coefficients in the 1,3 positions which makes the thienothiophenes good donor molecules for dienophilic reagents.

To summarize, the thienothiophenes are "aromatic" compounds like thiophene. Their high reactivity with respect to 1,3-additions follows from the HOMO energy and structure, as revealed by photoelectron spectroscopy. Thus, the hitherto unavailability of **1** appears to be a consequence of its high reactivity and not of its instability and **2** may be isolable because of a somewhat damped reactivity due to steric interference by the 1,3-phenyl substituents. Strictly speaking, these compounds are "nonclassical" only from the point of view of formal definition and representation.

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(12) These effects (orbital stabilization and charge transfer) are estimated on the basis of simple and well-known perturbational formulas.

(13) The reader is referred to Figure 2. Assuming a symmetrical splitting of the respective occupied subunit b_{3g} orbitals, the b_{3g} orbital of thienothiophene (filled) is expected to be located at $(-7.15 + 1.90)$ eV $= -5.25$ eV. The found lowering of the b_{3g} sulfur lone pair combination is -1.9 eV.

Electron Transmission Studies of the Negative Ion States of Substituted Benzenes in the Gas Phase

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Abstract: Temporary negative ions of benzene, aniline, phenol, anisole, fluoro-, chloro-, and bromobenzene, formed in the gas phase by capture of electrons into the low-lying π^* orbitals, are studied by means of electron transmission spectroscopy. The electron affinities are determined and their relative values are interpreted in terms of resonance and inductive effects.

Negative ions of aniline, phenol, anisole, fluoro-, chloro-, and bromobenzene may be formed in the gas phase by capture of impacting electrons into the low-lying π^* orbitals. As in benzene and the alkyl-substituted benzenes, which we discussed in a previous communication,[1] these anions are short lived and decay by ejecting the electron into the continuum in times of typically 10^{-14} s or less. The formation of these transient anions is observable as sharp variations or "resonances" in the cross section for electron scattering from the neutral molecules. The impact energies at which the resonant structures are observed yield the magnitudes[2] of the gas-phase electron affinities (EA). In this communication we report the electron affinities of the above listed benzene derivatives determined by means of electron transmission spectroscopy (ETS).[3,4]

In Figure 1, we present the electron transmission spectra[5] of benzene, phenol, fluoro-, and chlorobenzene. The structure in the benzene spectrum, which is in good agreement with that found by others,[3b,3c,6] corresponds to the capture of an incident electron into the doubly degenerate $e_{2u}(\pi^*)$ orbital, yielding the X $^2E_{2u}$ ground electronic state of the benzene anion.[7] The lifetime of the anion is sufficiently long that a progression of vibrational levels of the symmetric breathing mode is ob-

served.[8] With substitution on the ring, the degenerate $e_{2u}(\pi^*)$ orbital splits into $b_1(\pi^*)$ and $a_2(\pi^*)$ orbitals.[9] This splitting

$a_2 (\pi^*)$ $b_1 (\pi^*)$
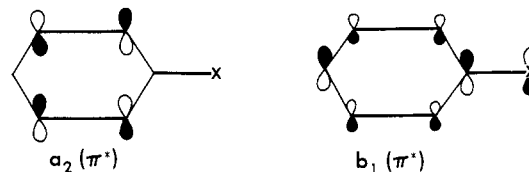
is particularly evident in the transmission spectrum of phenol. Similar results were found in aniline and anisole and the spectra are not shown. As shown below, the $a_2(\pi^*)$ orbital has nodes on the 1 and 4 carbons, while the $b_1(\pi^*)$ orbital does not possess nodes on any of the carbons.

The $-NH_2$, $-OH$, and $-OCH_3$ groups have small positive inductive effects[10] (which stabilize both A_2 and B_1 anion states) and large negative resonance effects[10] (which destabilize the B_1 state). We expect, therefore, that the ground state anions of aniline, phenol, and anisole will be slightly more stable than the ground state of $C_6H_6^-$ and will be of A_2 symmetry. On the other hand, the second anion states denoted by $\tilde{A}^2B_1$ should lie well above the $C_6H_6^-$ ground state. The
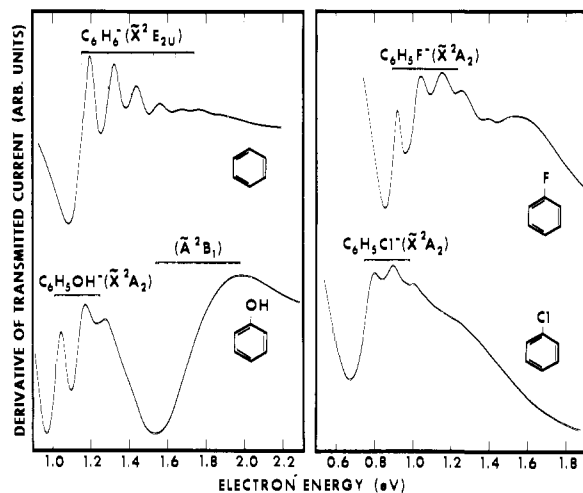
Figure 1. The derivative of the transmitted current as a function of electron impact energy in benzene, phenol, fluoro-, and chlorobenzene.

Figure 2. Correlations between the EA's and IP's of monosubstituted benzenes.

electron transmission spectra illustrate nicely the role of inductive and resonance contributions to anion stabilities. While the first EA of benzene is -1.15 eV, the first two EA's are -1.13 and -1.77 eV for aniline, -1.01 and -1.81 eV for phenol, and -1.00 and -1.63 eV for anisole. The $\tilde{X}\,^2A_2$ states of $C_6H_5OH^-$ and $C_6H_5OCH_3^-$ are lower than that of $C_6H_5NH_2^-$, corresponding to the greater inductive effects of the -OH and -OCH$_3$ groups relative to the -NH$_2$ group. The $\tilde{A}\,^2B_1$ state of $C_6H_5NH_2^-$ lies above those of $C_6H_5OH^-$ and $C_6H_5OCH_3^-$, consistent with the greater resonance contribution of the -NH$_2$ group. These symmetry assignments were confirmed for phenol by means of a SCF–MO calculation.[11] The ground states of the temporary anions exhibit well-defined vibrational structure,[12] thus allowing an accurate determination of the adiabatic EA's of each of the gases.[13] The excited states of the anions are apparently shorter lived and do not display measurable vibrational structure. We characterize the energy of these states by that of the midpoint of the structure. This energy corresponds to the negative of the vertical EA.

Although the fluoro, chloro, and bromo substituents also possess positive inductive and negative resonance effects,[10] induction is considerably more important for the halogens than for -NH$_2$, -OH, and -OCH$_3$. We expect, therefore, that the ground-state anions of C_6H_5F, C_6H_5Cl, and C_6H_5Br will be significantly stabilized relative to the $C_6H_6^-$ ground state. This is indeed the case. The first EA's for these three halobenzenes are -0.89, -0.75, and -0.70 eV, respectively. The latter two values are in good agreement with those reported by Nenner and Schulz[3c] using ETS.[14] The energies of the second anion states of the halobenzenes cannot be determined accurately from our transmission data. The lifetimes of these states appear
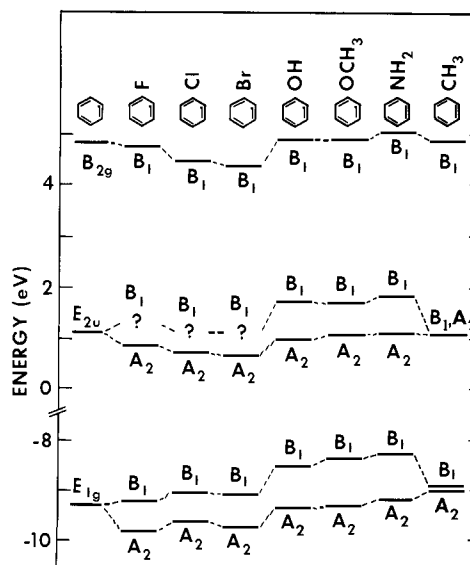
to be substantially shorter than those of the ground states and the associated spread in energy is sufficiently large to mask the splittings, which we anticipate to be $\sim$0.2–0.4 eV. A portion of the structure ascribed to a second anion state appears most visibly in C_6H_5F. With C_6H_5Cl this feature appears to broaden and disappears completely in C_6H_5Br. The spectra also suggest a progressive shortening in lifetime of the ground-state anions along the substituent sequence F, Cl, and Br.

Dissociative attachment under electron impact according to the reaction

$$C_6H_5X + e^- \rightarrow C_6H_5X^- \rightarrow C_6H_5 + X^-$$
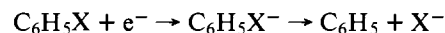
is energetically possible for C_6H_5Cl and C_6H_5Br throughout the range of electron energies employed in our investigation.[15] Experimental studies[16] have been performed which show that the Cl$^-$ and Br$^-$ production is maximum near electron energies of 0.86 and 0.84 eV, respectively. We suggest that dissociative attachment will proceed primarily from the $\tilde{A}\,^2B_1$ states rather than the $\tilde{X}\,^2A_2$ states, since the $b_1(\pi^*)$ orbital is antibonding between the halogen and the ring. It is important to note that the short lifetimes (10^{-15} s) of $C_6H_5Cl^-$ and $C_6H_5Br^-$ are due to electron autodetachment and not to dissociative attachment, which takes place on a longer time scale.

To summarize our results, in Table I we list the electron affinities of the molecules studied in this paper. For comparative purposes we have listed our earlier results for toluene.[1] We have also included the third electron affinities associated with capture of an electron into the $b_1(\pi_3^*)$ orbitals of the

Table I. Electron Affinities (eV) of Benzene and Monosubstituted Benzenes

Compound	First EA $(\pi_1^*)^a$	Second EA $(\pi_2^*)^b$	Third EA $(\pi_3^*)^b$
Benzene	-1.15	-1.15 (degenerate)	-4.85
Fluorobenzene	-0.89	Not observed	-4.77
Chlorobenzene	-0.75	Not observed	-4.50
Bromobenzene	-0.70	Not observed	-4.42
Phenol	-1.01	-1.73	-4.92
Anisole	-1.09	-1.72	-4.92
Aniline	-1.13	-1.85	-5.07
Toluene^c	-1.11	No splitting	-4.88

^{a} Determined from the zeroth vibrational level of the ion. The error in these values is less than ±0.05 eV. ^{b} Vibrational structure is not observed in the second and third negative ion states. The energies are determined from the center of the structure in the cross section. The error in these values is estimated to be ±0.08 eV. ^{c} Reference 1.

substituted benzenes and the $b_{2g}(\pi_3{}^*)$ orbital of benzene.[3b] For each of the molecules studied, the third electron affinity lies between -4.45 and -5.12 eV. The relative positions are in accord with our earlier discussion of inductive and resonance effects.

To provide an overview of the effects of substitution on the unfilled as well as filled orbitals, we present in Figure 2 a correlation diagram of the anion and cation states. For the latter, the splitting of the $e_{1g}(\pi)$ orbital of benzene into the $b_1(\pi)$ and $a_2(\pi)$ orbitals has been the subject of several investigations[17] employing photoelectron spectroscopy. We have not indicated the positions of the third π ionization potentials since, for some of the substituted benzenes, the assignment is still open to question.

These studies indicate that ETS provides a complement to photoelectron spectroscopy in yielding information about the shifts of levels due to substituent effects. Although the shifts in anion energies can be interpreted in terms of the same concepts invoked for cation states, the variations in anion lifetime are poorly understood and warrant further investigation.

Acknowledgment. We acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(12) The vibrational spacing of the ground state anions of C_6H_5OH, $C_6H_5OCH_3$, $C_6H_5NH_2$, C_6H_5F, C_6H_5Cl, and C_6H_5Br is 120, 125, 120, 115, 125, and $\sim$125 meV, respectively. Of the modes which are energetically possible, we favor the $a_2(\nu_{17a})$ ring puckering vibration. The excitation of this mode is consistent with the charge distribution of the $a_2(\pi^*)$ orbital.
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(14) I. Nenner and G. J. Schulz reported only a bound for the EA of C_6H_5F of >-1.0 eV.
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On the Development of Quantum Mechanical Solvent Effect Models. Macroscopic Electrostatic Contributions

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Abstract: Identification of the various kinds of interactions that are expected between a molecule and its environment is carried out and a model for the estimation of macroscopic electrostatic solvent effects using ab initio quantum mechanics is presented. Evaluation of all integrals in closed form when a spherical Guassian basis set is employed is shown to be possible and initial applications to CH_4, C_2H_6, C_3H_8, and n-C_4H_{10} in a n-hexane solvent are described. The need for inclusion of an additional potential to constrain the electrons within a sphere is described. It is shown how this constraining potential may be chosen to minimize the effect on the calculated interaction energy, while achieving the desired goal of constraining the electrons. Also, a strong dependence on choice of sphere radius is noted. Finally, the analysis necessary for inclusion of such a solvent effect model into a semiempirical formalism is described.

Interactions among molecular species clearly form one of the dominant and most pervasive preoccupations of chemists. However, not only the making and breaking of chemical bonds, but the effect of the environment on the physical and chemical properties of nonreactive systems, where lesser magnitude forces typically are involved, requires a detailed description of intramolecular interactions. Hence, the desirability of developing general approaches that will allow discussion of the various possible intermolecular interactions is self-evident.

In spite of the obvious need for such capabilities, previous approaches to the problem[1-23] have typically required serious approximations to be made, either in the model itself or in the techniques used to evaluate the model, so that computational