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Theoretical studies of multiple bonds in gallium–gallium and germanium–germanium compounds†

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A recent publication concerning the synthesis and structure of the compound $Na_2\{GaC_6H_3\text{-}2,6\text{-}Trip_2\}_2$ (Trip = C_6H_2-2,4,6-$^iPr_3$), which has a *trans*-bent geometry, has generated considerable discussion owing to the description of its gallium–gallium bond as a triple one.[1] To provide a theoretical perspective on this subject, we have studied a series of model compounds by the methods of molecular electronic structure theory. For the species *trans*-$Li_2MeGaGaMe$ we find a Ga–Ga bond order somewhat less than two, instead of a triple bond, owing to the antibonding character of one of the molecular orbitals. In the isoelectronic *trans*-MeGeGeMe we find an essentially Ge=Ge double bonded structure. The neutral *trans*-MeGaGaMe molecule has a weak Ga–Ga single bond rather than a Ga–Ga double bond. Each of these molecules features a lone pair orbital of b_u symmetry, with the main regions of electron density located on the gallium or germanium centers, formed by mixing a bonding π orbital and an antibonding σ* orbital in a second-order Jahn–Teller effect.

The stabilization of species that have multiple bonds between heavier main group elements has been studied extensively.[2] Nevertheless stable compounds featuring multiple bonding between heavier main group 13 elements have only been isolated and characterized within the past decade.[3] The first such compounds were the singly reduced ions $[R_2M\overset{\cdots}{-}MR_2]^-$ (M = Al[4] or Ga,[5] R = $-C_6H_2$-2,4,6-$^iPr_3$(Trip) or $-CH(SiMe_3)_2$) which have a formal bond order of 1.5 and bond distances 0.13–0.18 Å shorter than the unreduced neutral precursors $R_2M–MR_2$. Thus, the tetraaryl digallium species $Trip_2Ga–GaTrip_2$, which has a Ga–Ga single bond length of 2.515(3) Å, can be reduced to the anion $[Trip_2Ga\overset{\cdots}{-}GaTrip_2]^-$ which has a Ga–Ga distance of 2.343(2) Å and a formal Ga–Ga bond order of 1.5.[5a] Recent attempts at further reduction to give a dianion $[Trip_2Ga{=}GaTrip_2]^{2-}$ with a formal double bond have led to a rearrangement and the isolation of the compound $Na_2\{Ga(GaTrip_2)_3\}$ featuring the dianion $[Ga(GaTrip_2)_3]^{2-}$ with a trigonal planar arrangement of four galliums, a formal Ga–Ga bond order of 1.33, and an average Ga–Ga distance of 2.389(17) Å.[6]

The use of *m*-terphenyl ligands at gallium has also led to a number of interesting reduced organogallium species that have multiple bonding character. For example, reduction of $Cl_2GaC_6H_3$-2,6-Mes_2 (Mes = 2,4,6-trimethylphenyl) with Na or K leads to a cyclic Ga_3 species $M_2\{GaC_6H_3\text{-}2,6\text{-}Mes_2\}_3$ (M = Na or K)[7] which contains 2 π-electrons in conformity with the Hückel rule. It has a formal Ga–Ga bond order of 1.33 with an average Ga–Ga distance of *ca.* 2.44 Å (*cf. ca.* 2.39 Å in $\{Ga(GaTrip_2)_3\}^{2-}$ with the same formal bond order). With the larger $-C_6H_3$-2,6-$Trip_2$ substituent the reduced dimeric species $Na_2\{GaC_6H_3\text{-}2,6\text{-}Trip_2\}_2$ is obtained which has the shortest Ga–Ga distance (2.319(3) Å) seen in a molecular species.[1] Owing to the short Ga–Ga bond length and the fact that Group 13 ions of formula $[RMMR]^{2-}$ are isoelectronic to Group 14 species of formula RMMR (which are heavier congeners of alkynes), it was stated that this compound featured a triple Ga–Ga bond. However, the C–Ga–Ga–C backbone is bent (Ga–Ga–C = *ca.* 130°) and the Ga–Ga distance, *ca.* 2.32 Å, is not as short as might be expected on the basis of a comparison with the other multiply bonded Ga–Ga species (see above). These findings have led to questions[8] on the validity of the description of triple bonding in this molecule. Also, there has been a suggestion that close interactions between the alkali metal cations and the aryl ligand can shorten the Ga–Ga distance by as much as 0.1 Å. Thus in the free hypothetical dianion $\{GaPh\}_2^{2-}$ (with no Na^+–aryl interactions) the Ga–Ga distance is 2.461 Å, whereas in the contact ion pair $Na_2\{GaC_6H_3\text{-}2,6\text{-}Ph_2\}_2$, which features Na^+–aryl interactions, it is shortened to 2.362 Å.[9] Both of these Ga–Ga distances lie well within the normal single bonded range of *ca.* 2.33–2.54 Å.

The apparently intriguing Ga–Ga bonding in these reduced dimers led us to examine the electronic structures of the hypothetical species $Li_2\{GaMe\}_2$ and the corresponding neutral germanium molecule $\{GeMe\}_2$ in *trans* geometries. The results of these studies provide strong evidence that the Ga–Ga or Ge–Ge bond orders in such molecules are significantly less than three and, in the case of the gallium species, very probably between one and two.

Method

We determined structural parameters, total energies, orbital energies, and harmonic vibrational frequencies at stationary points using the self-consistent field (SCF) method, the Gaussian 94 program,[10a] and the Gaussian 98 program.[10b] The basis set was 6-31G*. The restricted Hartree–Fock (RHF) option was used for closed-shell states, unrestricted Hartree–Fock (UHF) for doublet states of radicals. An atoms-in-molecules (AIM)[11–18] program from Gaussian 94 was used for bond order determination. For a study at a level beyond SCF of *trans*-MeGaGaMe we employed the Generalized Valence Bond (GVB)[19,20] method, again using the program in Gaussian 94.

A comprehensive study of correlated wavefunctions was carried out for all molecules with second-order Møller–Plesset perturbation theory. The MP2 program of Gaussian 98 was used for this purpose. Again, the basis set was 6-31G*. Orbitals used for correlation included all occupied valence orbitals and all virtual orbitals. Thus the orbitals used for correlation were numbers 33–132 for the $Li_2MeGaGaMe$ species, 31–102 for MeGaGaMe and for MeGeGeMe, and 31–106 for MeHGaGaHMe and for MeHGeGeHMe. In general the SCF and MP2 results are very similar. Examples where this is not so are noted below at the appropriate points.

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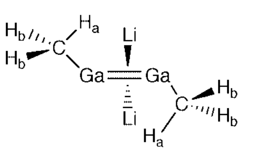
† Electronic supplementary information (ESI) available: more theoretical studies. See http://www.rsc.org/suppdata/dt/a9/a907421j/

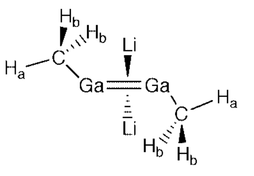
Table 1 Structures and energies of model compounds[a]

Molecule	MM bond length	MC bond length	MMC bond angle	H_aCMM[b] dihedral angle	Relative energy	No. of imaginary vibrational frequencies
trans-Li_2[MeGaGaMe], str 1	2.388	2.033	132.5	0.0	3.5	1
	2.391	2.039	133.1	0.0	0.8	0
trans-Li_2[MeGaGaMe], str 2	2.387	2.034	132.6	180.0	3.9	2
	2.392	2.040	133.4	180.0	1.4	2
"linear" Li_2[MeGaGaMe]	2.161	1.989	180.0	—	34.8	3
	2.203	2.000	180.0	—	37.5	3
bent Li_2[MeGaGaMe]	2.330	2.013[c]	128.9[d]	180.0, 0.0	0.0	0
	2.384	2.026[c]	133.2[d]	180.0, 0.0	0.0	0
trans-MeGaGaMe, str 2	2.654	2.017	123.0	180.0	0.0	0
	2.560	2.017	125.2	180.0	0.0	0
trans-MeGaGaMe, str 1	2.676	2.019	123.9	0.0	3.7	2
	2.566	2.020	126.8	0.0	4.6	2
trans-$MeGaGaMe^+$, str 2	2.476	1.959	148.7	180.0	0.0	0
	2.460	1.959	152.1	180.0	0.0	0
trans-$MeGaGaMe^+$, str 1	2.466	1.959	150.6	0.0	1.0	2
	2.447	1.959	154.4	0.0	1.4	2
trans-MeGeGeMe,[e] str 2	2.167	1.962	130.9	180.0	0.0	1
	2.197	1.968	129.9	180.0	0.0	0
trans-MeGeGeMe, str 1	2.171	1.962	130.5	0.0	0.2	1
	2.200	1.968	129.7	0.0	1.2	2
"linear" MeGeGeMe	2.014	1.932	180.0	—	63.6	2
	2.073	1.939	180.0	—	78.0	2
twist MeGeGeMe[e]	2.458	2.017	88.3	—	−32.5	0
	2.365	2.083	70.3	—	+22.8	0
trans-MeHGaGaHMe,[f] str 2	2.510	1.996	122.6	180.0	0.0	1
	2.515	1.999	122.3	180.0	0.0	1
trans-MeHGaGaHMe,[f] str 1	2.511	1.995	124.6	0.0	1.4	3
	2.514	1.997	124.4	0.0	0.7	3
trans-MeHGeGeHMe,[f] str 1	2.187	1.946	124.7	0.0	0.0	1
	2.218	1.947	124.1	0.0	0.0	1
trans-MeHGeGeHMe,[f] str 2	2.187	1.952	124.8	180.0	5.9	3
	2.218	1.953	124.3	180.0	4.9	3

[a] Structures having H_aCMM dihedral angles of 0.0° and 180.0° are designated str 1 and str 2, respectively. The structure of lower energy is listed first. Bond lengths are in Å, angles are in degrees, relative energies are in kJ mol^{-1}. Upper data are SCF or UHF, lower are MP2 or UMP2. All molecules have C_{2h} symmetry except bent Li_2MeGaGaMe (C_s), "linear" MeGeGeMe (D_{3d}), and twist MeGeGeMe (C_2). [b] H_a is the hydrogen atom bonded to C and lying in the CMMC plane. [c] Also 2.015 (2.051). [d] Also 153.6 (133.6). [e] The twist structure has the lowest energy at the SCF level, while *trans* structure 2 is lowest at the MP2 level. We have chosen the latter as the reference structure for relative energies. [f] The CHMMHC part of the molecule is planar.

We chose Li_2[MeGaGaMe], MeGaGaMe, and MeGeGeMe as model compounds, since they have Ga–C or Ge–C bonds, yet are simple enough for ease of study and interpretation. Since the compound in reference 1 has a *trans*-bent geometry, we emphasize those states of the model compounds having similar geometry. Typically, each state has two configurations, involving different orientations of the methyl groups, which have closely similar energies. We present results for both configurations, but in our analysis we emphasize the one of lower energy. We have also studied several other molecules which are helpful to an understanding of the nature of GaGa and GeGe multiple bonds. Results are summarized in Table 1. For clarity, the first two structures are illustrated below. Details, including absolute energies, are presented in Supplementary Information.



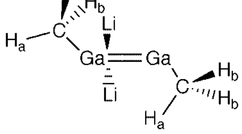


Discussion

We have chosen various states of two model compounds that are isoelectronic in the central part of the molecule with the gallium–gallium compound described in reference 1. They are Li_2[MeGaGaMe] and MeGeGeMe. The bonding in these states is now discussed.

The digallium species Li_2[MeGaGaMe] and related species

We have studied the electronic structure of Li_2[MeGaGaMe], where the lithium atoms are in bridging positions. We find that it has a triple bond only when the four heavy atoms have the linear structure C–Ga≡Ga–C. This structure, of C_{2h} symmetry, is not a minimum on the potential energy surface, but is instead a transition state lying 31.3 (36.7) kJ mol^{-1} above two equivalent *trans* structures, also of C_{2h} symmetry. (Throughout the text SCF results are listed first, with MP2 results in parentheses.) At the SCF level (but not the MP2 level), this *trans* structure is also a transition state. The normal mode of the imaginary frequency involves axial bending, where the two lithium cations both move into the region geminal to one of the methyl groups, with positions closer to the CGaGaC plane. This distorted structure, of C_s symmetry, is at an energy minimum lying only 3.5 (0.8) kJ mol^{-1} below the *trans* structure.



There is much less distortion with the MP2 results than with the SCF results (see Table 1 and Supplementary Information).

As it is the *trans* structure that is the appropriate model for comparison with the experimental structure of reference 1, we

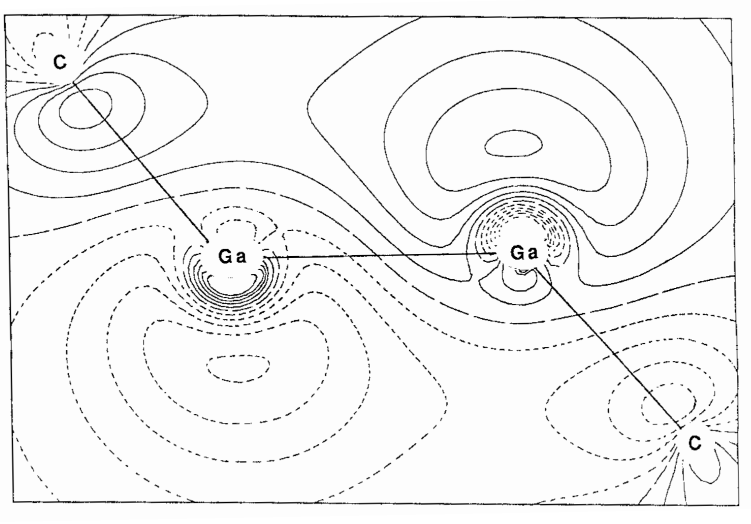
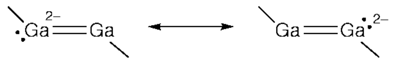


Fig. 1 Contour diagram of the $15b_u$ lone pair molecular orbital in *trans*-Li_2[MeGaGaMe], obtained with a 6-31G* basis set. The lithium atoms are in bridging positions above and below the CGaGaC plane.

focus attention on it. The *trans* species has a CGaGaC fragment that is planar, a GaGaC bond angle of 132.5° (133.1°), and a GaGa bond of length 2.388 Å (2.391 Å). One representation of this state in terms of simple Lewis structures is the resonance hybrid shown below:



Our characterization of the GaGa bond rests primarily on the nature of the canonical molecular orbitals. Using C_{2h} symbols, the $7a_u$ orbital (stabilized by the Li^+ ions) is the HOMO -1, and it is the π bond. The $16a_g$ orbital is the HOMO-2, and it is the σ bond. The $15b_u$ orbital is the HOMO, and it is an orbital representing lone pair electron density on the two gallium atoms in the regions geminal to the methyl groups (see Fig. 1). This behavior is consistent with the resonance hybrid shown above. There are also small contributions from the Ga–C σ bond regions, but the major contributions to the probability density come from the lone pair regions. (A homonuclear bonding orbital of π type would exhibit a maximum at the midplane between the heavy nuclei. Here the probability density in each lobe declines significantly in this region, reaching a minimum before rising to a smaller maximum in the Ga–C bonding region.) The orbital energies of both the *trans* and linear forms are shown in Fig. 2. (Note that the orbital energies of both the σ bond ($16a_g$) and the π bond ($7a_u$) are *less* negative in the *trans* structure than in the linear structure, suggesting that these bonds are weakened by the change to nonlinear geometry.)

By studying a related species, the neutral *trans*-bent MeGaGaMe, we have obtained strong evidence that the lone pair orbital has little or no bonding effect, and probably has some antibonding character. In this molecule the $15b_u$ lone pair orbital is the HOMO, and there is no π bond. The only GaGa bond is the $15a_g$ σ bond (HOMO-1). The GaGa bond length is 2.654 Å (2.560 Å), which is *longer* than that usually found in compounds with gallium–gallium single bonds (tetraorganodigallanes), where the experimental GaGa single bond lengths range from 2.333 Å[21] to 2.541 Å.[22] For *trans*-MeHGaGaHMe, we obtain 2.510 Å (2.515 Å). (This is a transition state, but it is the appropriate state for comparison of bond lengths here.) The AIM analysis of the SCF wavefunction yields a bond order of 0.821 for the GaGa bond in MeGaGaMe.

To further explore the interpretation of the $15b_u$ orbital, a generalized valence bond[19,20] (GVB) calculation replacing the

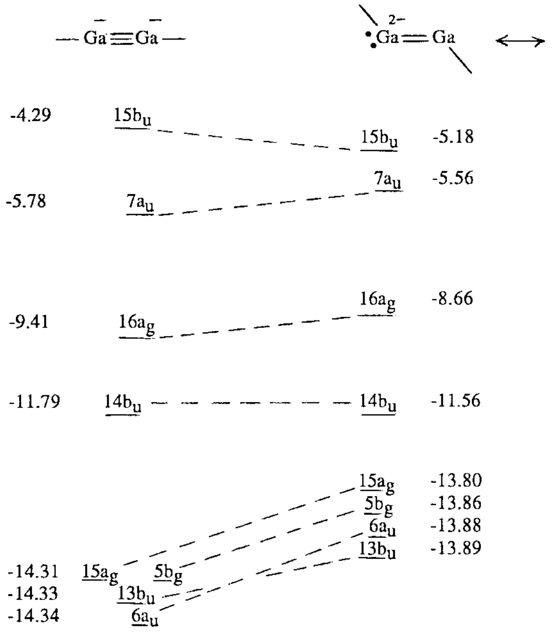
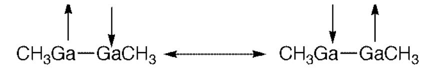


Fig. 2 Molecular orbital energy and correlation diagram for Li_2[MeGaGaMe]. Energies are in eV. The LUMOs are at 0.24 (linear, $17a_g$) and 0.21 (*trans*, $17a_g$).

$15b_u$ molecular orbital by separated spin-pair orbitals was performed in the hope that the GVB formalism could help to clarify the nature of this orbital. The geometry optimized with the closed shell Hartree–Fock (HF) formalism reported above was used for the calculation. The GVB calculation can be identified as a representation of the Lewis structures shown below,



where the spin paired electrons are occupying individual localized orbitals on the gallium atoms. This structure in valence bond language would emphasize the formation of the second bond between the gallium atoms. A contour diagram of one of the resulting generalized valence bond orbitals is shown in Fig. 3. The other orbital is, of course, simply an inversion image of the one shown. Each has a clear appearance of the distribution expected of a lone pair located primarily on the gallium atom. In particular there is a tilt to the axis of the orbital in a direction away from the gallium–gallium internuclear region. We

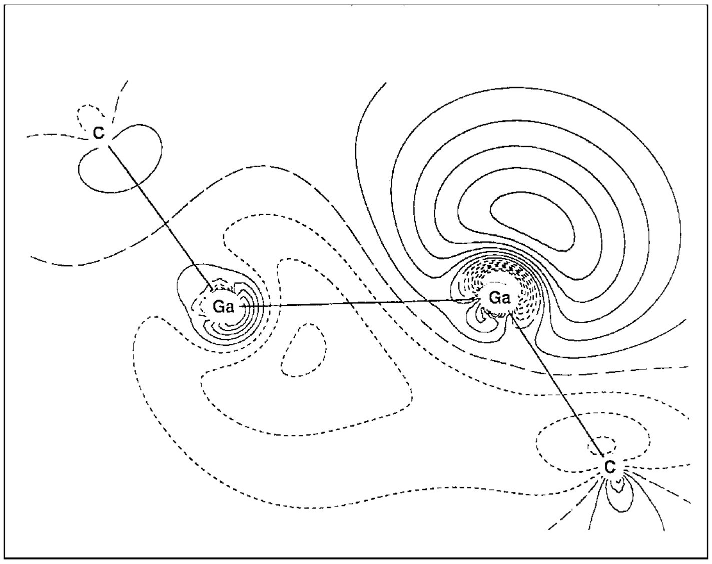


Fig. 3 Contour diagram of one of the two generalized valence-bond orbitals in the *trans*-MeGaGaMe molecule (lower-energy conformer).

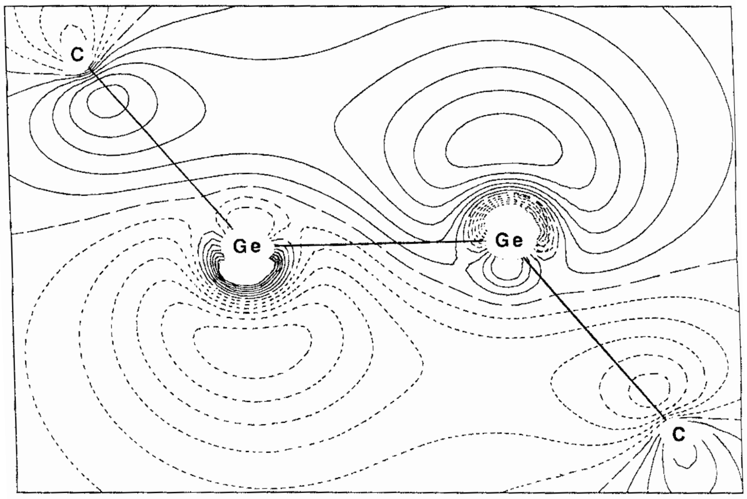


Fig. 4 Contour diagram of the $15b_u$ lone pair molecular orbital in *trans*-MeGeGeMe, obtained with a 6-31G* basis set.

note that this implementation of the GVB calculation has emphasized the spin-pair bond formation in contradistinction to the lone pair Lewis structures shown below, yet the resulting

$$CH_3\ddot{Ga}{-}GaCH_3 \longleftrightarrow CH_3Ga{-}\ddot{Ga}CH_3$$

orbitals are concentrated away from the Ga–Ga internuclear region into the lone pair regions. The GVB energy is 57.1 kJ mol^{-1} below the HF energy at this geometry. The GVB formalism has lowered the energy by spatially separating the spin pair, thereby improving the representation of electron correlation.

Even more striking are the results obtained with the MeGaGaMe$^+$ cation. When an electron is removed from the $15b_u$ HOMO of *trans*-MeGaGaMe, the resulting cation has the shorter GaGa bond length of 2.476 Å (2.460 Å) compared to 2.654 Å (2.560 Å) in the neutral molecule. Although the bond shortening is not so dramatic with the MP2 results (0.100 Å) as with the SCF data (0.178 Å), it is still quite substantial, and thus the $15b_u$ orbital in the neutral molecule must exert some antibonding effect, lengthening the GaGa bond. This conclusion is supported by an AIM study which yields a bond order of 1.069 for the cation, whereas the AIM bond order for the neutral molecule was 0.821. Also, the GaGaC bond angle in the cation is much larger: 148.71° (152.1°) *versus* 123.0° (125.2°) in the neutral molecule. No doubt the repulsion between the methyl group and the single $15b_u$ electron in the cation is smaller than that between the methyl group and the lone pair in the neutral molecule, allowing an increase in GaGaC bond angle. We find a similar effect in methyleneimine and its cation: the CNH bond angle increases from 111.5° (109.7°) in the neutral molecule to 148.66° (150.7°) in the cation. The near-identity of the two SCF cation bond angles must be regarded as a coincidence.

The germanium species MeGeGeMe and related species

As MeGeGeMe is isoelectronic with the [MeGaGaMe]$^{2-}$ dianion, it is not surprising that the results of our studies of this molecule are generally similar to the results presented in the previous section on Li_2[MeGaGaMe]. The main differences are in the relative orbital energies. Because of the absence of the Li^+ ions, the two highest occupied molecular orbitals of the unstable “linear” MeGeGeMe molecule are the doubly degenerate $15b_u$ and $6a_u$ pair, and they represent the two π bonds in this structure. As the GeGeC bond angle changes from 180.0° to 130.9° (129.9°), the $6a_u$ orbital becomes the HOMO, and it is still a π bond. The $15b_u$ orbital becomes the HOMO-1, changing into a lone pair orbital (see Fig. 4), similar to the lone pair orbital in Li_2[MeGaGaMe]. In both forms the $15a_g$ orbital is the HOMO-2, and it represents the σ bond. Fig. 5 shows the orbital energies of both forms.

There is also a twist form of MeGeGeMe. At the SCF level it lies 32.5 kJ mol^{-1} below the *trans* structure, but at the MP2 level it is 22.8 kJ mol^{-1} above the *trans* molecule. Both twist forms lie at minima on the potential energy surface. (This behavior is

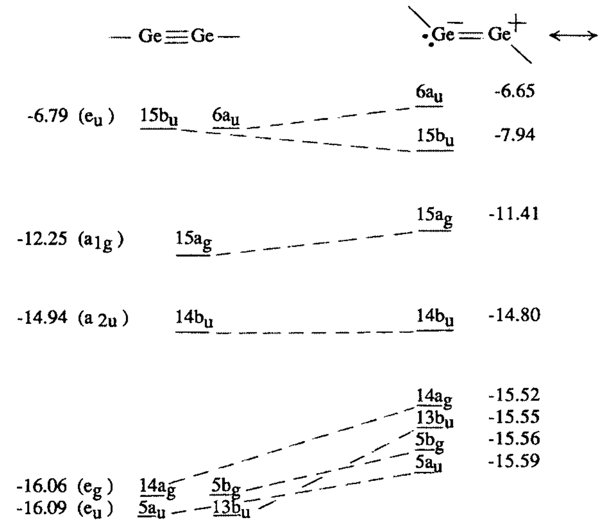


Fig. 5 Molecular orbital energy and correlation diagram for MeGeGeMe. Energies are in eV. The LUMOs are at 2.37 (linear, $16b_u$) and 0.43 (*trans*, $16a_g$).

somewhat similar to that of the silicon analog MeSiSiMe, where the twist form appears to be an artifact of the SCF method.[23]) The MP2 results show a remarkably small GeGeC bond angle (70.3°, compared to 88.3° in the SCF structure). The GeGe bond length of 2.365 Å is shorter than the SCF result of 2.458 Å, and the GeC bond length of 2.083 Å is longer than the SCF value of 2.017 Å.

Our characterization of the bonding in *trans*-MeGeGeMe as a double bond is consistent with other evidence: (a) the GeGe bond length of 2.167 Å (2.197 Å) lies between the triple-bond distance of 2.014 Å (2.073 Å) in the unstable linear structure, and the single-bond distance of 2.417 Å (2.415 Å) in H_3GeGeH_3 (obtained with the same basis set) and it affords a bond order of 1.98 (2.01), using the Pauling formula.[24] (b) With 2 additional hydrogen atoms, the ethylene-like analogue *trans*-MeHGeGeHMe with a coplanar CHGeGeHC fragment has a GeGeC bond angle of 124.7° (124.1°), a GeGeH bond angle of 120.5° (119.9°), and a GeGe bond length of 2.187 Å (2.218 Å). The close similarity in bond lengths between this state and MeGeGeMe suggests that the latter molecule also has a double bond. (Although *trans*-MeHGeGeHMe is a transition state, it is the appropriate state for comparison of double-bond lengths.) Other studies of digermenes with planarity at the double bond yield similar Ge=Ge bond lengths. These include the parent compound, Ge_2H_4 (2.201 Å,[25] 2.205 Å,[26] and 2.261 Å[27]), and $Ge_2(SiH_3)_4$ (2.249 Å[28]). (In the former molecule, the planar form distorts to a *trans*-bent structure.) (c) In a study of the *trans* isomer of HGeGeH, Grev, DeLeeuw, and Schaefer[26] point out that a triple bond "is certainly misleading as far as the geometry is concerned." They suggest a resonance hybrid with a single resonating lone pair (similar to the figure above) as possibly a better representation. (It might be argued that the resonance hybrid shown above should yield a bond that is somewhat stronger than a double bond, but this effect appears to be small in this molecule. Other examples of molecules having low resonance energies are known.) (d) While any analysis of the calculated electron density is arbitrary, one of the most self-defining is that of the topological theory of atoms-in-molecules (AIM).[11–18] We have carried out an AIM calculation for *trans*-MeGeGeMe, and obtained a GeGe covalent bond order of 2.097, which is reasonably close to 2. (e) We note that the b_u orbital may be viewed as arising from a second-order Jahn–Teller effect.[29] Starting from the "linear" structure, a bonding π orbital mixes with an antibonding σ* orbital to form the b_u orbital as the molecule bends to its *trans* structure. The situation here is analogous to pyramidalization in A_2H_4 molecules such as M_2H_4 (M = Si, Ge, Sn, or Pb), where an orbital increasingly n_+ in character, and of b_u symmetry, is formed by mixing of the π and σ* orbitals.[30]

Comparison with other work

The original characterization in $Na_2(GaC_6H_3\text{-}2,6\text{-}Trip_2)_2$ of the gallium–gallium bond as a triple one[1] rested on (1) the shortness of the GaGa bond; (2) the two-coordinate status of the gallium atoms; and (3) an assertion that Grev, Deleeuw, and Schaefer (our reference 26) had found a *trans* geometry for H–Ge≡Ge–H. However, (1) the GaGa bond length of the compound reported in reference 1 is appropriate for a bond order of 2 or less, as shown above; (2) coordination number 2 is equally consistent with a lower bond order; and (3) Grev, Deleeuw, and Schaefer find a GeGe triple bond only for the linear structure.

Other studies of this problem have appeared. In a recent paper, Klinkhammer[31] has studied the dinegative anion $Ga_2H_2^{2-}$. Using a natural bond orbital analysis, he finds what he describes as a "slipped" π bond, but his contour diagram of this orbital clearly shows an accumulation of electron density at the gallium atoms in the regions where lone pair electron density is to be expected. Furthermore, there remains the fundamental question of why a "π bond" between identical atoms should have such extreme asymmetry.

Using a different method, Cotton, Cowley, and Feng,[9] have reached conclusions similar to ours on the compound reported in reference 1. Furthermore, in a study of the hypothetical compound $Na_2[2,6\text{-}Ph_2H_3C_6GaGaC_6H_3\text{-}2,6\text{-}Ph_2]$ they show that the alkali metal cations also play a role in determining the GaGa bond length owing to their coordination to *ortho* aryl substituents. This may account for the fact that the GaGa bond length we find for $Li_2MeGaGaMe$ is longer than that in reference 1.

A recent article by Xie *et al.*[32] reports studies of several digallium model compounds. For example, in the *trans*-bent dianion $[HGaGaH]^{2-}$ the authors find three occupied localized molecular orbitals (LMOs) connecting the Ga atoms. One of these is the familiar π bond, concentrated about a plane perpendicular to the HGaGaH plane (analogous to the $6a_u$ orbital of our Fig. 2). It is a canonical MO as well as an LMO. The other two LMOs are equivalent. Each has a large lobe of electron density concentrated about one of the gallium atoms. They are described as dative bonding orbitals.

This description of the electronic structure is notable in that there is no GaGa σ bond. Nor is there any description of the molecular orbitals using the conventional C_{2h} symmetry designations. It appears that the canonical σ and n_+ MOs (analogous to the $15a_g$ and $15b_u$ orbitals of our Fig. 2) have been mixed to form the two LMOs (which do not have C_{2h} symmetry).

This situation is reminiscent of the long-standing controversy regarding the two equivalent descriptions of the electronic structure of ethylene: the σ-π description and the "bent-bond" or "banana-bond" description. Many years ago it was shown that, at the SCF level, the two descriptions are precisely equivalent. The bent bond orbitals are hybrids of the σ and π orbitals, and *vice versa*.

One virtue of these descriptions of ethylene is that in each case one has two bonding orbitals, so the molecule has a double bond regardless of which description is used. But if one replaces the canonical σ and n_+ orbitals of a digallium molecule with two equivalent hybrid LMOs, each weakly bonding, then in a formal sense the bond order has been artificially increased by one. Thus do single bonds become double, and double bonds become triple. As a consequence, the definition of bond order becomes ambiguous, and the connection between bond order and molecular properties (*e.g.*, bond length) is lost. In addition, in a homonuclear setting the LMOs should be symmetrically disposed, as in ethylene. But one LMO is strongly skewed toward one gallium atom, the other toward the other gallium atom. The reason for this skewing is their origin in the canonical lone pair MO.

Bytheway and Lin[33] have recently studied the $[\mathrm{Ga_2(CH_3)_2}]^{2-}$ dianion. Their GaGa bond length of 2.487 Å for the *trans*-bent optimized geometry is somewhat longer than our result of 2.388 Å for the neutral *trans*-$\mathrm{Li_2MeGaGaMe}$, but in general their results are similar to ours. Although they emphasize the decreased π-π overlap compared to the linear molecule, they characterize the controversial orbital as "a significantly weakened π bond which is *localized strongly on the Ga atoms*" (our emphasis). In our view this orbital is indistinguishable from a lone pair orbital.

Conclusions

A variety of models for the bonding in $\mathrm{Li_2[MeGaGaMe]}$ and MeGeGeMe and related species have been studied in this paper. The results of these studies are in agreement and point to a Ge–Ge bond order near two and a Ga–Ga bond order that lies between one and two. The calculated Ga–Ga distance (*ca.* 2.39 Å) and bent geometry (Ga–Ga–C = *ca.* 130°) at Ga, which resemble the experimentally observed structural parameters for $\mathrm{Na_2\{GaC_6H_3\text{-}2,6\text{-}Trip_2\}_2}$, are consistent with this bonding picture. Moreover, this view of the bonding is in agreement with structural and spectroscopic data for related Ga–Ga multiply bonded species such as $[\mathrm{Trip_2GaGaTrip_2}]^{-\cdot}$[5a] and $[\mathrm{Ga(GaTrip_2)_2}]^{2-}$[6] which have formal bond orders of 1.5 (Ga–Ga = 2.343(2) Å) and 1.33 (Ga–Ga = 2.389(17) Å) respectively. The MO approach to the bonding in $[\mathrm{RGaGaR}]^{2-}$ ions leads to the expectation of considerable Lewis base character at the Ga centers where electron density is accumulated. In addition, it is expected that in the (as yet unisolated) neutral compounds of formula RGaGaR, the Ga–Ga bond will be quite weak and that when the R substituent is very bulky (*e.g.*, $\mathrm{C_6H_3\text{-}2,6\text{-}Trip_2}$) the compound is likely to be either dissociated to monomers in solution (as are the bulky derivatives $[\mathrm{GaC(SiMe_3)_3}]_4$[34a] or $[\mathrm{GaC(SiMe_2Et)_3}]_4$[34b]) or may, perhaps, exist as monomers in the solid like its heavier congeners $\mathrm{MC_6H_3\text{-}2,6\text{-}Trip_2}$ [M = In[35a] or Tl[35b]].

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