The gallium–gallium triple bond in a realistic model. A density functional theory study of $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$

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Abstract

Density functional theory is employed to study the model molecule $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$ as a means to address the question of Ga–Ga triple bond formation in the recently reported gallyne, $Na_2[\{(i\text{-}Pr_3C_6H_2)_2 C_6H_3\}Ga\equiv Ga\{C_6H_3(i\text{-}Pr_3C_6H_2)_2\}]$. The structure is fully optimized with the B3LYP method utilizing a substantial basis set of 836 contracted Gaussian functions. Natural bond order analysis and a NLMO/NPA bond order of 2.79 for $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$ are in support of a weak Ga–Ga triple bond in the model compound and in the gallyne. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The synthesis and molecular structure of the novel compound $Na_2[\{(i\text{-}Pr_3C_6H_2)_2C_6H_3\}Ga\equiv Ga\{C_6H_3 (i\text{-}Pr_3C_6H_2)_2\}]$ was reported in 1997 [1]. The authors claimed that the Ga–Ga bond therein represented an unprecedented Ga–Ga triple bond, a *gallyne*. This provocative compound and the assertion of triple bond stabilization soon fueled a rather heated debate [2,3]. Cotton et al. [4] vigorously offered an opposing view in 1998 utilizing density functional theory (DFT), concluding that the bonding in $Na_2[\{(i\text{-}Pr_3C_6H_2)_2 C_6H_3\}Ga\equiv Ga\{C_6H_3(i\text{-}Pr_3C_6H_2)_2\}]$ is merely a Ga–Ga double bond which may be described by two canonical molecular orbitals. In notable contrast, mounting theoretical data support the original position that this compound contains a Ga–Ga triple bond – albeit a weak triple bond [5,6]. A previous study from this laboratory examined the dianions of HGaGaH and RGaGaR (R = Me) as simple models in an attempt to show that the bonding between the two Ga atoms in such model systems is reasonably as described a triple bond consisting of two dative bonds and a π bond [7]. While this study presented compelling data in support of the gallyne, it was criticized by Cotton for relying on too simplistic model molecules [3].

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Although the nature of the Ga–Ga bonding should remain the same if the bulky *m*-terphenyl substituents are replaced, the present theoretical study of a large molecule very similar to $Na_2[\{(i\text{-}Pr_3C_6H_2)_2 C_6H_3\}Ga\equiv Ga\{C_6H_3(i\text{-}Pr_3C_6H_2)_2\}]$ will provide more directly comparable geometrical parameters, and should further elucidate the nature of the Ga–Ga bond. This study examines the model molecule $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$ at a reliable level of theory. It is noteworthy that the model molecule is very similar to the experimental molecule, only differing in the fact that it lacks the *iso*-propyl substituents (below). It is important to note that this same model molecule, $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$, was utilized in Cotton et al.'s work. In the work described herein, the same $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$ model molecule has been fully optimized with the B3LYP method utilizing a substantial basis set of 836 contracted Gaussian functions. Herein we present additional data in support of the Ga–Ga triple bond.

Na2[(C6H5)2C6H3GaGaC6H3(C6H5)2]   Na2[{(*i*-Pr3C6H2)2C6H3}Ga≡Ga{C6H3(*i*-Pr3C6H2)2}]
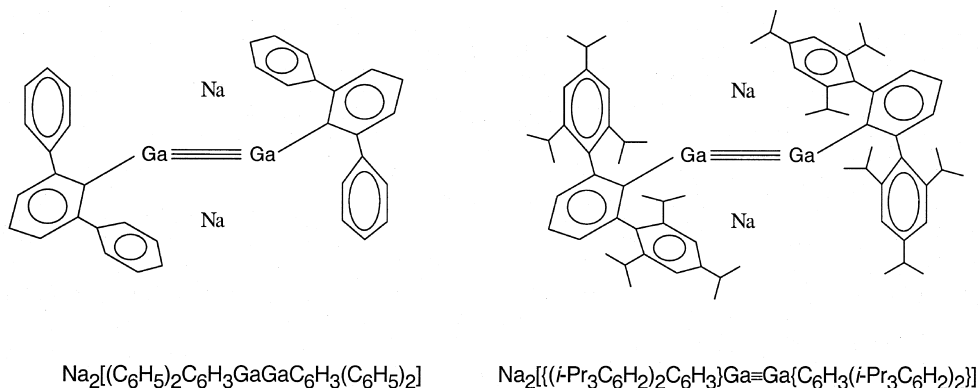
2. Method

The geometry of the model $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$ molecule with 66 atoms was fully optimized with DFT, specifically using Becke's hybrid three-parameter exchange functional [8] in conjunction with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) [9].

The basis sets employed here are of double-ζ quality augmented with polarization functions, and for the Ga atoms, with an additional set of s and p diffuse functions. For the Ga atoms, the basis functions are from Dunning's (14s11p5d) primitive functions [10] contracted to (8s6p2d) plus two sets of d and one set of f polarization functions with $\alpha_d(Ga) = 0.216, 0.068$, $\alpha_f(Ga) = 0.330$ plus a set of s and p diffuse functions with $\alpha_s(Ga) = 0.01838$ and $\alpha_p(Ga) = 0.01472$. For Na, the basis functions are from McLean and Chandler's (12s9p/6s5p) [11] plus a set of d polarization functions with $\alpha_d(Na) = 0.200$. For C and H, the basis functions are from Dunning's (9s5p/4s2p) and H (4s/2s) [12] plus a set of polarization functions with $\alpha_d(C) = 0.75$ and $\alpha_d(H) = 0.75$. The technical description of the final basis set is Ga(15s12p7d1f/9s7p4d1f), C(9s5p1d/4s2p1d), H(4s1p/2s1p), and Na(12s9p1d/6s5p1d). There are 836 basis functions in all.

The computation was carried out with the GAUSSIAN 94 [13] program, in which the natural bonding orbital (NBO) analysis is based on the work of Weinhold [14]. The Wiberg bond index (WBI) [15], which is used to screen atom pairs for the possible bonding in the NBO search, and the natural localized molecular orbital (NLMO) natural population analysis (NPA), are performed with the NBO program. We have modified the NBO subroutine (link 607 in GAUSSIAN 94) by increasing the limit on the number of basis functions to make the present job (with 836 basis functions) fit.

3. Geometry

The optimized geometry of the $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$ molecule (Fig. 1) has C_{2h} symmetry. Moreover, the structure is quite similar to the crystal structure of the experimental compound $Na_2[\{(i\text{-}Pr_3C_6H_2)_2C_6H_3\}Ga\equiv Ga\{C_6H_3(i\text{-}Pr_3C_6H_2)_2\}]$ molecule, showing a *trans*-bent C–Ga–Ga–C configuration with bond lengths and bond angles comparable to the experimental results. The Ga–Ga bond length is predicted to be 2.404 Å, which is similar to, but somewhat shorter than, that in the simplest model molecule $Na_2[HGaGaH]$ (2.441 Å), and substantially shorter than that in $Na_2[MeGaGaMe]$ (2.508 Å). This trend is the same as that reported for the Si–Si bond lengths in the disilyne series HSiSiH (2.111 Å), MeSiSiMe (2.123 Å), and RSiSiR (2.095 Å) (R is a larger substituent) [16].

Similar to Ref. [4], we notice that the optimized structure shows the twisting of the four substituent phenyl rings to face the sodium atoms. The distances from the Na atoms to the center of the phenyl rings are only 2.8 Å. This indicates an attractive interactions between the Na atoms and the phenyl rings, and then makes the Ga–Ga distance shorter than those in the simpler model molecules without the bulky substituents. However, our

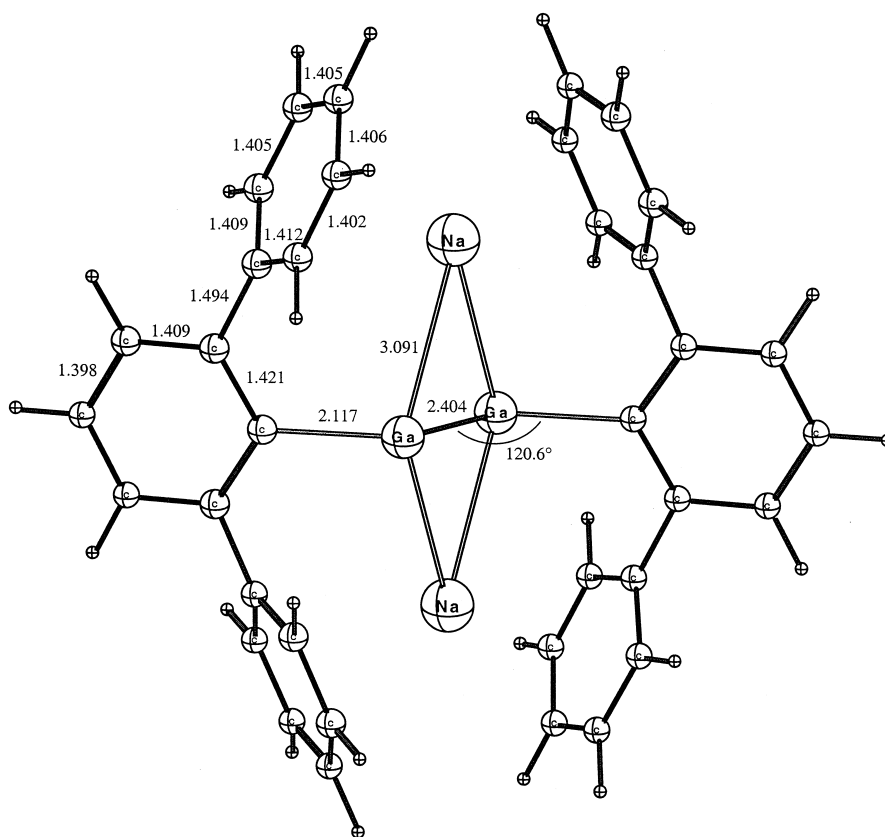$$Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2] \quad (C_{2h})$$

Fig. 1. The geometry of the title molecule optimized at the B3LYP level of theory with a basis set of 836 contracted Gaussian functions.

optimized Ga–Ga distance is not as short as obtained in Ref. [4]. This is presumably due to the relatively small basis sets used in Ref. [4] (6-31G and 6-311G, without polarization and diffuse functions).

In comparison with the experimental Ga–Ga distance 2.319 Å in the crystal structure, our predicted Ga–Ga bond distance for the isolated molecule is longer by 0.085 Å. This suggests that the gallium–gallium bond in the synthesized compound may be somewhat stronger than for the present model compound. The Ga–C bond lengths are predicted to be 2.117 Å, which is somewhat longer than the experimental value (2.044 Å). The theoretical Ga–Na bond distance 3.091 Å) is quite close to the experimental value (3.081 Å). The Ga–Ga–C bond angle is 120.6°, which is smaller than the experimental value 131.0°. The C–C bond distances in the phenyl rings fall in the range of 1.398 Å–1.421 Å, similar to that for the benzene molecule.

We have also performed the geometry optimization using GAUSSIAN 94 with the same DFT method but with a larger integration grid, having 96 radial shells and 434 angular points per shell. (The default of the GAUSSIAN 94 program is 75×302.) The modifications in the optimized geometry are negligible, having the bond lengths change less than 0.001 Å and the bond angles change by less than 0.1°. Final Cartesian coordinates are available from the authors.

4. The nature of the Ga–Ga bond

The nature of a chemical bond is determined primarily by the electronic structure, not by the molecular geometry. Relative to the gallyne, the Ga–Ga triple bond was described as three bonding localized molecular orbitals (LMOs) in our earlier paper. However, Cotton et al. concluded: ''... with or without hydrogen atoms [bonding to the Ga atoms], there can only be a Ga=Ga double bond.'' Their conclusion primarily rests upon the appearance of the highest occupied canonical molecular orbitals (CMOs). In Fig. 9 of their paper, two π-type CMOs were shown. They reported that ''while one of them is truly a π bonding orbital (A, Fig. 9), the other is clearly a nonbonding orbital (B, Fig. 9).'' In our opinion, this statement is worth further investigation.

The CMOs and LMOs are equivalent, being related to each other via a unitary transformation. Either set, taken as a whole, defines precisely the same wavefunction. Therefore, in principle, CMOs should lead to the same conclusions as the LMOs do. However, CMOs are known to be in general spatially delocalized over all the atoms in a given molecule [17]. Classical chemical bonds are thus more difficult to perceive. The LMOs, which are superposition of CMOs, are superior for such analyses. If the LMOs suggests the presence of a triple bond, it may be dangerous to use CMOs to draw the opposite conclusion.

Table 1
The coefficients from the primary natural atomic orbitals (NAOs) for the three Ga–Ga natural bond orbitals (NBOs)[a]

	Ga (4s)	Ga ($4p_x$)	Ga ($4p_y$)	Ga ($4p_z$)
Bond (1): Ga(1)–Ga(2)				
(50.00%) Ga(1)	−0.482	0.101	−0.867	0.000
(50.00%) Ga(2)	0.482	0.101	−0.867	0.000
Bond (2): Ga(1)–Ga(2)				
(50.00%) Ga(1)	0.671	−0.590	−0.443	0.000
(50.00%) Ga(2)	0.671	0.590	0.443	0.000
Bond (3): Ga(1)–Ga(2)				
(50.00%) Ga(1)	0.000	0.000	0.000	0.996
(50.00%) Ga(2)	0.000	0.000	0.000	0.996

[a]The Cartesian coordinates of the two Ga atoms are $(0.887, 0.800, 0.000)$ and $(-0.887, -0.800, 0.000)$, respectively.

In the present work, we have carried out Weinhold's NBO analysis on the title molecule [14]. In this procedure, NBOs and natural LMOs (NLMOs) are derived by transforming the atomic orbital basis to natural AOs. This analysis leads to three bonding Ga–Ga natural orbitals (Table 1). Interestingly, one of the NBOs [Bond(1), Table 1] is quite similar to the 'B orbital' in Fig. 9 of Cotton et al.'s work [4]. Cotton et al. had identified the 'B orbital' as a nonbonding orbital, primarily composed of hybrid orbitals on the two gallium atoms. The lack of bonding character in this orbital seems to have resulted from the contour levels (value not specified) used in the graphical representation. The bonding character in the NBO becomes evident on using a finer grid of orbital contour values. The two-dimensional orbital plot in Fig. 2 reveals that the contours corresponding to larger values (for magnitudes of the orbital = 0.03) are localized on the gallium atoms (just depicting the cross-section of the B orbital in Fig. 9 of Ref. [4]), but overlapping regions are also present at lower contour levels (for magnitudes of the orbital = 0.02). Therefore, the orbital seems to be a bonding in-plane π orbital.

This conclusion may also be drawn from accepted bonding concepts, since the 'B orbital' shown in Ref. [4] is composed of two in-phase hybrid atomic orbitals. They should have positive overlap and form a π MO, just
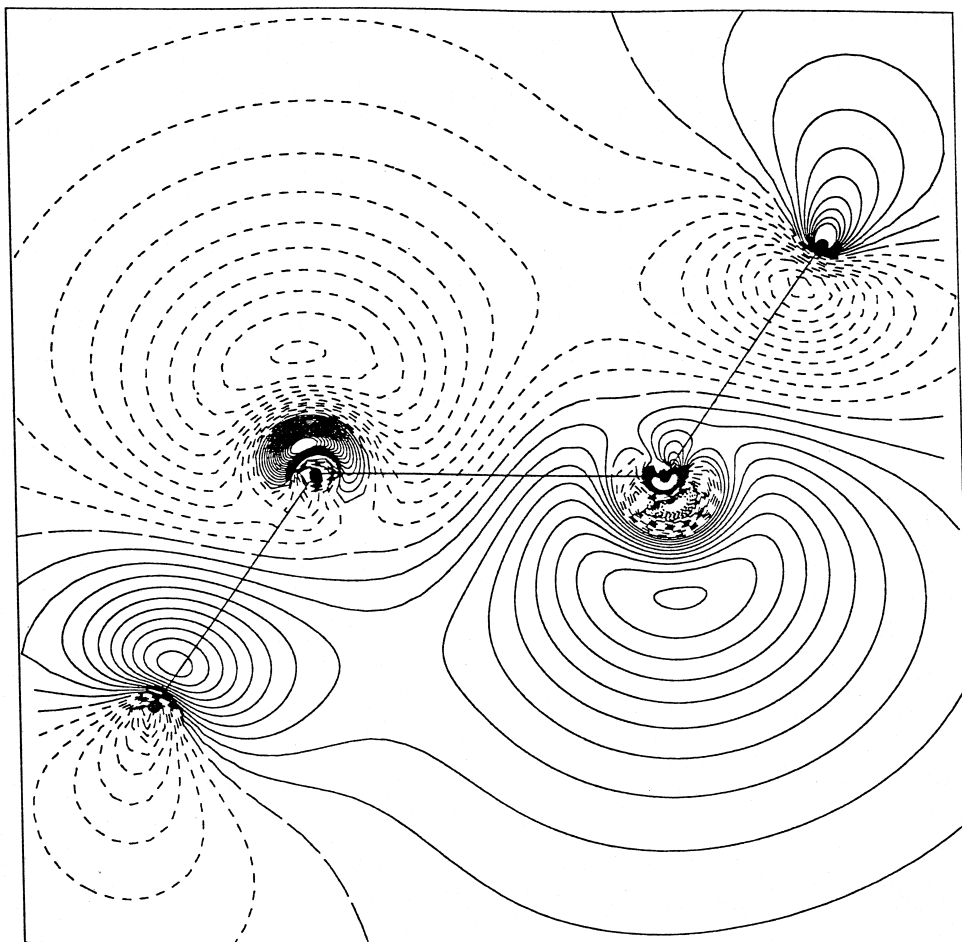

Fig. 2. A contour map of the first natural bonding orbital (in Table 1), which corresponds to the B orbital in Fig. 9 of Ref. [4]. The interval of the contour lines is 0.01.

in the same way for the normal π orbitals in other molecules (e.g., in ethene or acetylene). The only difference is that this π orbital has less symmetry than a conventional π orbital, due to the *trans* skeleton.

Fig. 9 of Ref. [4], nevertheless, gives an important message: the orbital B is weaker than orbital A in that figure, due to the smaller value of the orbital magnitude in the area between the two Ga atoms (we assume that the authors chose the same contour value for these two orbitals). Therefore, our conclusion is that there is a Ga–Ga triple bond, but a weak Ga–Ga triple bond – or perhaps a bond between triple and double – in the title molecule.

This point is verified by the NLMO/NPA bond order of 2.794 for the Ga–Ga bond in the $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$ molecule, thereby also indicating a triple bond. However, the WBI value of 2.019 adds confusion to the argument. Nonetheless, it must be noted that for many cases the WBI values are smaller than the corresponding formal bond orders. For example, the WBI value at the DZP SCF level of theory of the H–F bond in diatomic HF is 0.67, that of the O–H bond in H_2O) is 0.76, and that of the dative B–N bond in $H_3B–NH_3$ is 0.55. Compared with these values, the 2.019 WBI for the weak Ga–Ga triple bond, which is composed of two dative bonds and a normal π bond, should not be surprising.

From the results of the NBO analysis (Table 1), the MO shown in our contour map (Fig. 2), and the NLMO/NPA bond order the final conclusion should be that there is a weak Ga–Ga triple bond at the center of the $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$ molecule.

5. Conclusions

The geometry of the $Na_2[(C_6H_5)_2C_6H_3GaGaC_6H_3(C_6H_5)_2]$ molecule was fully optimized at the extended basis B3LYP level of theory. The Ga–Ga bond distance is predicted to be somewhat shorter than that in the simple model molecules HGaGaH and RGaGaR, but it is still longer than the experimental bond distance in the novel compound $Na_2[\{(i\text{-}Pr_3C_6H_2)_2C_6H_3\}Ga\equiv Ga\{C_6H_3(i\text{-}Pr_3C_6H_2)_2\}]$ by 0.08 Å.

The weak Ga–Ga triple bond in the molecule is supported by the natural bond orbital (NBO) analysis. We conclude that the reported nonbonding orbital in Cotton et al.'s study is actually a bonding orbital, thereby affording a triple bond.

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