The Use of Density Functional Theory To Understand and Predict Structures and Bonding in Main Group Compounds with Multiple Bonds

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Received August 27, 1997. Revised Manuscript Received November 12, 1997

Abstract: Density functional theory (DFT) calculations have been carried out on a number of compounds in which multiple bonds are formed by or between main group elements. The calculated and observed structures agree very well for P_2, P_4, P≡C−R, R−P═P−R, As≡C−R, R−As═As−R′, R−Bi═Bi−R, and R_2−Ge═Ge−R_2. For a recently reported compound alleged to contain a Ga≡Ga (triple) bond the calculations point to a different formulation in which there is only a double bond and a significant role for noncovalent interactions.

Introduction

As one of the frontier areas of chemical research, there has been a strong and still growing interest in syntheses of stable molecules containing multiple bonds between atoms of the heavier main group elements (E),[1] particularly, Ga, Ge, As, Sb, and Bi. In this article we deal with the interface between the synthetic challenge and another frontier of chemical research, namely, the application of the relatively new quantum chemical methodology called density functional theory (DFT).[2] The use of DFT in inorganic and organometallic chemistry has grown exponentially in the past few years with great success.[3,4] There are, however, only two reported DFT calculations on the multiply bonded main group compounds. In one case, the double bonds between Group 14 elements were studied in detail but for compounds in which the only ligands present were hydrogen atoms,[5] as in almost all previously reported calculations by traditional *ab initio* quantum chemical methods.[5] The other DFT calculation again dealt primarily with defining the bonding in a doubly bonded phosphorus compound without explicit report of structure optimization.[6] Other than these, we know of no other cases in which the DFT method has yet been applied to the types of molecules that we deal with here.

We report in this paper the results of DFT calculations on a number of molecules of Group 15 elements that contain multiple E−E bonds and on a few compounds involving bonding between germanium atoms and between gallium atoms. It is well-known that multiple E−E bonds are too reactive to be isolated unless protected from attack by bulky ligands that shelter them. Representative bulky ligands (specifically those occurring in compounds dealt with in this article) are shown in Figure 1. It is generally believed that these bulky ligands play a passive role, serving only to shelter the reactive E−E bonds, but not otherwise altering the essential structural and electronic features of the molecule. Thus, for computational purposes (as we have done in most of this study) it is assumed that it is acceptable to replace the ligand R1 in Figure 1 by CH_3, and the ligands R2, R3, and R4 by C_6H_5. Our work supports this view but sounds a note of caution in at least one case. The molecular structures of all compounds considered were obtained by complete geometry optimization. We will show that the optimized structures with the model ligands compare satisfactorily with those of corresponding compounds with the bulky ligand, except in one case where satisfactory results could be obtained only when more complicated model ligands were used to account for intramolecular, noncovalent interactions. The electronic structures and key bonding features of some of the molecules will also be examined by analyzing the DFT orbitals

Computational Details

All DFT calculations utilized Becke's hybrid method,[7a] which includes Perdew and Wang's 1991 gradient-corrected correlation functional[7b] for nonlocal correlation, namely, B3PW91. The calculations employed 6-311G(df), 6-311G(d), 6-311G, and 6-31G basis sets residing in the Gaussian program.[8a] All calculations were performed by using the Gaussian program and all molecular structure drawings were generated with atomic coordinates of the optimized structures and by using the SHELXL-93 program.[8b]

The calculations on $Na_2[Ga_2R_2]$ and $Na_2[Ga_2H_2R_2]$ were also carried out by using the Becke−Lee−Yang−Parr gradient-corrected density

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S0002-7863(97)03015-1 CCC: $15.00

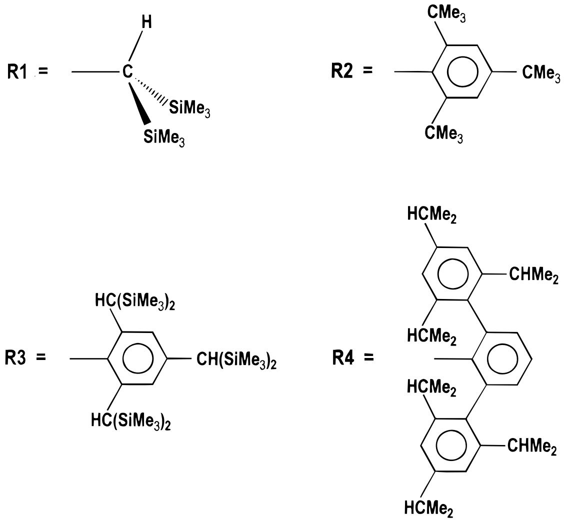

Figure 1. Some important bulky ligands found in compounds with E=E bonds.

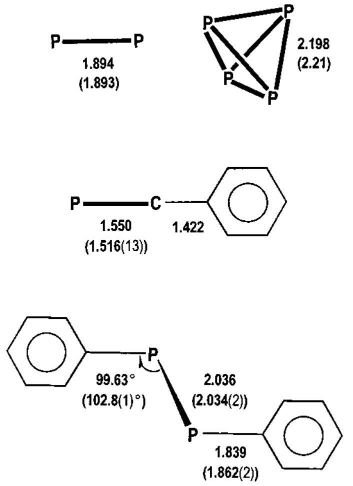

Figure 2. Calculated molecular structures (distances in Å in all figures) as compared with experimental data (in parentheses) for compounds containing phosphorus atoms. (Basis set information: 6-311G(df) for P, 6-311G(d) for C, and 6-311G for C_6H_5.)

functional,[9] BLYP, and the hybrid B3LYP functional. In addition to the 6-311G type of basis sets (including 6-311G(d), 6-311+G, 6-311G+(d), and 6-311G(df)), calculations on these two gallium compounds were also carried out by employing full double-ζ basis sets for both Ga[10a] and other atoms.[10b]

For compounds containing antimony and bismuth atoms, the calculations utilized relativistic effective core potential (ECP)[11] and associated basis functions (contracted to triple-ζ) for Sb and Bi, and for other atoms 6-311G basis sets were used.

All computations were carried out on SGI Power Challenge Computers.

Results and Discussion

Shown in Figure 2 are optimized bond distances and angles for four phosphorus compounds. The DFT calculations almost exactly reproduce the lengths of the P−P triple bond in the P_2 molecule[12] and the single bond in the tetrahedral P_4 molecule.[13] The P−C triple bond distance in $P{\equiv}C{-}C_6H_5$, which was calculated in C_{2v} symmetry, is also in very good agreement with that of the same bond in $P{\equiv}C{-}C_6H_2(CMe_3)_3$ characterized by X-ray crystallography.[14] Similarly, the pertinent bond parameters in $C_6H_5{-}P{=}P{-}C_6H_5$, the P−P double bond length (2.036 Å) and the P−P−C angle (99.63°), for example, compare satisfactorily to the crystal structure data for the similar compound but with much bulkier ligands, namely, $(CMe_3)_3C_6H_2{-}P{=}P{-}C_6H_2(CMe_3)_3$.[15]

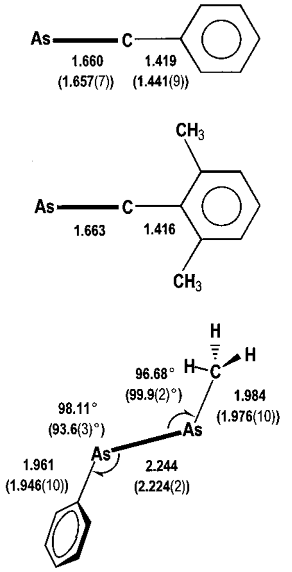

Figure 3. The same as in Figure 2 but for arsenic-containing molecules.

The situation in the molecules involving arsenic multiple bonds is very similar. The crystallographically characterized $As{\equiv}C{-}C_6H_2(CMe_3)_3$ compound[16] was considered in terms of two model molecules, in which the bulky $C_6H_2(CMe_3)_3$ ligand (ligand R2 in Figure 1) was replaced by C_6H_5 and $C_6H_3(CH_3)_2$, respectively. The results of geometry optimization of these two models (both in C_{2v} symmetry) are shown in Figure 3 and compared to the values from the crystal structure data of the real compound. There are insignificantly small differences in the calculated bond parameters between the two model molecules and, in both cases, the experimental As≡C bond length has been excellently reproduced. The DFT prediction of an As=As double bond in terms of simplified model ligands is also very accurate. This is shown in Figure 3 by the calculated structure for the $C_6H_5{-}As{=}As{-}CH_3$ compound (C_s symmetry) where the predicted As=As distance, 2.244 Å, compares satisfactorily to the value, 2.224(2) Å, in the real molecule of similar structure, namely, $(CMe_3)_3C_6H_2{-}As{=}As{-}CH(SiMe_3)_2$.[17]

Very recently, the crystal structure of a dinuclear bismuth compound, R−Bi=Bi−R, that contains the first stable Bi−Bi double bond was reported.[18] The ligand in this compound is the very bulky R3 ligand shown in Figure 1. DFT calculations employing relativistic core potentials were carried out for a model compound, namely, $C_6H_5{-}Bi{=}Bi{-}C_6H_5$ in C_{2h} sym-

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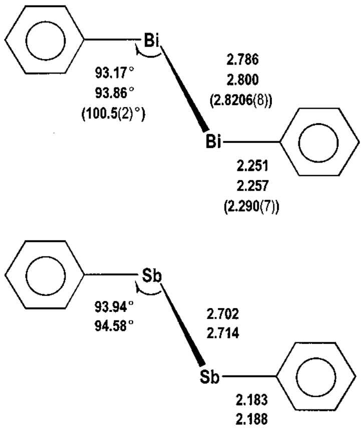

Figure 4. Comparison between calculated (first value by B3PW91 and second value by B3LYP) and experimental structural data (in parentheses) for the bismuth compound, and predicted structure parameters for the antimony analogue.

metry. Once again, as can be seen in Figure 4, the Bi−Bi double bond distance as well as other relevant bond parameters obtained from the model calculations represent quantitatively the main structural features of the real molecule. Shown also in Figure 4 are the predicted structural parameters for a dinuclear antimony analogue. A stable compound with a Sb═Sb double bond is yet to be characterized. It is reasonable to believe, after examining all the results presented above, that the distance of a Sb═Sb bond in such a molecule should be within a few hundredths of an angstrom of that shown in Figure 4 and the Sb−Sb−R bond angle should be around 95°.

The bonding interaction between a pair of E atoms (E = P, As, Sb, Bi) in the R−E═E−R compounds can be described by two bonding orbitals of σ and π types which are the two highest occupied DFT orbitals. The lowest unoccupied orbital in each is an E−E π^* antibonding orbital as would be expected. The energies of the σ and π bonding orbitals are very close. For E = P, As, and Sb, the π orbital is actually lower in energy than the σ orbital since the latter has also antibonding character from the E−C nonbonding interaction. It is very important to note that the valence s orbitals of the E atoms in all these compounds are very much localized as lone pairs without significant hybridization with the valence p orbitals, and that the molecular bonding interactions essentially involve only the orthogonal p orbitals. The calculated electronic structures, therefore, are in full accord with the structural fact that the E−E-C bond angles, either observed or calculated, are all roughly 90°.

In addition to the Group 15 molecules, we also calculated a doubly bonded germanium compound, $(CH_3)_2{-}Ge{=}Ge{-}(CH_3)_2$. This is a model molecule for the experimentally isolated compound with much bulkier ligands (R1 in Figure 1), namely, $[CH(SiMe_3)_2]_2{-}Ge{=}Ge{-}[CH(SiMe_3)_2]_2$.[19] The structure of the model molecule was optimized in C_i symmetry. The main features of the results are shown in Figure 5. We see again the true Ge═Ge bond length is well reproduced by using model ligands. Not surprisingly, the calculated structure is more symmetric than the crystal structure of the real bulky compound. The gallium analogue of the Ge═Ge compound has only a single Ga−Ga bond. The Ga−Ga bond distance, 2.541(11) Å, in $[CH(SiMe_3)_2]_2{-}Ga{-}Ga{-}[CH(SiMe_3)_2]_2$[20] is much longer than the corresponding Ge═Ge bond (2.347(2) Å). Such a difference was also predicted by DFT geometry optimizations as can be seen in Figure 5 by comparing the results for the Ga compound (C_{2h} symmetry) to those for the Ge compound. Also shown in Figure 5 are the theoretical (R = CH_3) and experimental (R = CMe_3) structural parameters for another singly bonded Ga compound with a very different ligand, namely, $(C_2H_2N_2R_2){-}Ga{-}Ga{-}(C_2H_2N_2R_2)$.[21] Again, the DFT structure (in D_{2d} symmetry) is in very good accord with the crystal structure. The very short Ga−Ga single bond (2.333(1) Å) in this compound is apparently associated with the largely reduced steric effects resulting from the perpendicular arrangement of the two five-member rings.

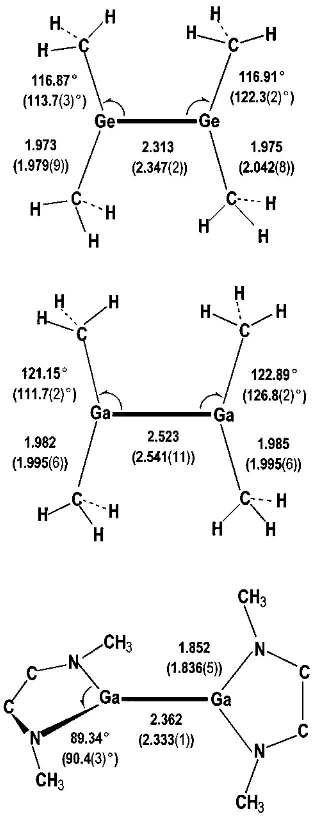

Figure 5. Calculated and experimental structures for dinuclear germanium and gallium compounds. (Basis sets: 6-311G for Ge, Ga, and C and 6-31G for H in $Ge_2(CH_3)_4$ and $Ga_2(CH_3)_4$; 6-311G(df) for Ga and 6-311G for N, C, and H in the Ga ring compound.)

We have seen by now that calculations by DFT methods provide accurate descriptions for both molecular and electronic structures of the dinuclear main group compounds of different bond orders and of various structural types. We can then proceed to use the same method to study the structural and electronic properties of a recently reported dinuclear compound of gallium, which has been claimed to contain the first Ga≡Ga triple bond.[22] As revealed by X-ray structural data, the compound $Na_2[Ga_2R_2]$, where R is the extremely bulky ligand R4 in Figure 1, has a rather short Ga−Ga bond (2.319(3) Å), but it is far from linear with the average Ga−Ga−C angle being 131° which would imply sp^2 hybridized Ga centers. As before, DFT calculations were carried out for a model molecule by replacing the bulky ligands with C_6H_5. The calculations predict a nonlinear structure for $Na_2[Ga_2(C_6H_5)_2]$ in which the Ga−Ga−C angle is very close to the observed angles, as shown in Figure 6. The calculated Ga−Ga distance, however, is not

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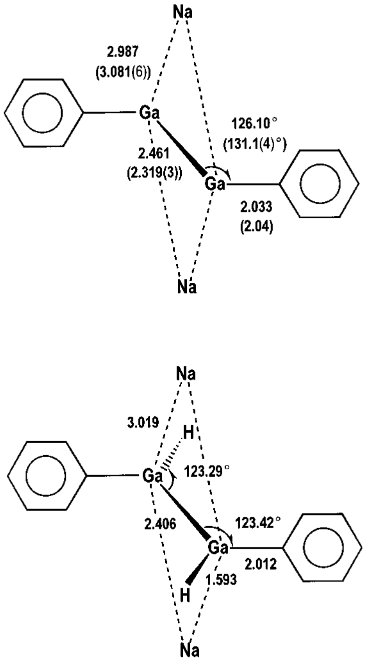

Figure 6. Calculated structures for $Na_2[Ga_2(C_6H_5)_2]$ and $Na_2[Ga_2H_2(C_6H_5)_2]$ with comparison to crystal structure data (B3PW91 calculations with 6-311G(df) set for Ga and 6-311G for all other atoms).

satisfactory and is always much longer than the experimental result. Various forms of DFT and different basis sets were used. The results, in general, are not particularly sensitive to the choice of basis sets, but better (or shorter) Ga−Ga distances are given by the hybrid DFT methods. The results shown in Figure 6 were obtained from the calculations employing the B3PW91 form and the 6-311G(df) and 6-311G basis sets for Ga and other atoms, respectively.

Because of the nonlinear structure, we also considered the possibility that there might be a hydrogen atom bonded to each of the Ga centers. The existing experimental evidence[22] for excluding such a possibility is neither very firm nor conclusive.[23] The $Na_2[Ga_2H_2(C_6H_5)_2]$ molecule was calculated in a way similar to that used for the compound without H atoms, and the results from the calculations with use of the same basis sets and the same form of DFT are shown in Figure 6. Indeed, the Ga−Ga distance is shortened considerably when two hydrogen atoms are added but is still not short enough to agree satisfactorily with the observed value.

There is no reason to believe that the DFT method would fail to provide a reliable structure only for this compound. The problem, as we know now, is actually associated with the model ligand used in the calculations. In general, one would expect that the sole consequence of close contacts between two bulky ligands would be repulsive steric effects. In this particular case, however, such contacts may have led to *attractive* interactions that could help to bring the two Ga atoms to a shorter distance. By examining the reported crystal structure with care, one can find the following very special structural features in this compound. Each of the two Na ions which sit above and below the Ga−Ga bond is "sandwiched" by two substituted phenyl rings which are the branching R groups in the bulky ligand, $C_6H_3R_2$, R = $C_6H_2(CHMe_2)_3$. The distances from an Na ion to the sandwich carbon atoms are only about 3 Å or even less. Therefore, it might well be that, relative to a system without the sandwiched structure, the compound could be further stabilized by noncovalent, attractive interactions between the Na atoms and sandwich rings. One effect of such interactions would be a reduced separation of the two $Ga-C_6H_3R_2$ fragments, which could then lead to shortening of the Ga−Ga distance. In order for this to happen, the total energy of the model compound must not change to any significant degree when the Ga−Ga separation varies over a pertinent range. In other words, the potential energy curve as a function of the Ga−Ga distance must be relatively flat in that range.

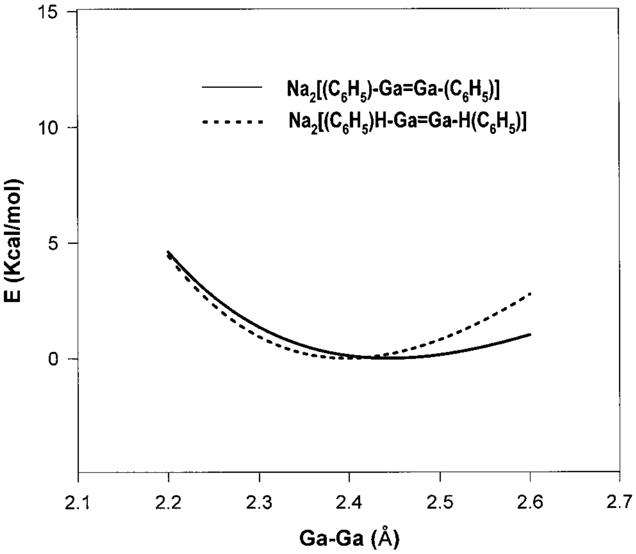

Figure 7. Potential energy curves for the two gallium model compounds as a functions of Ga−Ga distance.

This is exactly the case in both $Na_2[Ga_2(C_6H_5)_2]$ and $Na_2[Ga_2H_2(C_6H_5)_2]$ as shown in Figure 7. The potential curves in the figure were plotted by using energies obtained from geometry optimization at several fixed Ga−Ga distances with B3PW91 and 6-311G basis sets. Notably, the total energies increase by only 1.4 and 1.0 kcal/mol at Ga−Ga = 2.30 Å relative to those at the calculated equilibrium Ga−Ga distances for $Na_2[Ga_2(C_6H_5)_2]$ and $Na_2[Ga_2H_2(C_6H_5)_2]$, respectively. The importance of inclusion of the noncovalent interaction in the DFT structural calculations for this very compound has been ultimately confirmed by the results of geometry optimization on two much larger model compounds (both in C_{2h} symmetry), $Na_2[Ga_2(C_6H_3(C_6H_5)_2)_2]$ and $Na_2[Ga_2H_2(C_6H_3(C_6H_5)_2)_2]$ in which four C_6H_5 groups have been added to the original models. The results are shown in Figure 8. The calculated structures now are both very comparable with the crystal structure data. The distances from a Na atom to the carbon atoms on the C_6H_5 sandwiching rings are close to 3 Å. In particular, the Ga−Ga distance in $Na_2[Ga_2R_2]$ has been reduced from 2.46 Å when R = C_6H_5 to 2.36 Å when R = $C_6H_3(C_6H_5)_2$, which is very close to the value of 2.32 Å in the crystal structure. It is also to be noted that the calculated Ga−Ga distance, 2.34 Å, and other structural parameters for $Na_2[Ga_2H_2R_2]$ are now better than or very similar to the value shown above for the compound without

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(23) The possibility of two H atoms being present was said to "appear unlikely" in ref 22 only on the basis of a notoriously unacceptable spectroscopic argument, namely, that the nonobservation of an allegedly expected feature in a spectrum is proof of anything. In this specific case, the absence of "resonances in the expected range for gallium hydrides" was cited. The "expected range" was not actually stated. Previous observations (at δ 5.49 and 5.12) were cited, but these were for Ga−H bonds in two rather different compounds. Because both of the naturally occurring Ga isotopes have $I = {}^3/_2$ and rather large quadruple moments, ^1H signals for Ga−H protons are broad. If the signal were to occur in the δ 6−7 range (certainly a real possibility) where there are signals from 14 aromatic protons, it might go undetected. However, be it clearly understood, we are *not* asserting that hydrogen atoms are present, but merely noting that there is no experimental basis for asserting that they are not.

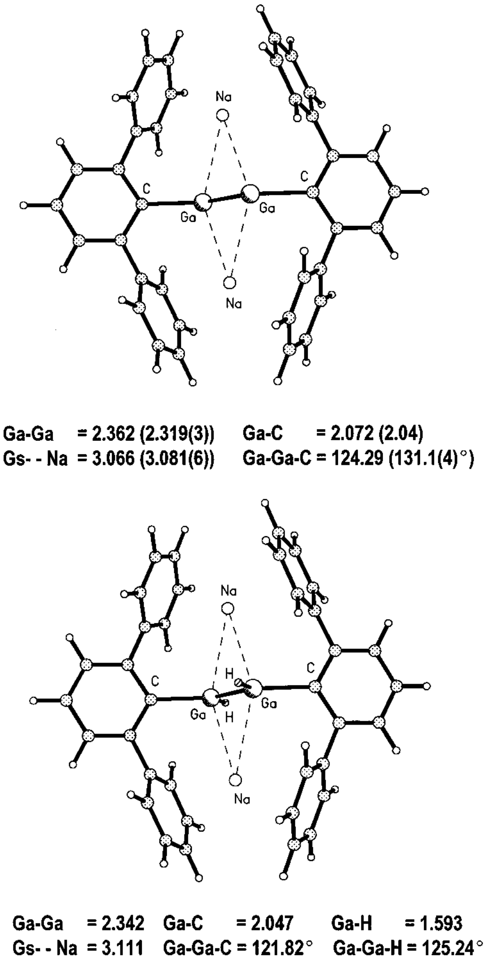

Figure 8. Calculated structures for $Na_2[Ga_2(C_6H_3(C_6H_5)_2)_2]$ and $Na_2[Ga_2H_2(C_6H_3(C_6H_5)_2)_2]$ (B3PW91 geometry optimization with 6-311G for Ga and 6-31G for all other atoms).

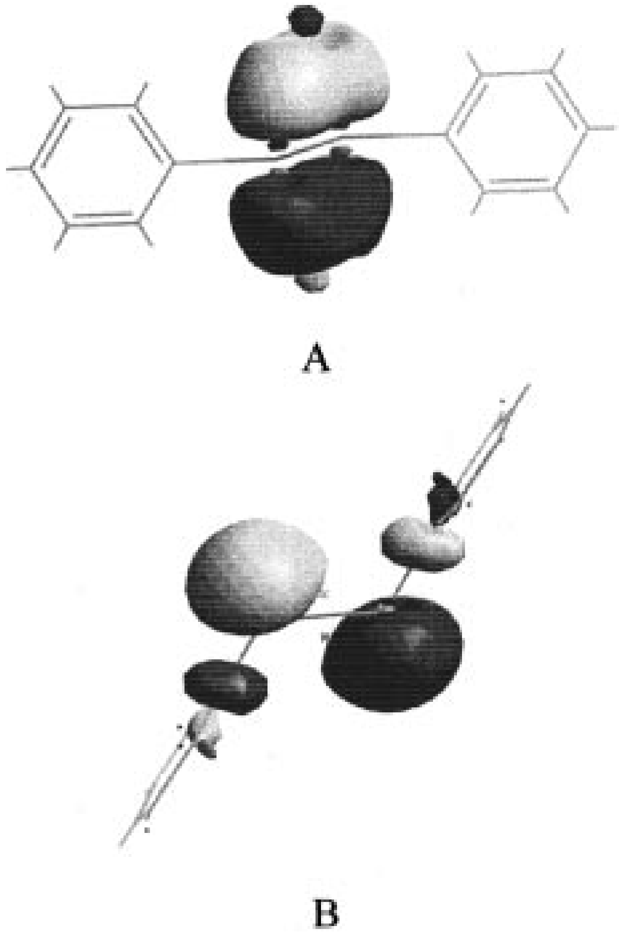

Figure 9. DFT orbital plots for the π bonding orbital (A) and the nonbonding orbital of π-type (B) in $Na_2[(C_6H_5){-}Ga{=}Ga{-}(C_6H_5)]$ corresponding to the calculated structure in Figure 6. Dark and bright portions of the plots represent positive and negative regions of the orbitals, respectively.

hydrogen atoms. While we do not claim that the optimized structures conclusively show the presence of the hydrogen atoms, our calculations do strongly raise the possibility of a $Na_2[Ga_2H_2R_2]$ compound. The total energy of the $Na_2[Ga_2H_2R_2]$ compound (Figure 6) is over 120 kcal/mol lower than the sum of the total energy of the $Na_2[Ga_2R_2]$ compound (Figure 6) plus the energies of two hydrogen atoms. It may be pointed out that these structural studies by the DFT calculations also allow us to make an interesting prediction. If a dinuclear gallium compound of similar structure could be isolated with the ligand R2 or R3 in Figure 1, the Ga−Ga distance might well be in the range from 2.40 to 2.45 Å because these systems could not have the sandwiched structure.

Finally we turn to another important aspect of the DFT studies on the dinuclear gallium compound, namely, formulation of the Ga−Ga bonding. If a Ga atom in the compound is coordinated by two ligands, an R group and a hydrogen atom, the situation is rather simple. (a) There can be only a double bond (one σ and one π bond) between the two Ga atoms, that is, $Na_2[RH{-}Ga{=}Ga{-}HR]$, and (b) the C−Ga−Ga−C chain must be bent. In the case where there are no hydrogen atoms present, our calculations again show that the chain should be bent. They also show that, in addition to the Ga−Ga σ bonding orbital, the two highest occupied orbitals in all DFT calculations have predominant contributions from the Ga atoms and have the character of π-type interactions. While one of them is truly a π bonding orbital (A, Figure 9), the other is clearly a nonbonding orbital (B, Figure 9). The energies of the two orbitals are similar, and in the simple model compound the nonbonding orbital is the HOMO while in the larger model compound the π bonding orbital is the HOMO. The conclusion is, therefore, unambiguous. With or without hydrogen atoms, *there can only be a Ga═Ga double bond, namely,* $Na_2[R{-}Ga{=}Ga{-}R]$, rather than $Na_2[R{-}Ga{\equiv}Ga{-}R]$ for the case of no hydrogen atoms.

Note Added in Proof: An article that appeared after this paper was submitted (Klinkhammer, K. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2320) has suggested that the in-plane nonbonding electrons are π-bonding electrons based on a calculation done by an undisclosed method on an oversimplified model (HGaGaH).

Acknowledgment. We thank the Robert A. Welch Foundation for support and the Supercomputing Center and the Department of Chemistry at Texas A&M University for granting computer time. We are grateful to Dr. S. Niu for helping with the generation of orbital plots.

JA973015E