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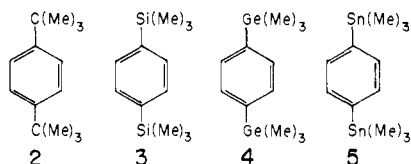
Anion States of Para-Disubstituted Benzenes: *p*-Di-*tert*-butylbenzene and Related Group 4 Molecules: *p*-Bis(trimethyl(silyl, germyl, and stannyl))benzene

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Abstract: The electron attachment energies to *p*-bis(M(Me)₃)benzene (M = C, Si, Ge, Sn) and the substituent parent compounds, M(Me)₄, were measured by electron transmission spectroscopy. Negative ion states associated with electron capture into benzene π^* orbitals as well as a substituent σ^* orbital were observed. The trends in the negative ion state energies can be explained on the basis of hyperconjugative interaction between the substituent σ^* orbital and the benzene π^* orbitals without appealing to $d \leftarrow p_x$ back-bonding arguments.

Organometallic substituents based upon group 4A elements (Si, Ge, Sn) exert a curious electron donor-acceptor effect upon π systems to which they are attached.¹ Organosilyl, germyl, and stannyl substituents are σ electron donors relative to the corresponding hydrocarbon substituent and are thus expected to increase the energy of π orbitals of the appropriate symmetry. However, photoelectron¹⁻³ and ESR spectroscopic⁴⁻⁹ measurements indicate that these substituents in fact often have the opposite effect. These results have been explained on the basis of electron delocalization through conjugation or $d \leftarrow p_x$ back donation. In this paper organometallic substituent effects on benzene (**1**) are investigated by examination of the electron transmission spectra of



For these para-disubstituted benzenes, the (π_2 , π_3) and (π_4^* , π_5^*) degeneracy will be removed and the substituent effect will be reflected in the energies of the symmetric (S) orbitals.⁴

There is presently available information on the energies of the filled π orbitals of these compounds from photoelectron spectroscopy¹⁻³ and on the lowest unfilled π^* orbital from ESR spectroscopy.⁴⁻⁹ Briefly put, it has been found that the symmetric π orbital energies of the trimethylsilyl, germyl, and stannyl substituted molecules are stabilized relative to the *tert*-butyl-substituted compound. It is suggested that this is because of the possibility for electron delocalization by $d \leftarrow p_x$ back-donation to the former three substituents, a mechanism not available to the latter. Interestingly, the π orbitals in the -Ge(Me)₃ substituted benzene (**4**) are not more stabilized than the -Si(Me)₃ substituted

benzene (**3**). Nor are they more stable in **5** than in **4**. This is attributed to an increase in the metal-(benzyl) carbon bond length across the series.¹ (Throughout this paper we often (incorrectly) treat orbitals as physical entities and thus use language such as "the orbital becomes more stable" to mean "the orbital eigenvalue decreases". We assume, however, that the reader is familiar with this terminology.)

Electron transmission spectroscopy^{10,11} (ETS) is the complement to photoelectron spectroscopy (PES). The latter (PES) measures the ionization potential which is the energy required to remove an electron from an occupied orbital. The former (ETS) measures the attachment energy, the energy to add an electron to an unoccupied orbital to create a radical anion. The data from both experiments can be interpreted in a Koopmans' theorem sense to elucidate the change in orbital energy accompanying a change of substituent. ETS has the advantage over ESR in that not only can electron capture into the lowest unoccupied molecular orbital (LUMO) be observed, but capture into higher orbitals is observed as well.

Experimental Section

Electron transmission spectroscopy is a technique for measuring the energy of a temporary negative ion formed by electron capture into an

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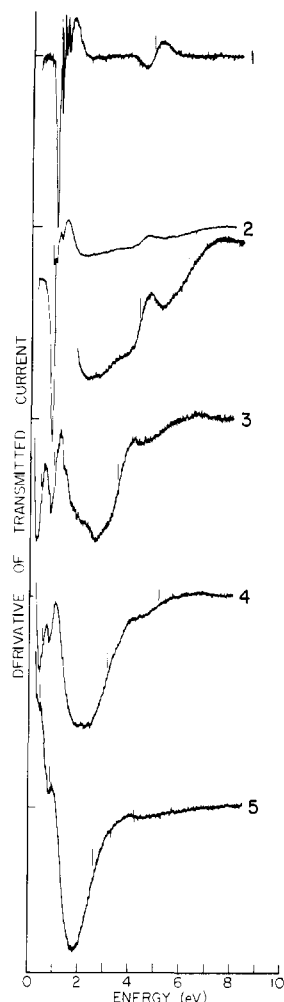


Figure 1. Derivative electron transmission spectra of benzene (1), *p*-di-*tert*-butylbenzene (2), *p*-bis(trimethylsilyl)benzene (3), *p*-bis(trimethylgermyl)benzene (4), and *p*-bis(trimethylstannyl)benzene (5).

unoccupied orbital of a molecule. The experiment involves the measurement of the transparency of a gas to an electron beam as a function of energy. The transparency depends in an inverse fashion upon the electron-scattering cross section. Temporary negative ion formation occurs with large cross section only over a narrow energy range. Since the negative ion promptly decays by giving up the trapped electron, the formation and decay process appears as a sharp fluctuation in the electron-scattering cross section. The process, as well as the corresponding feature in the transmission vs. electron energy spectrum, is referred to as a "resonance".

The electron spectrometer¹² consists of an electron source followed by an electron monochromator, a gas cell, and an electron collector. In practice the first derivative of the transmitted current as a function of energy is recorded since the derivative is sensitive to the abrupt change in transmitted current associated with a resonance.¹³ The energy associated with a resonance is known as an "attachment energy" (AE) and, with respect to the derivative spectrum, is defined as the point vertically midway between the minimum and maximum which characterize the resonance. For the present purposes an attachment energy may be identified with the negative of the corresponding electron affinity (EA).¹⁴

The resonances observed in the electron transmission spectrum are often broad and unstructured reflecting the very short lifetime of the negative ion¹⁰ as well as the Franck-Condon overlap between the anion and neutral states. A problem which arises is that of defining the attachment energies associated with two overlapping features. Consider for example the two features which appear in the expanded trace of the spectrum of **2** in Figure 1. Does this derivative spectrum correspond to two successive peaks in the resonant scattering cross section—one at 4.5

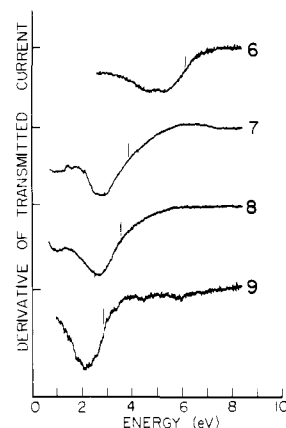


Figure 2. Derivative electron transmission spectra of 2,2-dimethylpropane (6), tetramethylsilane (7), tetramethylgermane (8), and tetramethyltin (9).

eV and one at 6.3 eV—or does the spectrum correspond to a peak at 4.5 eV superimposed upon a very broad peak extending from below 2 eV to above 7 eV with a maximum near 5 eV? Since the breadth of these features arises from natural limitations and not instrumental resolution, there is not clearcut means of distinguishing between two such possibilities. Thus the assignment of attachment energies to broad features must appropriately reflect this uncertainty.

The compounds **1**, **2**, **6**, **7**, **8**, and **9** were obtained from commercial sources and used without further purification. The *p*-disubstituted species, **3**, **4**, and **5**, were generously supplied by Dr. Wolfgang Kaim.

Results

The derivative electron transmission spectra of benzene (**1**), *p*-di-*tert*-butylbenzene (**2**), *p*-bis(trimethylsilyl)benzene (**3**), *p*-bis(trimethylgermyl)benzene (**4**), and *p*-bis(trimethylstannyl)benzene (**5**) are shown in Figure 1. For benzene there are two resonances: the first corresponds to electron capture into the degenerate orbitals (π_4^* , π_5^*), the second to π_6^* . The first of these resonant states is sufficiently long-lived that vibrational energy levels are defined accounting for the structure in the first resonance.¹⁰ The spectrum of **2** is quite similar to that of **1**. The two features appearing in the spectrum of **1** can be clearly discerned in the spectrum of **2**. There is in addition a broad, weak resonance as shown in the high-gain trace of the 2–8 eV portion the spectrum. The spectra of **3**, **4**, and **5** are similar to one another, consisting of two resonances between 0.5 eV and about 1 eV, a strong broad feature near 3 eV, and a weak, broad feature above. The presence of four features in these latter spectra indicates that in addition to resonances associated with electron capture into orbitals of essentially benzene π^* character, we have observed an attachment process involving a substituent-based orbital.

To ascertain the nature of the substituent-based orbital we have obtained spectra of the substituent parent compounds: 2,2-dimethylpropane (**6**), tetramethylsilane (**7**), tetramethylgermane (**8**), and tetramethyltin (**9**). These are shown in Figure 2. Each consists of a single broad resonance which decreases in energy across the series.

Discussion

The assignment of the observed attachment energies becomes straightforward when the ETS data and the corresponding PES data^{1,2,3,15–18} are arranged in a correlation diagram as shown in Figure 3. As noted above and as indicated on the correlation diagram, there is considerable uncertainty in assigning AE's to broad overlapping features. The spectrum of **2** can be interpreted

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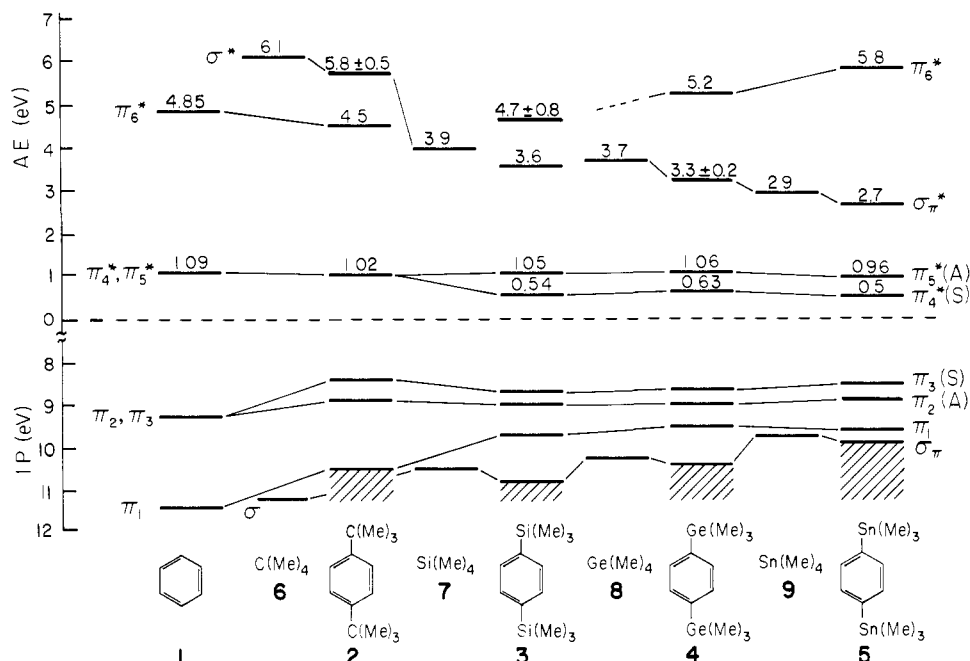


Figure 3. Diagram showing correlation of electron attachment energies and ionization potentials of 1-9. The uncertainty in the attachment energies reported to two decimal places is ± 0.05 eV. Except as noted, the uncertainty in the attachment energies reported to one place is ± 0.1 eV.

as two successive features at 4.5 and 6.3 eV or a relatively sharp feature at 4.5 eV superimposed upon a very broad feature centered at 5.2 eV. Similarly, the high-energy spectrum of 3 can be interpreted as successive peaks at 3.6 and 5.4 eV or as a relatively sharp feature at 3.6 eV superimposed upon a very broad feature centered at 3.9 eV. Finally, 4 can be interpreted as two successive features or as a feature at 5.2 superimposed upon a very broad feature. The high-energy spectrum of 5 is almost certainly two successive peaks.

The key to understanding the data lies in the identification of the orbital associated with the resonance in the tetramethyl compounds 6-9. From PES data coupled with theoretical calculations,¹⁵⁻¹⁸ the highest occupied molecular orbital (HOMO) in 6-9 is a bonding orbital of t_2 symmetry between the central atom and the methyl carbons. The C-H bonding orbitals and the occupied central atomic orbitals lie well below the HOMO. By the pairing theorem, the orbital associated with the resonance in 6-9 is a σ^* antibonding orbital between the central atom and the methyl carbons. This assignment is supported by the fact that the decrease (destabilization) in the $\sigma(t_2)$ ionization potential across the series 6-9 is reflected in a decrease (stabilization) in the σ^* attachment energy across the series. Further experimental proof of this assignment is presented in an accompanying paper. In the trimethyl substituents derived from 6-9, the symmetry change upon substitution will split the degenerate σ^* orbital; however, an orbital of similar character can be expected. This substituent-based orbital in the *p*-disubstituted benzenes (2-5) can interact in a hyperconjugative manner with the symmetric benzene π orbitals and is thus identified here as σ_π^* . The presence of a low-lying σ_π^* orbital localized on the substituent has been suggested by recent ETS work¹⁹ as well as calculations on related compounds.²⁰

Assuming the existence of a substituent-based σ_π^* orbital, we assign the resonance at 6.3 eV in *p*-di-*tert*-butylbenzene (2) to temporary anion formation by electron capture into this orbital. The bonding (hyperconjugative) interaction between σ_π^* and π_6^* of the benzene moiety stabilizes π_6^* to give the resonance at 4.5 eV. Because σ_π^* is quite high in energy it does not significantly perturb (π_4^* , π_5^*), which are only slightly stabilized in 2 relative to benzene (1) and are not noticeably split. The σ^* orbital in tetramethylsilane (7) is much lower in energy than in 6 and the

σ_π^* in the -Si(Me)₃ substituted benzene (3) can be expected to be correspondingly low in energy. It is evident from the spectrum and the correlation diagram that σ_π^* in 3 is very close in energy to π_6^* . The low energy of σ_π^* in 3 is reflected in the fact that the (π_4^* , π_5^*) pair is split to give a resonance at 1.05 eV, unperturbed from that in benzene, and a resonance at 0.54 eV. Continuing across the series 6-9, the σ^* orbital becomes more stable. Similarly, across the series 2-5, the σ_π^* orbital becomes more stable. In 4 and 5 it is clear that σ_π^* lies below π_6^* , which is thus destabilized relative to benzene. Whether the π_6^* resonance lies above or below the σ_π^* resonance in *p*-bis(trimethylsilyl)benzene (3) is not clear from our spectra or correlation diagram. In the ETS spectrum of trimethylsilylbenzene, Modelli et al. conjecture that the σ_π^* lies below the π_6^* resonance.¹⁹

The PES data also display consistent trends. Across the series 6-9 the highest occupied σ orbital increases in energy, while across the series 2-5 the energy of the σ onset, and presumably also the energy of σ_π , increases. This results in a systematic destabilization of π_1 across the series. The interaction of the substituent σ_π orbital with the π system also removes the (π_2 , π_3) degeneracy.

Both the ETS and the PES data imply that the substituent effect upon the degenerate benzene orbitals, (π_2 , π_3) and (π_4^* , π_5^*), is such that when the degenerate pair is split, one orbital is not perturbed from its original position. This is because one member of each pair is antisymmetric (A) and is largely unaffected by para substitution. Thus, π_2 and π_5^* are antisymmetric (A) and π_3 and π_4^* are symmetric (S). As noted above, (π_4^* , π_5^*) of 2 is not split because σ_π^* in this molecule is quite high in energy. This is consistent with ESR experiments⁵ where it was found that 2 does not give a radical anion, presumably because the (π_4^* , π_5^*) splitting is not sufficient to give a LUMO of low enough energy to permit formation of a stable anion in solution. It is also noteworthy that both ETS and ESR¹ experiments imply that conjugative interaction between σ_π^* and π_4^* does not appear to increase in magnitude for the germyl- and stannyl-substituted benzenes (4 and 5) relative to the silyl-substituted compound (3), although the σ_π^* - π_4^* energy difference decreases across the series 3 to 5. However, while the energies of σ_π^* and π_4^* approach one another on going from 3 to 5, the overlap between these two orbitals decreases dramatically. The bond distances between the metal atom and the benzene carbon are 193, 198, and 218 pm for 3, 4, and 5, respectively.²¹

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Conclusion

The most important conclusion to be drawn from this work is that with the observation of a low-lying antibonding σ^* orbital it is possible to understand the silyl, germyl, and stannyl substituent effects upon π systems without appealing to a model which involves electron delocalization onto the metal d orbitals. This is consistent with a number of theoretical studies which find that the inclusion of d orbitals in the description of π systems with substituents containing group 4A atoms does not improve the agreement between the computations and PES and other experimental observations.^{16,20,22} The trends in the energies of unfilled π^* orbitals of substituted benzenes as inferred from the measurement of

electron attachment energies can be explained on the basis of hyperconjugative interactions between the π^* orbitals and a low-lying σ^* orbital. This conclusion is at odds with ESR studies of the *p*-disubstituted benzenes; however, the calculations performed to explain the ESR results explicitly exclude hyperconjugative interactions by treating the substituent simply as a heteroatom.⁴

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Registry No. 1, 71-43-2; 2, 1012-72-2; 3, 13183-70-5; 4, 21364-16-9; 5, 1012-73-3; 6, 463-82-1; 7, 75-76-3; 8, 865-52-1; 9, 594-27-4.

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Negative Ions: Effect of α - vs. β -Silyl Substitution on the Negative Ion States of π Systems

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Abstract: To elucidate the effects of α - vs. β -silyl substituents on the π -electronic properties of unsaturated hydrocarbons, the gas-phase electron affinities of tetramethylsilane (TMS) (**1**), 3,3-dimethyl-1-butene (**4**), vinyltrimethylsilane (**5**), propyne (**7**), 3,3-dimethyl-1-butyne (**8**), (trimethylsilyl)acetylene (**9**), 1-butene (**10**), 4,4-dimethyl-1-pentene (**11**), allyltrimethylsilane (**12**), and silane (**13**) were determined by electron transmission spectroscopy. The trends in the energies obtained for the silylated compounds are proposed to arise from hyperconjugative interactions between low-lying, silicon-substituent-based unoccupied molecular orbitals and occupied π -type orbitals.

The dual donor-acceptor effect of silyl substituents on various properties of π systems has long been an intriguing topic. Ionization energies, as determined by photoelectron and mass spectroscopies,¹⁻³ ESR spectra,⁴ characteristic vibrational frequencies,⁵ NMR signals,⁶ and theoretical molecular orbital energies⁷ have been determined over the years for various series of unsaturated alkyl- and silyl-substituted compounds and the data interpreted in terms of the difference in electronegativity of carbon vs. silicon and π -electron back donation from carbon to low-lying unoccupied orbitals on silicon. In particular, the trends in the energies of the occupied orbitals of these systems, as obtained from ionization potential data using Koopmans' theorem,⁸ have been instrumental in elucidating the silylation effects. However, a thorough description of the electronic properties also requires information on the energies of the low-lying, unoccupied orbitals. This can be obtained from electron transmission spectroscopy (ETS).^{9,10} The conjugate experiment to photoelectron spectroscopy (PES), ETS measures the energy of a negative ion state resulting from temporary capture of an electron into an unoccupied orbital while PES measures the energy required to remove an electron from an occupied orbital. Although the technique of ETS has been used to study atoms and di- and triatomics^{10,11} as well as properties of π^* orbitals in unsaturated hydrocarbons,^{9,12a} it has only recently been applied to systems containing transition metals¹³ and selected silicon compounds.¹⁴ We report here the application of this technique to an investigation of the effect of α - vs. β -silyl substitution on the energies of the unoccupied orbitals of unsaturated hydrocarbons.

Experimental Section

Electron transmission spectroscopy is a technique for measuring the energy of a temporary negative ion formed by electron capture into an

unoccupied orbital of a molecule. The experiment involves the measurement of the transparency of a gas to an electron beam as a function

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