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Do Lead Analogues of Alkynes Take a Multiply Bonded Structure?

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*Summary: It is found from theoretical calculations that Ar*PbPbAr* (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-iPr$_3$)$_2$) has a multiply bonded structure in solution, although a singly bonded structure with a highly trans-bent core skeleton has been reported from the X-ray crystal study.*

Multiple bonds between heavier elements are of wide interest in main-group chemistry. Among these, the heavier group 14 element analogues of alkynes, REER (E = Si, Ge, Sn, Pb), have attracted special interest.[1] Thus, $R^{Si}SiSiR^{Si}$(R^{Si} = Si*i*Pr-{CH($SiMe_3$)$_2$}$_2$),[2] Ar′GeGeAr′ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-*i*Pr_2)$_2$),[3] BbtGeGeBbt (Bbt = C_6H_2-2,6-{CH($SiMe_3$)$_2$}$_2$-4-C($SiMe_3$)$_3$),[4] Ar′SnSnAr′,[5] and Ar*PbPbAr* (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-*i*Pr_3)$_2$)[6] have been successfully synthesized and isolated up to now. Bulky silyl and aryl groups play an important role in making these heavier analogues synthetically accessible and isolable as stable compounds.[7] As shown by X-ray crystal analysis, the heavier analogues have a trans-bent core skeleton,[8] unlike the alkyne case. However, the Si−Si distance of $R^{Si}SiSiR^{Si}$ is considerably shorter than those of Si−Si double bonds,[2] while the Ge−Ge and Sn−Sn distances of Ar′GeGeAr′, BbtGeGeBbt, and Ar′SnSnAr′ are close to those of Ge−Ge and Sn−Sn double bonds.[3−5] In contrast, the X-ray crystal analysis of the heaviest analogue, Ar*PbPbAr*, has shown that the trans-bending is greatly increased and the Pb−Pb distance is much longer than the Pb−Pb single-bond distances of diplumbanes such as $Ph_3Pb-PbPh_3$.[6] The singly bonded structure having no Pb−Pb π bond has been also confirmed by model calculations.[9] The exceptional structure of Ar*PbPbAr* has been explained by the fact that the heaviest Pb atom has the strongest tendency to preserve the valence 6s electrons as lone-pair electrons in making bonds (see Figure 1).[1,6]

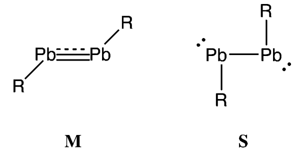

Figure 1. Multiply (M) and singly bonded (S) structures.

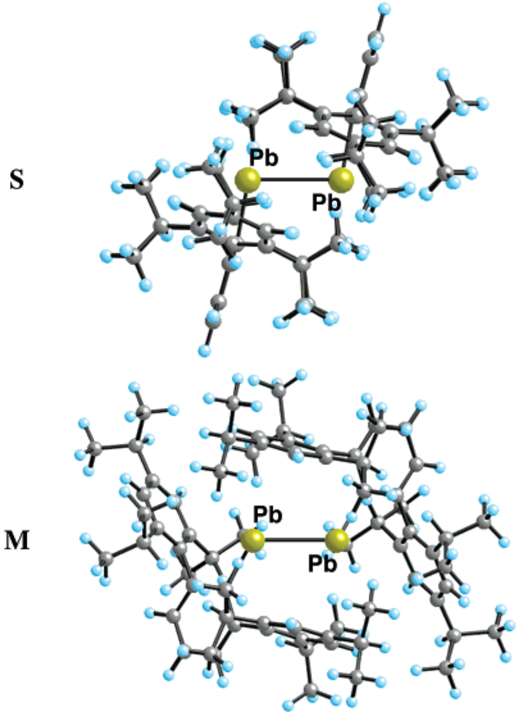

Figure 2. Multiply (M) and singly bonded (S) structures of Ar*PbPbAr* optimized at the B3PW91 level.

To investigate whether Ar*PbPbAr* takes a multiply bonded structure, we have carried out theoretical calculations. Geometries were fully optimized without symmetry constraint with hybrid density functional theory at the B3PW91 level[10] using the Gaussian 03 program.[11] The triple-ζ basis set[12] augmented by two sets of d polarization functions (d exponents 0.213 and 0.062)[13] and relativistic effective core potentials[12] were used for Pb, while the 6-31G(d) basis set was used for other atoms.[14]

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[8] The stabilization of REER due to trans-bending is due to the mixing of the low-lying vacant σ^* orbital into the in-plane π orbital, known as a second-order Jahn−Teller effect. This σ^* mixing is enhanced, as the E atom becomes heavier, and makes the π orbital slipped and weakened.

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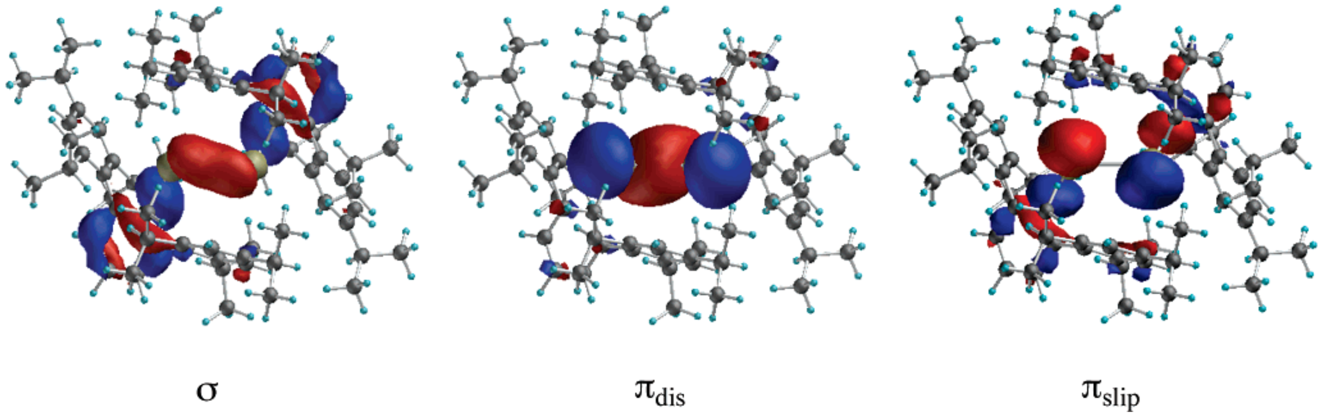

Figure 3. σ, π_{dis}, and π_{slip} orbitals of the multiply bonded structure of Ar*PbPbAr* at the B3PW91 level, plotted with a value of 0.03 au.

Single-point calculations were also performed using the MP2 (second-order Møller−Plesset perturbation) and TD (time-dependent)-B3PW91 methods.[15]

The singly bonded structure of Ar*PbPbAr* found from the X-ray crystal study was first optimized. As Figure 2 shows, the optimized structure has C_2 symmetry. The Pb−Pb distance and Pb−Pb−C trans-bent angle (θ) are 3.260 Å and 100.4°, respectively. These agree reasonably well with the experimental values of 3.188 Å and 94.3° in the crystal structure, despite packing forces. The optimized core skeleton is nearly planar, as indicated by the C−Pb−Pb−C dihedral angle (ω) of 175.2°. Interestingly enough, a new structure with C_2 symmetry was also located as an energy minimum by switching the HOMO and LUMO levels of the singly bonded structure. The newly located structure is much less trans-bent ($\theta = 117.7°$) and has the shorter Pb−Pb distance of 3.071 Å, while it is 119.8° twisted around the Pb−Pb bond because of the bulk of the Ar* group. The Pb−Pb distance is longer than those of typical Pb−Pb single bonds. As is apparent from Figure 3, however, the newly located structure corresponds to a multiply bonded structure, since the central Pb−Pb bond consists of a σ bond, a somewhat distorted π_{dis} bond (resulting from the twisting of the out-of-plane π orbital), and a slipped π_{slip} bond (resulting from the mixing of σ^* and in-plane π orbitals due to trans-bending[8]). It is notable that the multiply bonded structure is 1.0 (B3PW91) and 0.5 kcal/mol (MP2) more stable than the singly bonded structure.[16]

In this context, important information can be obtained from UV−vis spectra. For Ar*PbPbAr*, two absorptions with different intensities have been observed at 397 nm ($\epsilon = 29\,000$) and 719 nm ($\epsilon = 5200$) in *n*-hexane solution,[6] as in the cases of Ar′GeGeAr′ (371 and 501 nm)[3] and Ar′SnSnAr′ (410 and 597 nm).[5] For the multiply bonded structure of Ar*PbPbAr*, the two absorptions were calculated at 413 nm ($f = 0.141$) and 822 nm ($f = 0.025$) at the TD-B3PW91 level, which are assignable to the $\pi_{\mathrm{slip}} \rightarrow \pi_{\mathrm{slip}}^* + \pi_{\mathrm{dis}} \rightarrow \sigma^* + \pi_{\mathrm{dis}} \rightarrow$ Ar* and $\pi_{\mathrm{dis}} \rightarrow \pi_{\mathrm{dis}}^*$ transitions, respectively.[17] For the singly bonded structure of Ar*PbPbAr*, however, only one strong absorption was calculated at 416 nm ($f = 0.383$) at the same level, which is assignable to the $\pi_{\mathrm{slip}}^* \rightarrow \sigma^*$ transition. Obviously, these results indicate that Ar*PbPbAr* has a multiply bonded structure in solution.

It has been known that the lead analogues of alkenes (R_2PbPbR_2) dissociate in solution to provide two singlet divalent species (PbR_2) because of the weak Pb−Pb bonding.[18] The dissociation of the multiply bonded Ar*PbPbAr*, which leads to two PbAr* fragments in the ground doublet state, was calculated to be endothermic by 12.2 kcal/mol. For the PbAr* fragment, two weak p_π(Pb) → Ar* absorptions with almost equal intensities were calculated at 420 nm ($f = 0.026$) and 388 nm ($f = 0.024$), which differ considerably in both absorption positions and intensities from the two absorptions observed (or calculated) for Ar*PbPbAr*. These confirm that the multiply bonded structure of Ar*PbPbAr* is present in solution, unlike the R_2PbPbR_2 case.

In conclusion, Ar*PbPbAr* takes a multiply bonded structure in solution,[19] although a singly bonded structure with a highly trans-bent skeleton has been found by X-ray crystal analysis. The singly bonded structure of Ar*PbPbAr* in the crystalline

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(16) Isolation and crystallization of Ar*GeGeAr* and Ar*SnSnAr* have not been successful (for example, see: Pu, L.; Phillips, A. D.; Richards, A. F.; Stender, M.; Simons, R. S.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 11626). In contrast, isolation and crystallization have been successful using the somewhat less crowded Ar′ group, which has no *i*Pr group at the para positions of the flanking aryl ring.[3,5] For Ar′PbPbAr′, the multiply bonded structure (Pb−Pb = 3.047Å, $\theta = 117.2°$, and $\omega = 131.3°$) was calculated to be 0.1 kcal/mol (B3PW91) less stable and 2.1 kcal/mol (MP2) more stable than the singly bonded structure (Pb−Pb = 3.200Å, $\theta = 103.3°$, and $\omega = 179.5°$).

(17) It should be noted that the potential energy of the multiply bonded structure is rather flat for the changes in the C−Pb−Pb−C dihedral angle (ω). For example, the structure optimized by fixing the angle at $\omega = 140°$ is only 0.7 kcal/mol less stable than the fully optimized structure ($\omega = 119.8°$). It is interesting that the two absorptions of 420 and 752 nm calculated at the less twisted structure ($\omega = 140°$) are much closer to the experimental values of 397 and 719 nm (especially for the $\pi_{\mathrm{dis}} \rightarrow \pi_{\mathrm{dis}}^*$ absorption, which is very sensitive to the ω angle).

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(19) For REER, it has been known that electropositive silyl groups decrease the trans-bending and shorten the E−E distance.[7a−c,f,g] Therefore, the silyl group (R^{Si} = Si*i*Pr{CH(SiMe$_3$)$_2$}$_2$)[2] employed for the synthesis and isolation of $R^{Si}SiSiR^{Si}$ was tested. A very short Pb−Pb distance of 2.696 Å was optimized for $R^{Si}PbPbR^{Si}$ ($\theta = 128.9°$ and $\omega = 155.6°$). However, this multiply bonded structure was calculated to be 4.3 kcal/mol (B3PW91) less stable than the singly bonded structure (Pb−Pb = 3.080 Å, $\theta = 100.2°$, and $\omega = 134.4°$). It is expected that bulky silyl groups effective for the stabilization of multiply bonded structures are developed to realize a sufficiently short Pb−Pb bond.

phase is ascribable to packing forces. In addition, crystallization is significantly affected by the bulk of the substituent groups. These have been very recently demonstrated[20] also for tin analogues of alkynes: Ar*SnSnAr* and 4-$SiMe_3$-Ar′SnSnAr′-4-$SiMe_3$ (Ar′-4-$SiMe_3$ = C_6H_2-2,6-(C_6H_3-2,6-*i*Pr_2)$_2$-4-$SiMe_3$).[21]

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