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Published on Web 06/19/2002

Intramolecular Electron Transfer in Heterosubstituted Benzene Derivatives as Probed by Dissociative Electron Attachment

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Received March 13, 2002

Abstract: The electron transmission and dissociative electron attachment spectra of the 1-chloroalkyl benzene derivatives, $C_6H_5(CH_2)_3Cl$ and $C_6H_5(CH_2)_4Cl$, and of the sulfur and silicon derivatives, $C_6H_5SCH_2Cl$, $C_6H_5Si(CH_3)_2CH_2Cl$ and $C_6H_5CH_2Si(CH_3)_2CH_2Cl$, are presented for the first time. The relative Cl^- fragment anion currents generated by electron attachment to the benzene π^* LUMO are measured in the series $C_6H_5(CH_2)_nCl$, with $n = 1-4$, and in the heteroatomic compounds. The Cl^- yield reflects the rate of intramolecular electron transfer between the π-system and the remote chlorine atom, which in turn depends on the extent of through-bond coupling between the localized π^* and σ^*_{Cl-C} orbitals. In compounds $C_6H_5(CH_2)_nCl$ the Cl^- current rapidly decreases with increasing length of the saturated chain. This decrease is significantly attenuated when a carbon atom of the alkyl skeleton is replaced with a third-row heteroatom. This greater ability to promote through-bond coupling between the π^* and σ^*_{Cl-C} orbitals is attributed to the sizably lower energy of the empty σ^*_{S-C} and σ^*_{Si-C} orbitals with respect to the σ^*_{C-C} orbitals. In the sulfur derivative the increase of the Cl^- current is larger than in the silicon analogue. In this case, however, other negative fragments are observed, due to dissociation of the S−C bonds.

Introduction

Long-range intramolecular electron transfer processes play an important role in photochemistry and biochemistry. In addition, systems capable of transmitting variations of charge density between different parts of a molecule are increasingly important in the field of nanoscale technology, that is, organic conductors, molecular wires, and molecular devices.[1]

Intramolecular electron-transfer processes can be revealed with experiments of gas-phase electron−molecule collisions, when an incident electron is first trapped into a localized functional group and then is transferred to a remote group (or atom) where bond dissociation and formation of a negative fragment takes place.

An isolated molecule can temporarily attach an electron of proper energy into a vacant orbital, producing a shape resonance in the scattering cross section.[2] Electron transmission spectroscopy (ETS)[3] is one of the most suitable means for detecting the formation of these short-lived anions. Electron attachment is rapid with respect to nuclear motion so that temporary anions are formed in the equilibrium geometry of the neutral molecule. The impact energies at which electron attachment occurs are properly denoted as vertical attachment energies (VAEs) and are the negative of the vertical electron affinities. When suitable energetic and kinetic conditions occur, the decay of the unstable molecular anions can follow a dissociative channel which generates long-lived negative fragments. Dissociative electron attachment spectroscopy (DEAS) measures the yield of these fragments as a function of the incident electron energy.

While in saturated halohydrocarbons[4−7] production of halogen negative fragments follows electron attachment to the σ^* lowest unoccupied molecular orbital (LUMO), with mainly halogen character, in unsaturated halohydrocarbons[8−19] the maximum yield of halide fragments occurs close to the energy of the lowest π^* resonance observed in ETS. Pearl, Burrow et al.[18,19] used

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10.1021/ja0203768 CCC: $22.00

DEAS as a probe for intramolecular electron transfer in chloronorbornene derivatives and demonstrated the role of symmetry and, more generally, the extent of through-bond coupling between the empty $\sigma^*_{\mathrm{Cl-C}}$ and π^* MOs in the efficiency of the electron-transfer mechanism.

In $H_2C{=}CHCH_2Cl$ (allyl chloride) and $C_6H_5CH_2Cl$ (benzyl chloride), where strong σ^*/π^* mixing occurs, the Cl^- current is an order of magnitude larger[8-11] than in chloroethene and chlorobenzene, respectively, where σ^*/π^* mixing (forbidden by symmetry in the rigid planar structure of the molecule) relies on vibronic coupling. We have recently found[11] that in 1-chloro-2-phenylethane, $C_6H_5(CH_2)_2Cl$, where $\sigma^*_{\mathrm{Cl-C}}/\pi^*$ mixing is relatively small, the Cl^- current following electron attachment to the π^* LUMO is about the same as in chlorobenzene, that is, still 2 orders of magnitude larger than in 1-chlorobutane, where Cl^- is directly generated by dissociation of the σ^* resonance. In a detailed DEAS and theoretical study of the chloroalkene series $H_2C{=}CH(CH_2)_nCl$, with $n = 0-4$, Moore and co-workers[10] demonstrated that the Cl^- yield rapidly decreases with increasing length of the alkyl chain, owing to the inefficiency of the intermediate higher-lying empty $\sigma^*_{\mathrm{C-C}}$ MOs to promote through-bond coupling between the π^* and $\sigma^*_{\mathrm{Cl-C}}$ MOs.

ETS has shown[13] that third-row (or heavier) substituents in saturated hydrocarbons cause a sizable stabilization of the lowest-lying σ^* orbitals. Replacement of carbon atoms with third-row heteroatoms in the alkyl chain should thus favor through-bond $\pi^*/\sigma^*_{\mathrm{Cl-C}}$ coupling, owing to the energy proximity of the intermediate σ^* MOs.

Here we extend our previous[11] ETS and DEAS analysis of the compounds $C_6H_5(CH_2)_nCl$ with $n = 0-2$ to the analogues with $n = 3$ and 4, where the benzene π-system is separated from the chlorine atom by a longer alkyl chain, and to heterosubstituted derivatives obtained by replacement of a CH_2 group with a $Si(CH_3)_2$ group or a sulfur atom. The following labels are used through the text for designating the corresponding molecules:

1 $C_6H_5CH_2Cl$
2 $C_6H_5(CH_2)_2Cl$ **2a** $C_6H_5Si(CH_3)_2CH_2Cl$ **2b** $C_6H_5SCH_2Cl$
3 $C_6H_5(CH_2)_3Cl$ **3a** $C_6H_5CH_2\,Si(CH_3)_2CH_2Cl$
4 $C_6H_5(CH_2)_4Cl$

The aim of this work is to verify if the presence of third-row heteroatoms in the alkyl skeleton can significantly improve the efficiency of the intramolecular electron-transfer mechanism. Possible production of fragment anions other than Cl^- is also monitored. Dissociation of the saturated chain could in fact represent a limit to practical applications of these molecular systems under conditions of excess negative charge.

Quantum mechanical density functional theory (DFT) calculations are employed to determine the most stable molecular conformations of the neutral states. The relative Cl^- intensities measured in the DEA spectra are compared with the $\sigma^*_{\mathrm{Cl-C}}$ contribution to the π^* LUMO (which should reflect the extent of σ^*/π^*mixing) evaluated with Hückel-type calculations.

Experimental Section

ET and DEA spectra. Our electron transmission apparatus is in the format devised by Sanche and Schulz[20] and has been previously described.[21] To enhance the visibility of the sharp resonance structures, the impact energy of the electron beam is modulated with a small ac voltage, and the derivative of the electron current transmitted through the gas sample is measured directly by a synchronous lock-in amplifier. The present spectra have been obtained by using the apparatus in the "high-rejection" mode[22] and are, therefore, related to the nearly total scattering cross sections. The electron beam resolution was about 50 meV (fwhm). The energy scale was calibrated with reference to the $(1s^12s^2)^2S$ anion state of He. The estimated accuracy is ±0.05 or ±0.1 eV, depending on the number of decimal digits reported.

The collision chamber of the ETS apparatus has been modified[12] to allow for ion extraction at 90° with respect to the electron beam direction. Ions are then accelerated and focused toward the entrance of a quadrupole mass filter. Alternatively, the total anion current can be collected and measured (with a Keithley 485 picoammeter) at the walls of the collision chamber (about 0.8 cm from the electron beam). The DEAS data reported here were obtained with an electron beam current about twice as large as that used for the ET experiment. The energy spread of the electron beam increased to about 120 meV, as evaluated from the width of the SF_6^- signal at zero energy used for calibration of the energy scales.

The relative total anion currents were evaluated from the peak heights with the same pressure reading for all compounds (2×10^{-5} mbar, measured in the main vacuum chamber by means of a cold cathode ionization gauge). Preliminary measurements showed that the total anion current reading is proportional to the pressure, at least in the 1×10^{-5}–4×10^{-5} mbar range.

All the compounds except for (benzyl)(chloromethyl)dimethylsilane were commercially available. **3a** was prepared by standard literature method[23] based on the reaction between benzylmagnesium chloride and chloro(chloromethyl)dimethylsilane in Et_2O.

Computational Details. The electronic structure calculations and geometry optimizations on the neutral molecules were carried out with the Gaussian 98 set of programs.[24]

Geometry optimizations were performed using the B3LYP density functional method[25] with the standard 6-31G* basis set. To explore most of the local energy minima of the neutral molecules, all available initial guesses were first generated applying the C_s symmetry group constraints. Then, to find more local energy minima, new initial guesses with lower symmetry were generated from the minima found with the previous procedure.

Due to the occurrence of mixing of the LUMO with discretized continuum orbitals[26] when ab initio methods with more extended basis sets are employed, the atomic $\sigma^*_{\mathrm{Cl-C}}$ contributions to the π^* LUMO were evaluated with a simple (Hückel-type) LCBO approach.[27]

Results and Discussion

Molecular Conformations. The total energies of the most stable geometries of the neutral molecules were obtained with

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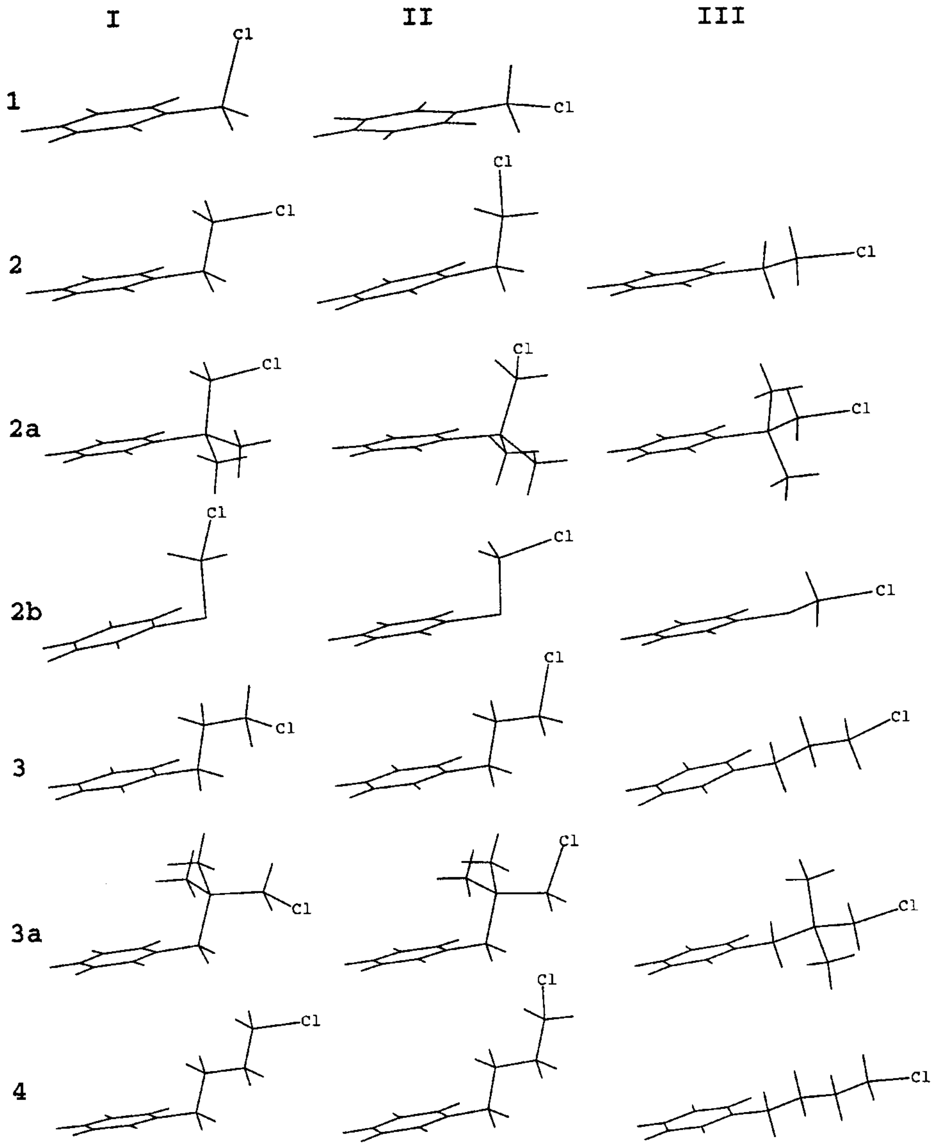

Figure 1. Representation of the most stable conformations, as obtained by B3LYP/6-31G* calculations.

Table 1. B3LYP/6-31G* Relative Energies (kJ/mol) of the Most Stable Conformers (Sketched in Figure 1).

	conformer	Δ*E* (kJ/mol)		conformer	Δ*E* (kJ/mol)
1 $C_6H_5{-}CH_2{-}Cl$	II	8.04	**3** $C_6H_5{-}CH_2{-}CH_2{-}CH_2{-}Cl$	III	6.36
	I	0		II	0.33
2 $C_6H_5{-}CH_2{-}CH_2{-}Cl$	III	9.28		I	0
	II	4.87	**3a** $C_6H_5{-}CH_2{-}Si(CH_3)_2{-}CH_2{-}Cl$	III	17.54
	I	0		II	0.76
2a $C_6H_5{-}Si(CH_3)_2{-}CH_2{-}Cl$	III	3.43		I	0
	II	2.68	**4** $C_6H_5{-}CH_2{-}CH_2{-}CH_2{-}CH_2Cl$	III	6.31
	I	0		II	1.03
2b $C_6H_5{-}S{-}CH_2{-}Cl$	III	15.99		I	0
	II	10.03			
	I	0			

B3LYP calculations using the 6-31G* basis set. The molecular conformations lying within 20 kJ/mol from the ground state (except for compound **3**, where a fourth minimum with a relative energy of 6.68 kJ/mol was found) are sketched in Figure 1. The relative energies are reported in Table 1. As a test, we carried out preliminary calculations on thioanisole where HF/6-31G* calculations predict a conformer with the $S{-}C(H_3)$ bond out of the ring plane to be more stable than that with the S−C bond in the ring plane, in contrast with photoelectron spectroscopy data.[28] The present B3LYP calculations correctly predict the planar conformer to be the most stable.

In benzyl chloride (**1**), for the dihedral angle determined by the C−Cl bond and the ring plane there are only two minima, one at 90° (i.e., the conformer where σ^*/π^* mixing is maximum) and one at 0°, the energy of the latter (planar) conformer being 8.04 kJ/mol higher.

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Table 2. VAEs (eV) Measured in the ET Spectra and Peak Energies (eV) and Relative Anion Currents Measured in the DEA Spectra.

	ETS		DEAS (total anion current)		
	VAEs	(fwhm)	peak energy	int. rel. to C_6H_5–Cl	int. %
C_6H_5-Cl [a]	2.44				
	0.75	(0.59)	0.75	1	5.7
1	2.8				
$C_6H_5-CH_2Cl$ [a]	1.05		$1.0_{sh.}$	11.49	
	0.65	(0.65)	0.52	17.68	100
2	2.7				
C_6H_5-$(CH_2)_2Cl$ [a]	0.87	(0.63)	0.76	0.94	5.3
2a	2.4−3.3				
$C_6H_5-SiMe_2CH_2Cl$	0.97		$0.9_{sh.}$	1.36	
	0.55	(0.35)	0.44	2.06	11.7
2b	<3.6				
$C_6H_5-SCH_2Cl$	2.18				
	0.90		0.7	2.61	
	0.36	(0.18)	0.2	4.35	24.6
3	2.65				
C_6H_5-$(CH_2)_3Cl$	0.95	(0.60)	0.9	0.084	0.48
3a	3.0				
$C_6H_5-CH_2SiMe_2CH_2Cl$	0.91	(0.6)	0.82	0.62	3.5
4	2.6				
C_6H_5-$(CH_2)_4Cl$	1.00	(0.60)	1.0	0.065	0.37
$H_2C{=}CH-CH_2Cl$	1.01	(0.85)	0.79	6.42	36.3
$CH_3(CH_2)_3Cl$ [a]	2.39	(1.8)	1.4	≤ 0.006	≤0.03
$(CH_3)_3CCl$ [a]	1.80	(1.2)	1.54	0.093	0.52

[a] Taken from ref 11.

In the most stable conformer of 1-chloro-2-phenylethane (**2**) the ethane C atoms and the Cl atom lie in a plane perpendicular to the ring, with the Cl atom and the ring in a trans arrangement (see conformer I in Figure 1). Rotation of about 120° around the C−C bond (which puts a hydrogen atom in this plane instead of the chlorine atom, conformer II) causes an energy increase of 4.9 kJ/mol. The conformer (III) with the C and Cl atoms in the plane of the ring has an even higher (9.3 kJ/mol) energy. Similar results are obtained for the silicon analogue **2a**, although the energy gaps among the three conformers are smaller, whereas in the sulfur derivative **2b** the relative energy of the first two conformers is reversed.

In the two most stable (and close in energy, see Table 1) conformers of 1-chloro-3-phenylpropane (**3**) and of 1-chloro-4-phenylbutane (**4**) all the alkyl C atoms lie in a plane perpendicular to the ring plane. In the next two higher-lying (more than 6 kJ/mol) conformers, the alkyl C skeleton lies in the plane of the ring. Analogous results are obtained for the silicon derivative **3a**, where the relative energy of the planar conformation is even higher.

A common feature can be noticed in the optimized geometries; in the most stable conformer of each compound, the first σ bond of the saturated skeleton always forms a dihedral angle of 90° with the benzene ring. This is the crucial requirement for the occurrence of a large σ^*_{Cl-C}/π^* mixing, the orientation of the following σ bonds being less important. In agreement, according to semiempirical PM3 calculations on compounds **2** and **2b**, the chlorine contributions to the π^* LUMO are quite close to each other in conformers I and II (which differ in the orientation of the C−Cl bond, see Figure 1), whereas essentially no chlorine character is predicted for the LUMO of the planar conformer (III).

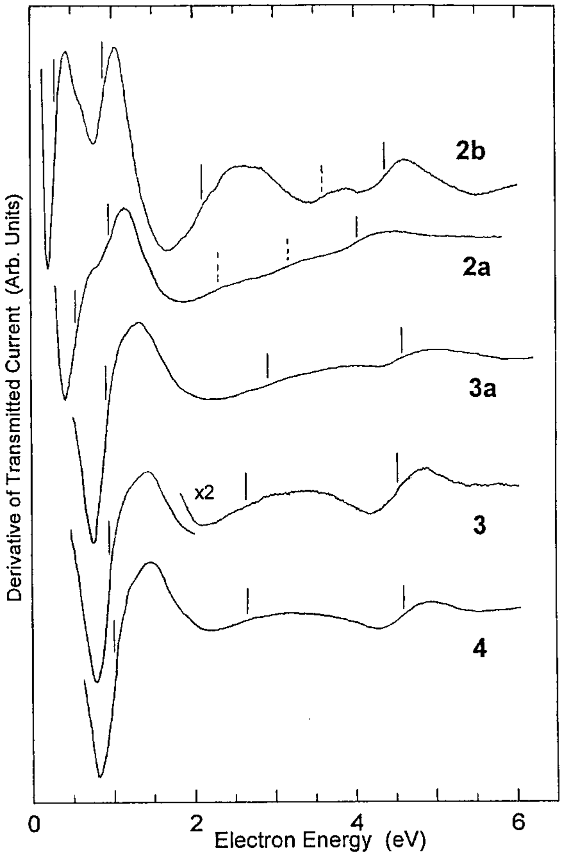

Figure 2. Derivative of transmitted current, as a function of electron energy, in compounds **2b**, **2a**, **3a**, **3**, and **4**. The vertical lines locate the VAEs.

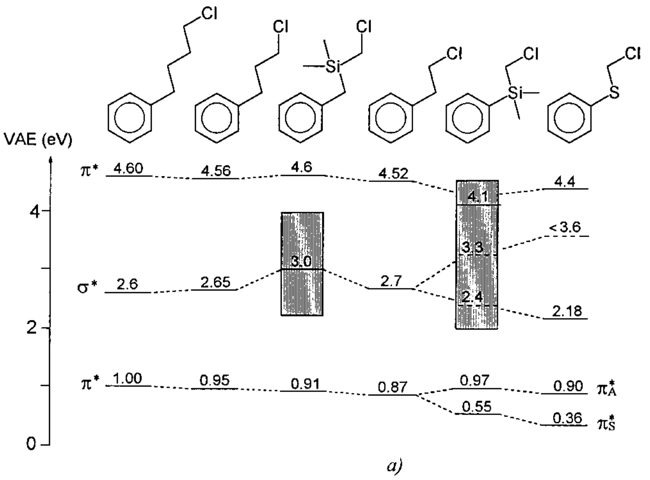

Figure 3. Diagram of the VAEs measured in the ET spectra of **4**, **3**, **3a**, **2**, **2a** and **2b**. a) VAEs taken from ref 11.

ET Spectra. Figure 2 reports the ET spectra in the 0−6 eV energy range of the silyl (**2a**) and thio (**2b**) derivatives of 1-chloro-2-phenylethane, 1-chloro-3-phenylpropane (**3**), its silyl derivative **3a**, and 1-chloro-4-phenylbutane (**4**). The measured VAEs are given in the correlation diagram of Figure 3 and in Table 2.

The ET spectra of **3** and **4** are similar to that of **2**, where the first resonance is due to the unresolved contributions of both the symmetric (π^*_S) and antisymmetric (π^*_A) components of the benzene e_{2u} LUMO, in agreement with unrestricted Hartree−Fock and DFT/B3LYP calculations.[11] The main difference on going from **2** to **4** seems to be a gradual small shift to higher energy of the center of the resonance (see Figure 3), consistent with the increasing length of the alkyl chain and consequent attenuation of the electron-withdrawing inductive effect exerted by the chlorine atom on the benzene ring.

In the ET spectrum of (chloromethyl)dimethylphenylsilane (**2a**), the analogue of **2** where the CH_2 group attached to the ring is replaced by a $Si(CH_3)_2$ group, the two lowest π^* resonances are well resolved in energy. Mixing with the lowest empty σ^* orbital localized at the (out-of-plane) Si−C bond causes a stabilization of the benzene π^*_S anion state (VAE = 0.55 eV) 0.1 eV greater than in benzyl chloride (**1**),[9,29] thus indicating the possibility of a relatively large coupling between the π^* LUMO and the empty σ^* MO with mainly Cl character through the Si−C bond. The σ^*_{Cl-C} and σ^*_{Si-C} resonances (tentatively located at 2.4 and 3.3 eV, respectively) give rise to a broad and unresolved signal starting at about 2 eV.

In the ET spectrum of the corresponding thio derivative **2b**, phenylchloromethyl sulfide, the first σ^* resonance is well resolved and lies at lower energy (VAE = 2.18 eV) with respect to **2a**. In agreement, the σ^* resonance displayed in the ET spectrum of thioanisole[30] is significantly lower in energy (VAE = 2.70 eV) and narrower than in trimethylsilylbenzene.[21] Consistently, in the sulfur derivative **2b** the extent of σ^*/π^* mixing, as evaluated from the stabilization of the π^*_S anion state (VAE = 0.36 eV), is larger than in the silicon analogue **2a**.

The ET spectrum of **3a**, the analogue of 1-chloro-3-phenylpropane (**3**) where the central CH_2 group is replaced by a $Si(CH_3)_2$ group, displays a single unresolved resonance at low energy (centered at 0.91 eV). The π^*_S anion state thus lies at about 0.3 eV higher energy with respect to **2a,** where the silicon atom is adjacent to the π-system. The sizable reduction of the stabilizing effect when the silicon atom is placed in a β position is in line with the VAEs measured in the $-Si(CH_3)_3$ and $-CH_2Si(CH_3)_3$ derivatives of benzene,[21,29] thiophene, and furan[31] and was ascribed[31] to a larger localization at the silicon atom of the empty σ^* (Si−C) MOs.

At higher energy, a broad signal centered at 3.0 eV is due to the unresolved contributions of the σ^*_{Cl-C} and σ^*_{Si-C} MOs.

DEA Spectra. Figure 4 displays the total yield of negative ions measured at the collision chamber in compounds **2**−**4**, **2a**, **2b**, and **3a**, as a function of the incident electron energy, in the 0−4 eV energy range. Although the negative ion current at the walls of the collision chamber can, in principle, be affected by spurious trapped electrons, these measurements are more reliable with respect to the current detected through the mass filter because of kinetic energy discrimination in the anion extraction efficiency in the latter experiment. In a previous test[32] with normal and branched monochloro alkanes our relative total anion currents reproduced to within 1% the ratios in the absolute cross sections found by Pearl and Burrow.[6] The peak energies and intensities relative to chlorobenzene (evaluated from the peak heights under our experimental conditions, with the same electron beam intensity and the same pressure reading for all the compounds) are given in Table 2. Mass analysis revealed that, except for the thio derivative **2b** (see below), the total anion current is essentially due only to the Cl^- fragment.

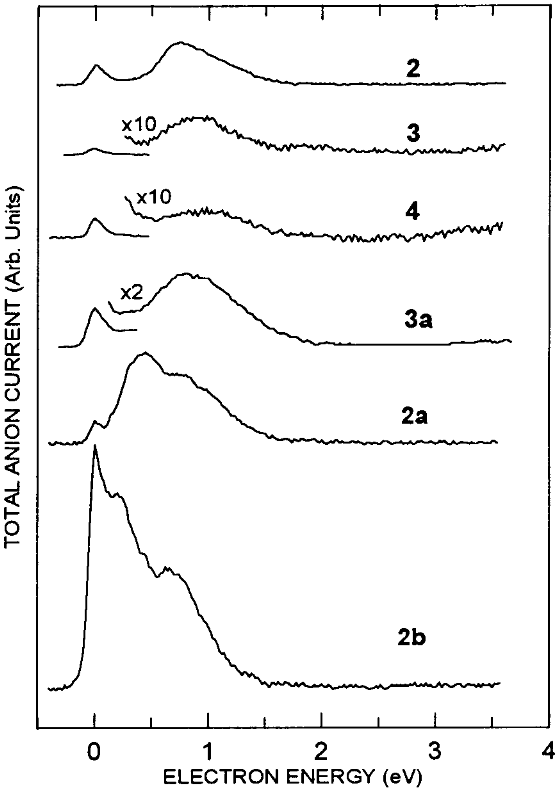

Figure 4. Total anion current, as a function of the incident electron energy, in compounds **2-4**, **2b**, **2a**, **3a**.

The zero-energy signals in the DEA spectra are attributed to the low-energy wing of the first resonance, owing to the inverse energy dependence of the electron attachment cross section[33] which causes the yield to climb at zero energy, although some contribution from traces of impurities cannot be excluded. In compounds **1**−**4** the energy of the first peak is slightly shifted to lower energy with respect to the corresponding VAE measured in the ET spectra (see Table 2). This shift is well understood in terms of the shorter lifetime and of the larger distance from the crossing between the anion and neutral potential curves for the high-energy side of the resonance.[34] In these compounds, in contrast to the saturated chloroalkanes,[4] the shifts are small (~0.1 eV), indicating that the lifetime of the temporary π^* anion states is sufficiently long to allow the nuclei to reach the separation at which dissociation of the C−Cl bond can occur.

On going from benzyl chloride to **2** and **3** each CH_2 group added to the alkyl chain causes a reduction of 1 order of magnitude in the Cl^- fragment current (see Table 2). The effect produced by a fourth CH_2 group is smaller: on going from **3** to **4** the negative current decreases by only 1.3 times. In 1-chloro-4-phenylbutane (**4**) the Cl^- production is 270 times smaller than in benzyl chloride, but still 1 order of magnitude larger than in 1-chlorobutane (where the Cl^- current peaks at 1.4 eV,[4] see Table 2). Thus, even in **3** and **4** the contribution from direct dissociation of the σ^* resonance (VAE = 2.6 eV) is very small and hidden by the high-energy wing of the π^*

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signal centered at about 1.0 eV. The observed reduction of Cl^- production with increasing length of the alkyl chain is consistent with the exponential decay of the charge-transfer rate predicted for through-bond interactions between localized π^* and σ^* orbitals.[35]

The Cl^- production in the $C_6H_5(CH_2)_nCl$ series can be compared with that observed by Moore and co-workers[10] in the corresponding ethene derivatives $H_2C{=}CH(CH_2)_nCl$, where the (percent) relative intensities [100 ($n = 1$), 6.22 ($n = 2$), 0.55 ($n = 3$), 0.42 ($n = 4$)] are surprisingly close to those found here in the corresponding benzene derivatives (100, 5.3, 0.48, 0.37, see last column of Table 2). It is to be noticed, however, that in the benzene derivatives the absolute Cl^- yields are higher. In allyl chloride ($n = 1$, see Table 2) we find the anion current to be 2.75 times smaller (36.3%) relative to that in benzyl chloride (**1**), in very good agreement with literature data.[9] A second difference between the two series is that in compounds **2**−**4** the benzene π^*_S and π^*_A MOs are nearly degenerate in energy, so that the measured negative current is due to the unresolved contributions of two π^* resonances. In fact, the DEA spectra of 4-haloanisoles (where the LUMO is the π^*_A MO) and of 4-halopyridines show[12] that the maximum halogen anion yield occurs close in energy to the lowest π^* resonance, regardless of its symmetry. On the other hand, in the DEA spectra of compounds **2a** and **2b** (see Figure 4) the shoulder at 0.9 eV and the maximum at 0.7 eV, respectively, clearly demonstrate that the π^*_A resonance also follows a dissociative decay channel.

The DEA spectra of **2a** and **2b**, the analogues of **2** where the carbon atom attached to the ring is replaced by a silicon or sulfur atom, display the first maximum (excluding the zero-energy signal) at 0.44 and 0.2 eV, respectively, following the energy trend of the π^*_S resonance observed in the ET spectra. The intensity increase of the negative current in **2a** and **2b** relative to that in **2** (more than 2 times and more than 4 times larger, respectively, see Table 2) support the above-mentioned expectation of increasing π^*/σ^*_{Cl-C} coupling with decreasing energy of the intermediate empty σ^* orbitals.

The increase of the dissociative electron attachment cross section is even larger on going from **3** to the silicon derivative **3a**, where the Cl^- yield is 7 times more abundant with respect to that for the alkyl counterpart and of the same order of magnitude as that of **2**.

As noted above, the total anion current measured in **2b** is about twice as large as that in **2a**, so that replacement of carbon atoms with sulfur (rather than silicon) atoms in the alkyl skeleton would seem to be a better choice for enhancing the rate of intramolecular electron transfer. However, mass analysis through a quadrupole filter showed that in **2b**, in contrast to the other compounds considered, Cl^- is not the only negative species generated by dissociative electron attachment. About 71% of the signal detected around 0.2 eV comes from the Cl^- fragment (with a maximum at 0.23 eV and a shoulder at 0.7 eV), but the remaining current (see Figure 5) is due to the SCH_2Cl^- and $C_6H_5S^-$ fragments, which involve cleavage of each the S−C bonds. This proneness to dissociation of the S−C bonds, as well as of S−S bonds in di- and trisulfides,[36] upon addition of slow electrons is of course an unwanted effect and suggests possible damage to materials with thioalkyl chains under conditions of excess negative charge.

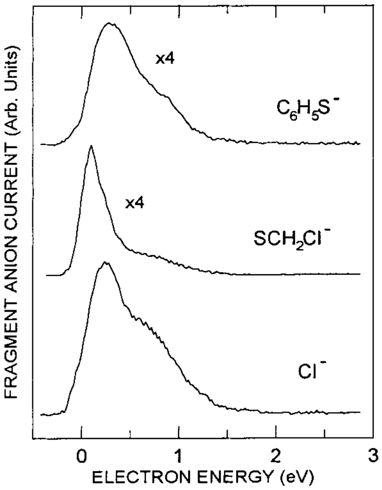

Figure 5. Mass-selected anion currents, as a function of the incident electron energy, in $C_6H_5SCH_2Cl$.

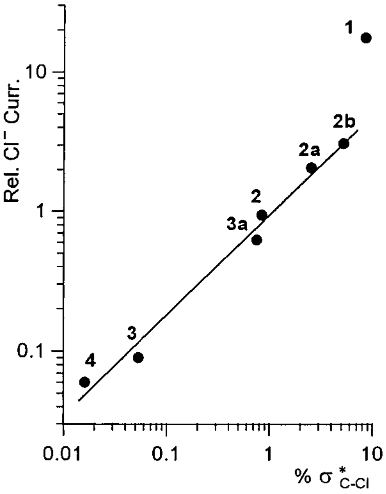

Figure 6. Relative Cl^- yields as a function of the percent of σ^*_{Cl-C} character of the π^* LUMO, as supplied by Hückel-type calculations.

Figure 6 correlates (on a logarithmic scale) the relative Cl^- intensities associated with the first π^* resonance to the (percent) σ^*_{Cl-C} character of the LUMOs in the neutral molecules, that is, with the extent of π^*_S/σ^*_{Cl-C} coupling. For **2b** only the Cl^- contribution (71%, as evaluated from the mass spectroscopy analysis) to the total anion current was considered. Evaluation of the σ^*_{Cl-C} participation was obtained with a simple (Hückel-type) LCBO approach,[27] applied to the interaction among the π^*_S and the σ^* bond orbitals. Direct through-space interaction between the benzene ring and the chlorine atom is assumed to be negligible, in line with studies[37] on long-range electron transfer. The following Coulomb integrals (A), derived from the experimental VAEs of reference molecules, were used: $A(\pi^*) = 1.0$ eV, $A(\sigma^*_{C-C}) = 5.0$ eV, $A(\sigma^*_{Cl-C}) = 2.5$ eV, $A(\sigma^*_{Si-C}) = 3.3$ eV, $A(\sigma^*_{S-C}) = 2.5$ eV. The resonance integrals $B(\pi^*/\sigma^*) = -0.5$ eV and $B(\sigma^*/\sigma^*) = -1.0$ eV were chosen arbitrarily, but such to account for σ^*/σ^* interactions larger than the interaction between the π^*_S MO and the adjacent out-of-

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[35] Larson, S.; Braga, M. *Chem. Phys.* **1993**, *176*, 367 and references therein.
[36] Modelli, A.; Jones, D.; Distefano, G.; Tronc, M. *Chem. Phys. Lett.* **1991**, *181*, 361.
[37] Paddon-Row, M. N.; Shephard, M. J.; Jordan, K. D. *J. Phys. Chem.* **1993**, *97*, 1743.

plane σ^* MO. The following $\sigma^*_{\mathrm{Cl-C}}$ percentage contributions to the LUMOs were obtained: 8.41 (**1**), 5.198 (**2b**), 2.528 (**2a**), 0.828 (**2**), 0.74 (**3a**), 0.053 (**3**), 0.016 (**4**).

Despite the roughness of this model, not only does the intensity increase monotonically with the calculated $\sigma^*_{\mathrm{Cl-C}}$ character, but except for **1**, the data are also nicely fitted by a linear correlation. The exception of benzyl chloride is expected. Due to direct strong $\pi^*/\sigma^*_{\mathrm{Cl-C}}$ mixing, this molecule does not fit the model of localized weakly (through-bond) interacting orbitals.[35] An analogous different behavior was noted in allyl chloride,[10] the corresponding ethene derivative.

It is to be noticed that the dissociative attachment cross section increases exponentially with the lifetime (with respect to autodetachment of the extra electron) of the temporary molecular anion.[34] In turn, the anion lifetime increases in an inverse fashion with VAE.[6,7] Therefore, other conditions being the same, π^*/σ^* mixing favors the $\mathrm{Cl^-}$ yield not only by increasing the rate of transfer of the π^* electron to the chlorine atom but also by stabilizing the π^* resonance, with consequent increase of its survival time.

Conclusions

This ETS and DEAS study provides the gas-phase empty level structures and the relative $\mathrm{Cl^-}$ fragment anion currents generated by dissociative electron attachment to the π^* LUMO of 1-chloroalkyl benzene derivatives and of related molecules where one carbon atom of the alkyl chain is replaced by a silicon or sulfur atom.

The $\mathrm{Cl^-}$ yield can be used as a probe for the rate of intramolecular electron transfer from the benzene ring (where the electron is first temporarily trapped) to the opposite end of the saturated chain. The fragment anion current rapidly decreases with the length of the alkyl chain, in line with the inefficiency of the C−C bonds to promote coupling between the empty π^* and $\sigma^*_{\mathrm{Cl-C}}$ orbitals, due to the high energy of the intermediate $\sigma^*_{\mathrm{C-C}}$ orbitals. However, the presence of a third-row heteroatom in the saturated chain causes a significantly higher halide anion yield with respect to the corresponding carbon analogues, due to the energy proximity of the $\sigma^*_{\mathrm{Si-C}}$ or $\sigma^*_{\mathrm{S-C}}$ orbitals to the π^* and $\sigma^*_{\mathrm{Cl-C}}$ orbitals and consequent increase of through-bond coupling. Except for benzyl chloride, where strong $\pi^*/\sigma^*_{\mathrm{Cl-C}}$ mixing occurs, a linear correlation is found between the measured $\mathrm{Cl^-}$ current and the extent of $\sigma^*_{\mathrm{Cl-C}}$ character of the π^* LUMO, as determined by simple Hückel-type calculations.

Sulfur substitution causes a larger increase in the $\mathrm{Cl^-}$ yield. However, whereas in the silicon derivatives (as well as in the carbon analogues) $\mathrm{Cl^-}$ is essentially the only negative fragment produced, in the thioderivative analyzed about one-third of the total anion current involves cleavage of the S−C bonds. This suggests possible damage to materials with thioalkyl chains under conditions of excess negative charge. According to the present data, a saturated *molecular wire* whose skeleton is constituted by third-row atoms or, at least, alternate third-row and carbon atoms, enhances the rate of electron transfer between two π-centers, and silicon is a suitable candidate as far as the stability of the material is concerned.

Acknowledgment. We thank the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica, the University of Bologna (Funds for Selected Topics) and the Hungarian Ministry of Education (Grant Number FKFP 0162/1999) for financial support.

JA0203768