively that, compared to the isolated dianion, electron population is being shifted both into the Ga–Ga bonding region as well as toward the Na atoms.

The net effect of this can be addressed by looking at the relative ELF electron populations and delocalization indices in Table 3B. Based on the delocalization index ratios and assuming that the h6, h4, and linear h2 are single, double, and triple in nature, we must conclude that the Ga–Ga bond in both salts and

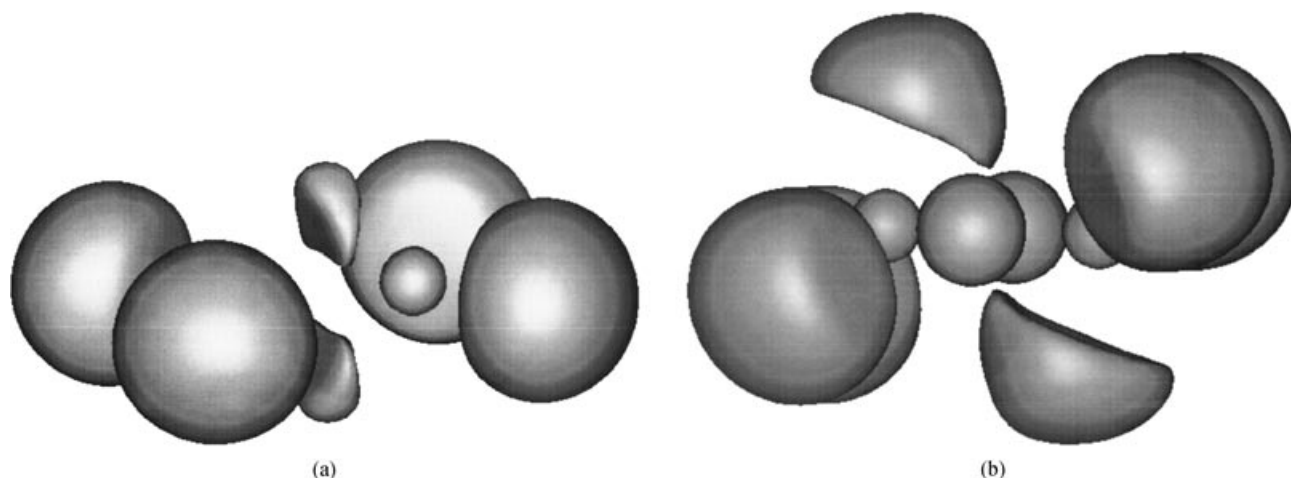


FIGURE 2 ELF isosurfaces ($\eta = 0.70$) for (a) planar $[\text{H}_2\text{GaGaH}_2]^{2-}$ viewed from slightly above the molecular plane exhibiting the twin basins above and below the molecular plane characteristic of a double bond between the Ga atoms, and (b) for $\text{Na}_2[\text{H}_2\text{GaGaH}_2]$ where the $[\text{H}_2\text{GaGaH}_2]^{2-}$ moiety is in a trans-bent form. Gallium core and hydrogen basins are apparent in both figures. In case (b) the Ga-Ga bond basin is distinctly in the Ga-Ga bonding region.

in the dianion is roughly *midway* between a double and triple bond; the ratios are not large enough to characterize it as triple, yet with a value of 2.40 it is clearly larger than double. That is, in terms of the schematic representation of contributing single- and triple-bonded structures appearing in Scheme 2, the triply bonded structure need be given higher weight.

Neutral Gallium Compounds

Data for a selected set of neutral gallium compounds are given in Table 4. Here one could choose as reference either the planar (D_{2h}) or D_{2d} H_2GaGaH_2 species; because it seems clear that only a single bond

can exist between the gallium atoms in the twisted D_{2d} form, we define it to have a bond order of 1.00. This leads to bond orders of essentially 1.00 and 2.00 for the planar (transition state) H_2GaGaH_2 and linear HGaGaH compounds as one might expect. Somewhat unexpectedly, the trans-bent (C_{2h}) HGaGaH molecule exhibits a Ga-Ga bond of order 1.00 according to the delocalization index. The $\eta = 0.70$ ELF isosurfaces are shown in Fig. 4 and it does appear that a great deal of the Ga-Ga bond basin is not in what one would call the bonding region. The fact that the relative ELF bond order is 1.86 suggests that some of what we term the bond basin population must be associated with the gallium lone pairs.

TABLE 3 Absolute Basin Populations and Delocalization Indices, and Ratios of These Parameters Relative to the $[\text{H}_2\text{GaGaH}_2]^{2-}$ Dianion

| | N_i | | | δ_{ij} | | |
|--|----------|----------|-----------------------------------|---------------|---------|---------------------------|
| | Na salt | Li salt | Dianion | Na salt | Li salt | Dianion |
| A. ELF Ga-Ga basin populations (N_i) and AIM delocalization indices (δ_{ij}) for the species involving $[\text{HGaGaH}]^{2-}$ (h2), $[\text{H}_2\text{GaGaH}_2]^{2-}$ (h4), and $[\text{H}_3\text{GaGaH}_3]^{2-}$ (h6) in the Na and Li salts and in the isolated dianionic species | | | | | | |
| h2 | 6.53 (4) | 6.63 (4) | 6.30 (2) 6.28 ^a (1) | 1.44 | 1.75 | 1.47 2.12 ^a |
| h4 | 4.36 (2) | 4.34 (2) | 3.94 (2) | 1.22 | 1.24 | 1.23 |
| h6 | 2.31 (2) | 2.28 (2) | 1.86 (6) | 0.73 | 0.72 | 0.56 |
| B. Parameter ratios relative to the δ_{ij} and N_i for the planar h4 species in the dianion defined as 2.00 | | | | | | |
| h2 | 3.32 | 3.37 | 3.20 3.19 ^a | 2.35 | 2.86 | 2.40 3.45 ^a |
| h4 | 2.22 | 2.20 | (2.00) | 1.98 | 2.02 | (2.00) |
| h6 | 1.17 | 1.16 | 0.94 | 1.19 | 1.18 | 0.91 |

The number of basins contributing to the Ga-Ga basin populations is shown in parentheses.

^aLinear $[\text{HGaGaH}]^{2-}$, a transition state.

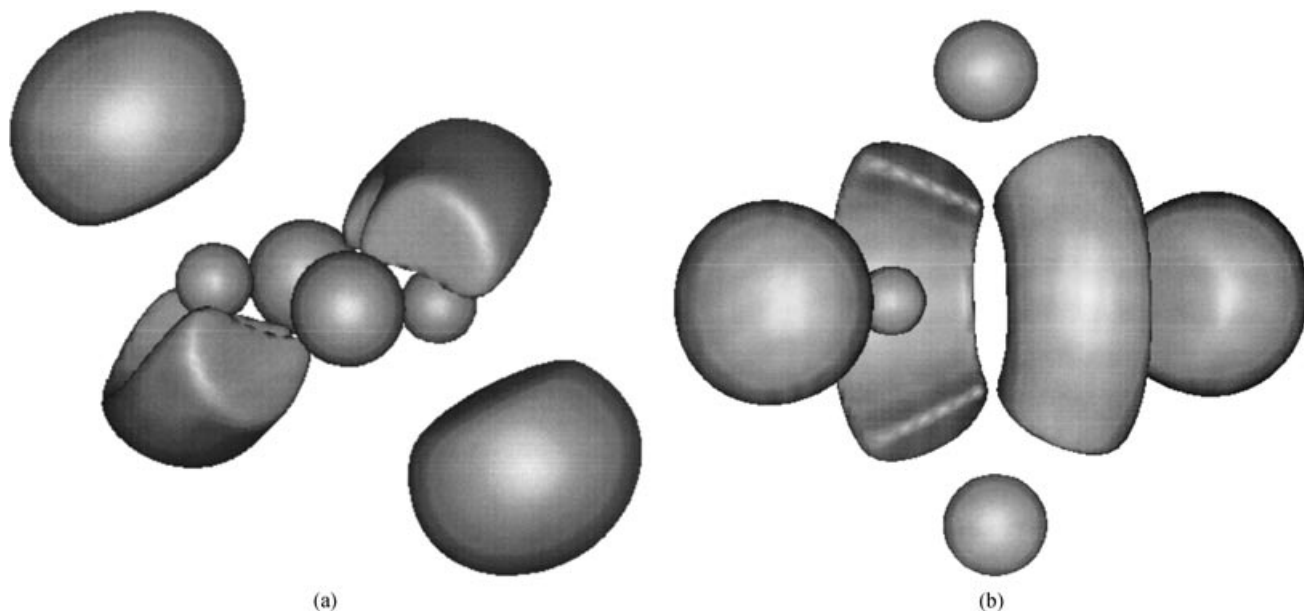


FIGURE 3 Two views of the ELF basins ($\eta = 0.71$) for $\text{Na}_2[\text{HGaGaH}]$ from (a) nearly along the line connecting the two Na atoms (larger core basins) and (b) from the edge of the $[\text{HGaGaH}]^{2-}$ moiety clearly exhibiting the Ga–Ga bond basin elongated toward the polarizing Na atoms (top and bottom of the graphic).

In terms of an earlier scheme one might indicate the situation as in Scheme 3 with an unusual no-bond contributing structure! We note too that the Ga–Ga bond distance is very long, consistent with the idea of a single bond.

Isoelectronic Germanium Compounds

Data for some selected germanium compounds isoelectronic with the h2, h4, and h6 gallium species are given in Table 5. In addition we have included the three Ge_2H_2 stable isomers where the dibridged (**D**, C_{2v}) or butterfly structure is lowest in energy, followed by the monobridged (**M**, C_s) structure some

11.3 kcal/mol higher, and the digermavinylidene (**V**, C_{2v}) at 11.8 kcal/mol above the **D** structure; while the planar trans-bent (C_{2h}) structure is stable in HSiSiH , the corresponding germanium compound is a transition state in our studies. These four molecules have the structures shown in Scheme 4.

We again choose the planar (D_{2h}) H_2GeGeH_2 compound to reference the double bond for the

TABLE 4 Data for Neutral Gallium Species

| | R_{GaGa} | N_i | $N_{i,\text{rel}}$ | δ_{ij} | $\delta_{ij,\text{rel}}$ |
|--------------------------------|-------------------|----------|--------------------|---------------|--------------------------|
| Ga_2H_2 | | | | | |
| Planar trans-bent (C_{2h}) | 2.635 | 4.48 (2) | 1.86 | 0.89 | 1.08 |
| Linear* ($C_{\infty h}$) | 2.252 | 4.54 (2) | 1.88 | 1.63 | 1.98 |
| Ga_2H_4 | | | | | |
| D_{2d} | 2.476 | 2.41 (2) | (1.00) | 0.83 | (1.00) |
| Planar* (D_{2h}) | 2.526 | 2.34 (2) | 0.97 | 0.81 | 0.98 |

Ga–Ga bond distances (R_{GaGa} , Å), Ga–Ga ELF basin populations (N_i), Ga–Ga delocalization indices (δ_{ij}), and their ratios ($N_{i,\text{rel}}$, $\delta_{ij,\text{rel}}$) relative to planar Ga_2H_4 defined as 2.00. The number of basins contributing to the GaGa basin populations is shown in parentheses. Transition states are indicated by an asterisk.

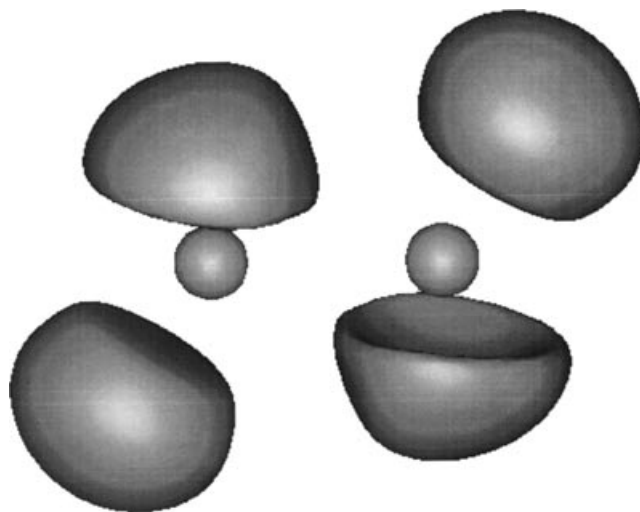
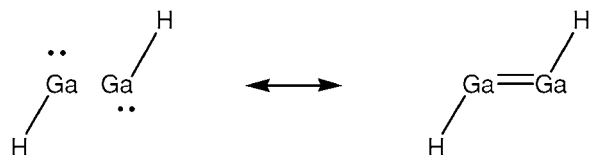


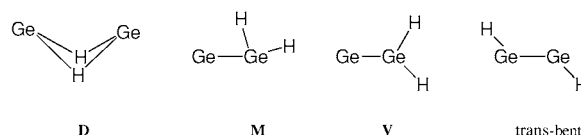
FIGURE 4 ELF isosurfaces ($\eta = 0.70$) for neutral trans-bent $[\text{HGaGaH}]$ that shows that the Ga–Ga bond basin is located nearly as much in the lone pair region as in the bonding region.



SCHEME 3

germanium molecules even though it is a transition state (4.30 kcal/mol above the minimum energy trans-bent H_2GeGeH_2). The results are quite similar to the associated gallium compounds, as one would expect. As the relative bond parameters in Table 5 show, the Ge—Ge bonds for D_{3d} H_3GeGeH_3 , trans-bent H_2GeGeH_2 , and linear HGeGeH are single, double, and triple, as expected. As is the case for the gallium compounds, the trans-bent (C_{2h}) HGeGeH molecule exhibits a Ge—Ge bond that has a bond order larger than double but smaller than triple; accordingly, some of the electron population in the Ge—Ge ELF basin must be described in terms of lone pairs.

The low-energy form for H_2Ge_2 is the C_{2v} dibridged (butterfly) form as is the case for H_2Si_2 . Its $\eta = 0.7$ ELF isosurfaces are shown in Fig. 5 where the core and bridging hydrogen basins clearly exhibit the dibridged geometry. The bridging hydrogens represent three-center, two-electron bonds, while there is a bent bond connecting the two germanium atoms. What is unusual here is the fact that the relative bond orders predicted by the ELF basin populations for the **D**, **M**, and **V** Ge_2H_2 structures are smaller than those predicted by the delocalization indices, as is also the case in HSiSiH [4]. To this point the two



SCHEME 4

measures of bond order either have agreed in their predictions, or the ELF bond orders have been larger, an indication we have taken to imply partial lone pair character of the basin.

The ELF basins observed (not all shown here but very close to those seen for HSiSiH [4]) make clear suggestions regarding the nature of the bonds in these molecules. They reflect the structures shown in the orbital diagrams of Scheme 5 where tetrahedral or sp^2 hybrids or $p\pi$ orbitals are used, again paralleling the situation found earlier [4] for Si_2H_2 : the dibridged molecule is predicted to have one bent single bond connecting the Ge atoms, there are two bent bonds between the Ge atoms in the **M** and **V** cases (double bonds), and lone pairs completing the electron pair count are exactly where we would expect them to be chemically. The structure we have drawn for the planar dibridged transition state molecules (**PLD** in Scheme 5) is based on the fact that, while there is no longer a separate Ge—Ge ELF bond basin, the delocalization index only falls from 1.48 to 1.32 in moving from the stable **D** form to the **PLD** form. In addition, the $\eta = 0.70$ ELF isosurfaces shown in Fig. 6 for the **PLD** form suggests from the comma-shaped character of the non-core, non-hydrogen basins the presence of a single weak π bond in this case, replacing the bent bond of the **D**

TABLE 5 Ge—Ge Bond Distances (R_{GeGe} , Å), Ge—Ge ELF Basin Populations (N_i), Ge—Ge Delocalization Indices (δ_{ij}), and Their Ratios ($N_{i,\text{rel}}$, $\delta_{ij,\text{rel}}$) Relative to Planar Ge_2H_4 Defined as 2.00

| | R_{GeGe} | N_i | $N_{i,\text{rel}}$ | δ_{ij} | $\delta_{ij,\text{rel}}$ |
|------------------------------------|-------------------|----------|--------------------|---------------|--------------------------|
| Ge₂H₂ | | | | | |
| Planar trans-bent* (C_{2h}) | 2.224 | 6.48 (4) | 3.01 | 2.04 | 2.47 |
| Linear* ($C_{\infty h}$) | 2.056 | 6.56 (1) | 3.05 | 2.65 | 3.20 |
| D (C_{2v}) | 2.384 | 2.12 (1) | 0.99 | 1.23 | 1.48 |
| Planar D * (D_{2h}) | 2.569 | — | — | 1.10 | 1.32 |
| M (C_s) | 2.248 | 3.49 (2) | 1.62 | 1.71 | 2.07 |
| V (C_{2v}) | 2.314 | 3.54 (2) | 1.64 | 1.77 | 2.14 |
| Ge₂H₄ | | | | | |
| trans-Bent (C_2) | 2.306 | 4.27 (2) | 1.98 | 1.43 | 1.73 |
| Planar* (D_{2h}) | 2.225 | 4.31 (2) | (2.00) | 1.66 | (2.00) |
| Ge₂H₆ | | | | | |
| D_{3d} | 2.445 | 2.15 (1) | 1.00 | 0.83 | 1.00 |

Transition states are indicated by an asterisk. The number of basins contributing to the Ge—Ge basin populations is shown in parentheses.

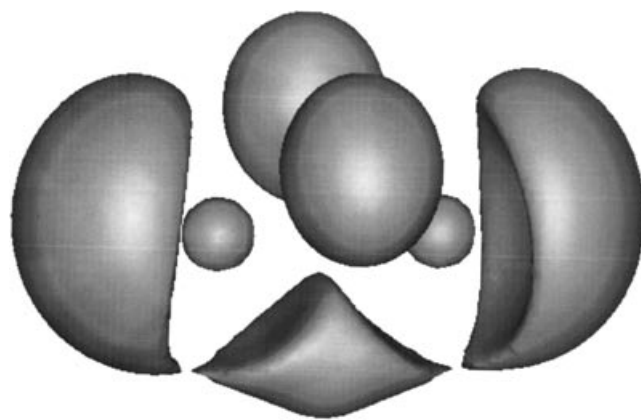
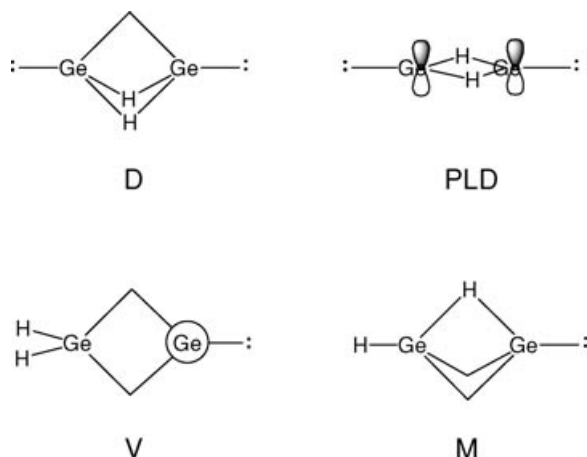


FIGURE 5 ELF isosurfaces ($\eta = 0.72$) for the minimum energy dibridged (butterfly) Ge_2H_2 molecule showing the germanium core and bridging hydrogen basins, the germanium lone pair basins (at the extreme left and right), and a bent single bond Ge—Ge bond basin.



SCHEME 5

case. The HOMO for this case is, indeed, a bonding (in phase) π orbital.

While this assignment of bonds seems appropriate, the **M** and **V** ELF relative bond orders are too low, and the delocalization index relative bond order for the **D** molecule is too high. It is unusual to have relative delocalization bond orders that are larger than those for the ELF basin populations.

These unusual characteristics occur for the rather unusual structures these structures exhibit. The **M** and **V** cases may be explained in terms of the lone pair basin populations for these two molecules, 3.08 and 2.92 electrons, respectively. These populations are considerably larger than that of the **D** molecule of 2.25 (for each of two lone pairs). If we assume that some of the bonding basin populations are actually contained in those basins representing

the lone pairs and add in the difference between the lone pair populations and that for the **D** case to the bonding basin populations, relative ELF bond orders of 2.00 and 1.96 result for the **M** and **V** molecules, respectively.

This still leaves the problem of why the AIM relative bond order for the **D** case is midway between 1.00 and 2.00. It is an unusual molecule, and even when made planar so that one might not expect any direct Ge—Ge bonding, the relative index is 1.32. It may be that in this particular case the delocalization index is measuring more than just the electron sharing expected for a single bond. For example, in diborane the (unnormalized) index between the two boron atoms separated by the two bridging hydrogens is 0.11, and in cyclobutadiene we find an index between nonadjacent carbon atoms of 0.14. Of course, this argument might also be made for the **M** and **V** cases which tend to behave “normally.” As was the case for this isomer in Si_2H_2 , the high value of the delocalization index for the **D** molecule remains somewhat of an anomaly.

SUMMARY

Using the ratio of delocalization indices and bond basin populations referenced to reasonable standards, formal bond orders have been derived for two-, three-, and four-coordinate gallium hydrides present in Na and Li salts and as the isolated dianionic species, for some isoelectronic germanium compounds, and for several neutral gallium hydrides. While chemically expected bond orders are found in most cases, the situation in the $[\text{HGaGaH}]^{2-}$ species appears to lie intermediate between a bond of order 2.00 and 3.00, and that for neutral trans-bent HGaGaH is found to be best described as a bond of order 1.00. In these cases the larger bond order predicted by ELF bond basin populations evidently results from overlap of the bond basin into the lone pair (nonbonding) region of the molecule.

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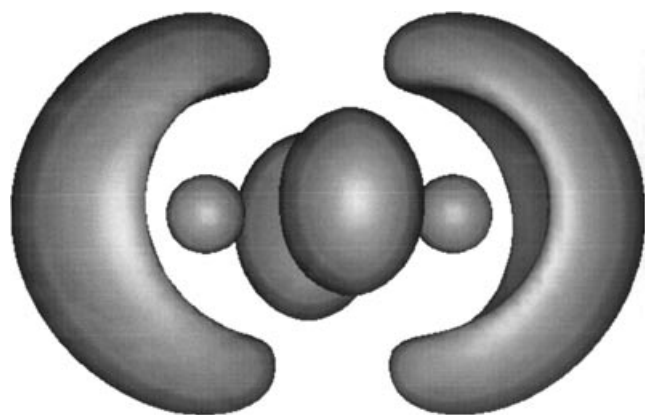


FIGURE 6 ELF isosurfaces ($\eta = 0.70$) for the planar dibridged Ge_2H_2 transition state. There is no longer a single bond Ge—Ge bond basin but rather that electron population has been incorporated into the lone pair bond basins whose comma-shaped form is indicative of a weak π bond between the Ge atoms.

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