

Unusual Long Distances of Germanium-Carbon Bond of Organogermyl-
alkali Metals Probed by EXAFS

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Extended X-ray absorption fine structure (EXAFS) spectra were analyzed for a series of organogermylalkali metals in solutions. The germanium-carbon bond lengths of the germylalkali metals were found to be longer as much as 10% than those of the corresponding neutral species.

Carbanions, R_3C^- , play an important role as reaction intermediates in organic chemistry. Similarly, the chemistry of the heavy carbanion analogues, silyl anions R_3Si^- , germyl anions R_3Ge^- , and stannyl anions R_3Sn^- , has received much attention in organic synthesis as reaction intermediate in recent years.¹⁾ However, structural data of the heavy carbanion analogues have little been determined because of their instability.²⁾ Only a few spectroscopic studies (NMR and UV) of these anions have been reported.³⁾ To determine the structures of these anions is essential for the understanding of the nature of the bonding and physical and chemical behavior of these systems. In this report we describe structural features of organogermylalkali metals in solution determined by EXAFS spectroscopy for the first time. These results prove that EXAFS is a very useful tool to determine the structure of organogermanium compounds which are stable in solution.

EXAFS measurements were performed by using the laboratory EXAFS spectrometer reported elsewhere.⁴⁾ The alkyl- or aryl-substituted germylalkali metal in hexamethylphosphoric triamide (HMPA)-ether solvents^{5,6)} was transferred from a reacting vessel to a Pyrex flat cell (path length ≈ 2 mm) in an argon atmosphere in order to avoid decomposition by moisture, and the cell was sealed after the sample was degassed.

The EXAFS spectra of two aryl-substituted germanium compounds (Ph_4Ge and Ph_3GeH) and two alkyl-substituted germanium compounds (Et_4Ge and Et_3GeH) were measured as reference materials. The EXAFS spectra and the associated k^1 weighed Fourier transforms of these germanium compounds are shown in Figs. 1 A-D.

The peak a, b, and c in Fig. 1 correspond to the interatomic distances of germanium and the first, second, and third nearest carbon of the aryl ring in Figs. 1 A-B and the alkyl group in Figs. 1 C-D, respectively. Indeed, a calculation including phase factors show the peaks a represent interatomic distance of 1.96 Å.

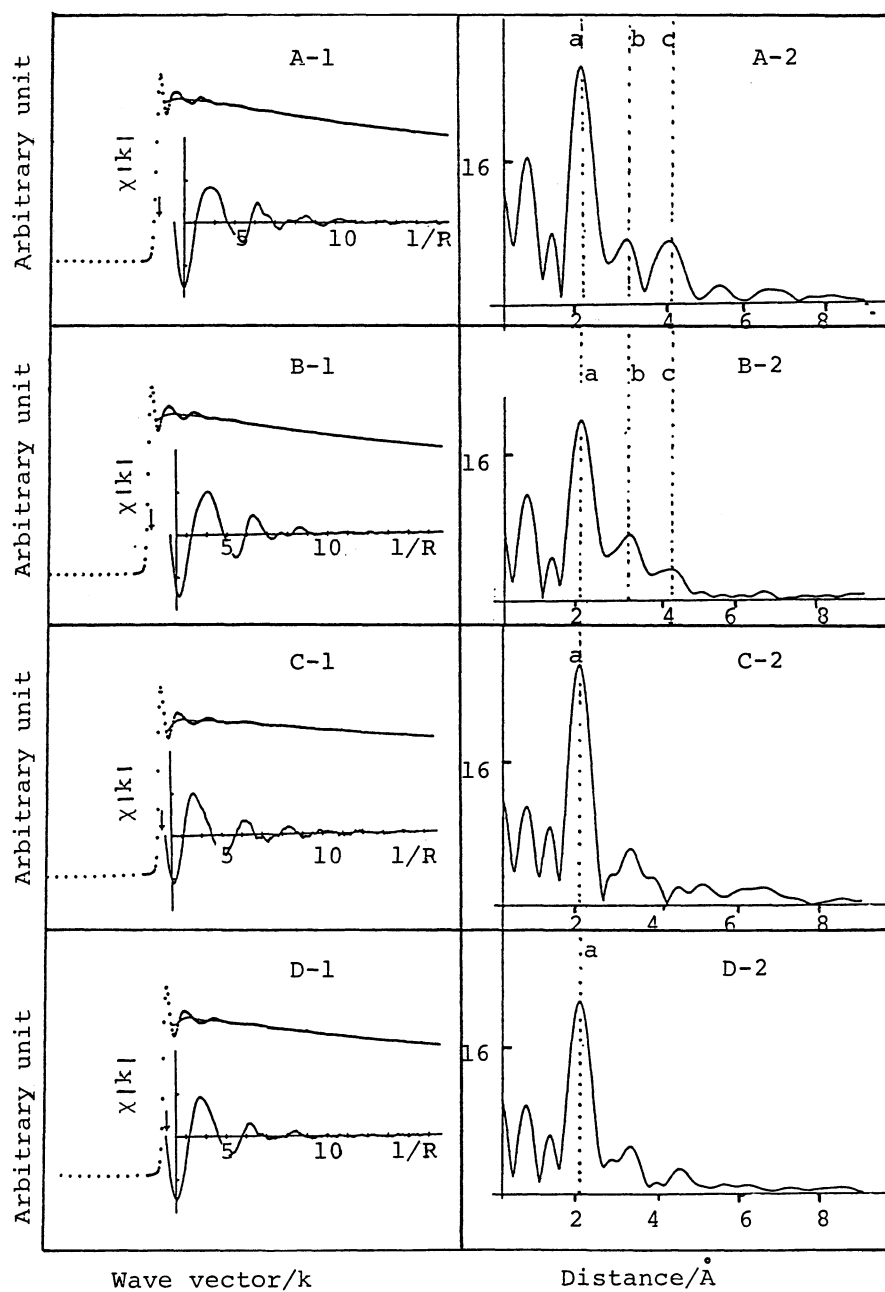


Fig. 1. EXAFS spectra and associated Fourier transforms of Ph_4Ge (A), Ph_3GeH (B), Et_4Ge (C), and Et_3GeH (D).

This is in very good agreement with the known germanium-carbon bond distances.⁷⁾

Extracted oscillations used to Fourier transform were taken over the same wavevector range of $3.0 < k < 9.0 \text{ \AA}^{-1}$. Therefore, the comparison of the coordination number can be made directly from the peak height of radial structure functions.

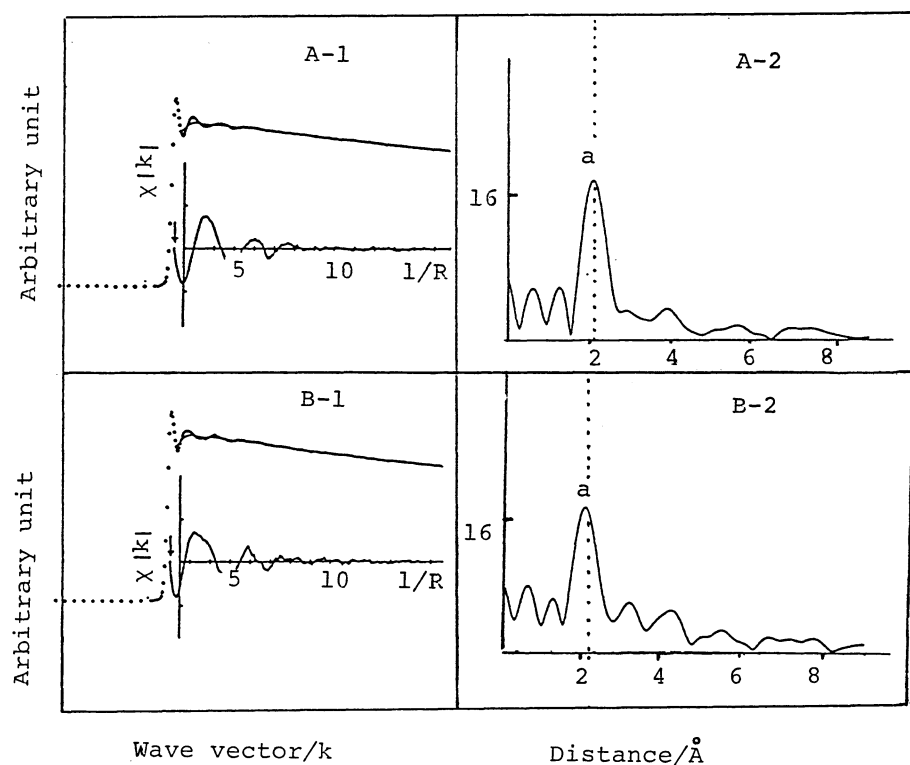


Fig. 2. EXAFS spectra and associated Fourier transforms of Me_3GeNa (A) and Ph_3GeLi (B).

Table 1. The Distance of Germanium-Carbon Bond of Aryl- and Alkyl-Substituted Germylalaki Metals and Related Compounds

No.	Compound	Ge-C bond/Å
1	Et_4Ge	1.96
2	Et_3GeH	1.96
3	Ph_4Ge	1.97
4	Ph_3GeH	1.96
5	Me_3GeLi	2.07
6	Me_3GeNa	2.17
7	Me_3GeK	2.10
8	Et_3GeLi	2.06
9	Ph_3GeLi	2.04

As is expected, the peak height increases with the increase of the substituent. Therefore, it is evident that peak heights can serve as a substituent number marker for unknown compounds. The interatomic distances obtained for the reference com-

pounds are summarized in Table 1.

The EXAFS spectra of aryl- and alkyl-substituted germylalkali metals were measured. As typical examples, EXAFS spectra and the associated Fourier transforms of trimethylgermysodium (Me_3GeNa) and triphenylgermyllithium (Ph_3GeLi) are shown in Figs. 2 A-B. From a comparison of the amplitude of the extracted oscillations and the peak heights with those of the reference compounds it is immediately clear that the three substituents remain around Ge in these solutions. However, peak positions of radial structure functions are appreciably different, suggesting the Ge-C bond lengths are longer in the anions. The values obtained from the calculated including phase factors are also summarized in Table 1.

The most reasonable explanation for the long distance of Ge-C bond of the anions would seem to be that a large negative charge on a germanium atom causes rehybridization at germanium, placing more s character in the unpaired electrons-bearing hybrid. As a result, p character in bond orbitals of the germanium atom is increased, and Ge-C bond lengths of the anions are increased.

We have no information on the degree of association of the anions in this EXAFS study.

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