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# INFLUENCE OF ALKYL SUBSTITUENTS ON THE $\pi^*$ NEGATIVE ION STATES OF BENZENE AND ITS DERIVATIVES

## ELECTRON TRANSMISSION SPECTROSCOPY OF *p*-ALKYLANILINES

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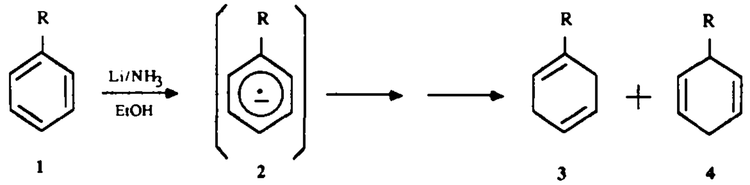
**Abstract**—Electron affinities and electron attachment energies associated with the $\pi^*$ orbitals of several *p*-alkylanilines (alkyl = Me, Et, i-Pr, and t-Bu) have been determined in the gas phase by electron transmission spectroscopy and have been analyzed by *ab initio* molecular orbital calculations at the STO-3G and 6-31G levels of basis set. The results lead to the conclusions that (a) the $^2A_2$ negative ion state in toluene lies below the $^2B_1$ state, (b) the $^2A_2$ state is stabilized in toluene relative to benzene by bonding overlap between the *ortho* carbon ($C_2(2p_z)$) and the Me H(1s) orbitals in the LUMO, (c) the $^2B_1$ state is stabilized on adding Me groups to toluene to form t-butylbenzene through reduced antibonding interactions between $C_1(2p_z)$ and Me $C(2p_z)$ orbitals, and (d) the lowest resonance in t-butylbenzene is extensively overlapped with the second resonance and may involve strong mixing of the $^2A_2$ and $^2B_1$ states.

## INTRODUCTION

Radical anions of alkylbenzenes (1) have generated considerable interest, both from an experimental and a theoretical standpoint. These species are key intermediates in the widely used Birch reduction of aromatic rings (Eq. 1) and the stability of the various negative ion (or radical-anion) states (2) involved in these reactions strongly influences both the rate and the regioselectivity (i.e. the ratio 3 : 4) of this reaction.



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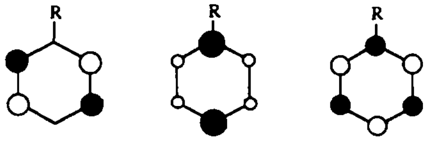
Some years ago Krapcho and Bothner-By determined that the rate of reduction of alkylbenzenes (Eq. 1) decreased in the order R = H > Me > Et > i-Pr > t-Bu by a factor of 20 over the complete range.[1] These results were subsequently reflected more or less quantitatively by ESR studies of Lawler and Tabit, who determined the relative adiabatic electron affinities ($EA_a$) of benzene and alkylbenzenes on reduction with Na–K alloy in tetrahydrofuran (THF)–dimethoxyethane (DME) at −100°.[2] These authors found the EA of 1 to decrease in the order H > Me > Et > i-Pr > t-Bu by a factor of 110, corresponding to a $\Delta EA_a$ of 0.07 eV, over the complete range.

It was initially believed that solvation and ion pairing effects do not play a role and that these EAs were a good approximation of the corresponding gas phase values.[3] However, several subsequent studies have forced a change in this view. Most significantly, Jordan *et al.* found by electron transmission spectroscopy (ETS) that the corresponding gas phase $EA_a$s of 1 follow *exactly the opposite* order of the solution values, i.e. t-Bu > i-Pr > Et > Me > H, covering a total range of 0.09 eV.[3] This reversal in order was supported by subsequent studies of Stevenson *et al.*, who found that the enthalpy of solvation of $(K^+)_g + (2,6\text{-di-t-butylnaphthalene}^{\bar{\cdot}})_g$ in DME was about 17 kcal mol$^{-1}$ less exothermic than that for $(K^+)_g + (\text{naphthalene}^{\bar{\cdot}})_g$.[4] This difference was attributed to steric inhibition of solvation and (possibly) ion association by the t-Bu groups.

A minor diene product is sometimes found in the Birch reduction of alkylbenzenes. Benkeser *et al.* reported the formation of 6% 3-t-butyl-1,4-cyclohexadiene (4, R = t-Bu) when Na was employed (Eq. 1).[5] We have confirmed this result with Li. Other data of Benkeser *et al.* suggest that larger values of 3 : 4 are obtained as R becomes smaller (e.g. i-Pr and Et).[5]

These results are consistent with a number of ESR studies which indicate that alkyl substitution favors occupation of the $\pi^*(2a_2)$ orbital‡ over the $\pi^*(3b_1)$ orbital‡ in the radical anions of alkylbenzenes.[6] These



$\pi^*(2a_2)$ $\pi^*(3b_1)$ $\pi^*(4b_1)$

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‡ These $C_{2v}$ symmetry classifications are, strictly speaking, only valid when R (e.g. $CH_3$) is rapidly rotating (spherically symmetrical) on the time scale of the experiment, and do not apply to instantaneous conformations. With this caveat in mind we will continue to use these classifications, which refer to the $\pi^*$ orbitals in $C_{2v}$ benzene.

orbitals are degenerate in benzene, but this degeneracy is split on alkyl substitution. However, the ESR spectrum of the radical anion is not that of a pure $^2A_2$ state since the $^2B_1$ state can contribute through thermal averaging with the $^2A_2$ state and these two states can mix through vibronic coupling.[7] Ihrig *et al.* have estimated that the ESR spectrum of toluene$^{\dot{-}}$ is about 20% $^2B_1$ and 80% $^2A_2$ in character at −95° and that about half of this distribution results from vibronic interaction and the rest from thermal population of excited states.[8] This proportion of vibronic interaction generally agrees with previous theoretical treatments of de Boer and Colpa[6b] (74–88% $^2A_2$), Hobey[7a] (92% $^2A_2$), and Purins and Karplus[7b] (88% $^2A_2$). However, Jones *et al.* have suggested that these theoretical treatments underestimate the extent of vibronic interaction and have calculated that the $^2B_1$ vibronic mixing term contributes 17% to the ground state.[6d]

An interesting aspect to the ESR spectra of alkylbenzenes (1) is the observation that the absolute values of the hyperfine coupling constants for the *ortho* protons are usually smaller than those for the corresponding *meta* protons and this difference decreases in the order R = Me > Et > i-Pr > t-Bu.[6] Although this trend has been observed by a number of workers, it has not been dealt with theoretically, although Hobey has suggested that it may be caused by mixing with higher-energy ring configurations.[7a]

There are several important problems which are raised in this brief introduction, some of which have already been settled. It now seems clear that (a) larger alkyl groups decrease the EA in solution due to steric hindrance to solvation and/or ion pairing but increase it in the gas phase, and (b) the $^2A_2$ state lies below the $^2B_1$ state in solution. However, important questions remain unanswered. (c) Why is the EA increased by alkyl groups in the gas phase? (d) Which is the lower energy state ($^2A_2$ or $^2B_1$) in the gas phase? Several authors have discussed the possibility that the relative energies of these states may be reversed in the gas phase relative to solution.[3,9] (e) More specifically, what are the effects of larger alkyl groups on each of these negative ion states in the gas phase and what are their origins?

## ELECTRON TRANSMISSION SPECTROSCOPY

We have employed the technique of electron transmission spectroscopy (ETS) to study this problem as it relates to negative ion states in the gas phase.[10] In this experiment, a monoenergetic beam of electrons (FWHM = 20–50 meV) is passed through a static sample in the gas phase. The electrons then enter a retarding region where a variable potential prevents a portion of the scattered electrons from reaching the collector. The ET spectrum is plotted as the derivative of the transmitted current vs electron energy. At certain energies sharp variations in the electron-scattering cross section, and especially in the derivative of the transmitted current, can be seen.

These variations, as well as the actual scattering events (which occur on a time scale of $10^{-12}$–$10^{-15}$ s) are called "resonances". They result from the capture of an electron by an orbital angular momentum barrier to form an unbound temporary negative ion state. If the lifetime of this state approaches the time required for certain vibrations, then "vibrational structure" can be observed in the resonance. The center of the resonance is taken as the vertical midpoint between the minimum and maximum of the first derivative curve. The corresponding energy is termed the electron "attachment energy" (AE). This value, which is always positive, is usually taken to be the negative of the "vertical electron affinity" ($EV_v$) associated with a particular orbital. Note that positive EAs cannot be determined by ETS. The AE of the first vibrational feature in a resonance (when it can be observed) is termed $AE_a$ and is taken to be the negative of the adiabatic electron affinity ($EA_a$). The theoretical foundations of electron–molecule collisions have not been dealt with to a significant extent beyond diatomics (e.g. $N_2$)[11] and much theoretical work remains to be done.

As in photoelectron spectroscopy, current practice is to assume the validity of the relative form of Koopmans' approximation in ETS. This relationship (Eq. 2) equates the negative of the

$$\Delta\varepsilon_i = -\Delta IE_{v,i} \text{ (or } -\Delta EA_{v,i}) \qquad (2)$$

change in the vertical ionization energy ($\Delta IE_v$) (or $\Delta EA_v$) upon substitution with the change in the energy of the appropriate SCF orbital (*i*) of the neutral molecule ($\Delta\varepsilon_i$).[12] We have recently shown[13] that Koopmans' theorem is just as valid for the *relative* energies of $\pi^*$ negative ion states as it is for *relative* $\pi$ positive ion states at the 6-31G[14] level of basis set, but *not* at the less diffuse STO-3G[15] or the more diffuse 6-31+G*[16] levels. Therefore, calculations are expected to be most reliable in a relative sense for split valence basis sets such as 6-31G.

In this paper we shall discuss our results in terms of attachment energies (AEs). Not only do changes in AEs parallel changes in orbital energies, but this terminology may avoid confusion caused by the term "electron affinity", which has historically referred to the energy difference between the ground state and the relaxed first negative ion state.

## EXPERIMENTAL

*Materials.* Compounds **5–9** were purchased from Aldrich Chemical Co. Milwaukee, WI, U.S.A. The purification of **5** was effected by GLPC on a 1 m 20% silicone SE-30 on 100/120 mesh Chromosorb P column. Compound **6** was recrystallized from hexane/ether, whereas **7** and **8** were used without further purification. *p*-t-Butylaniline (**9**) was prepared by the reduction[17] of *p*-t-butylnitrobenzene[18] and was purified by GLPC on the above-mentioned column.

*Electron transmission spectroscopy.* As mentioned above, a variable potential in the retarding region of the spectrometer prevents a portion of the scattered electrons from reaching the collector. If the potential barrier is sufficiently high (high-rejection conditions), then essentially all of the scattered electrons will be rejected and the transmitted current will be a measure of the total scattering cross-section. On the other hand, if no potential barrier is employed (low-rejection conditions), then all of the electrons except a small portion which are backscattered (i.e. elastically scattered into a cone centered around a 180° scattering angle) will be collected. This measurement provides a differential scattering cross-section.[19] We routinely obtain our ETS data under both high- and low-rejection conditions. Although high-rejection spectra are normally published, the corresponding low-rejection spectra often contain valuable and unique information.

In this paper we primarily discuss AEs derived from low-rejection spectra. Under these conditions the $^2A_2$ and $^2B_1$ states of the alkyl-substituted anilines appear as distinct resonances. In contrast, these resonances are typically barely discernible as discrete features in the high-rejection spectra.

The resonance profile differences can be principally attribute to two factors.[19] First, the resonances are superimposed on a falling background in the low-rejection spectra whereas the retarding cusp causes the background to be more constant under high-rejection conditions. Second, the relative profiles may appear to be different in the total and differential scattering cross-section of resonances arising from the capture of electrons by orbitals possessing dissimilar angular momentum components ($a_2$: $l = 3,2$; $b_1$: $l = 2,1$) due to constructive and destructive interference between the resonant and background partial waves. Despite the enhanced visibility of the alkyl-substituted aniline $^2A_2$ and $^2B_1$ resonances in the low-rejection spectra, there is still some overlap of the two resonances.

The $^2P_{3/2}$ resonance in argon[20] was used to calibrate the spectra. We have found this to be a useful calibration gas due to the narrow width, symmetrical profile, and relatively low energy of the resonance.

Vibrational features were obtained from spectra obtained when the electron beam was modulated at 20 meV. The modulation voltage was set at 200 meV in order to obtain attachment energies (corresponding to the centers of the resonances) for resonances which displayed vibrational structure under low-rejection conditions. Control experiments were run to ascertain that the centers did not shift under these conditions.

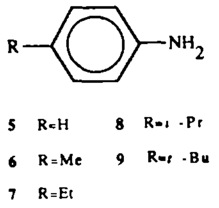
The relative errors are estimated to be ±0.02 eV for the first resonance and ±0.05 eV for the second and third resonances. The second resonance may suffer some additional uncertainty owing to overlap with the first resonance. The actual errors associated with these energies are probably much larger, on the order of ±0.05 eV for the first resonance and ±0.1 eV for the second and third resonances.

*Calulations.* All calculations employed Pople's GAUSSIAN 70 series of programs.[21] Calculations were performed at both the minimal (STO-3G)[13] and split valence (6-31G)[14] basis set levels on the best available experimental geometries.

## RESULTS AND DISCUSSION

Our goal in the present investigation was to define the effect of alkyl groups (Me, Et, i-Pr, and t-Bu) on the individual negative ion states in alkyl-substituted benzenes. Jordan *et al.* had previously shown that these alkyl groups decrease the $AE_a$ relative to benzene.[3] However, because of the small perturbing effect of the alkyl groups (we calculate a 0.2 eV separation between the $a_2$ and $b_1$ orbitals in toluene at the 6-31G level; see Table 2), they were not able to separately observe the $^2A_2$ and $^2B_1$ resonances, nor were they able to determine which configuration predominated in the ground state of the negative ion.

Our motivation in using aniline derivatives to study the effect of alkyl substituents on the $^2A_2$ and $^2B_1$ states of alkylbenzenes was three-fold. First, in order to assign the resonances, it was necessary to perturb the benzene ring in a known manner. The effect of the amino substituent on these states is well documented,[22] and was expected to be large relative to the alkyl perturbation. The amino substituent can effectively interact only with the $^2B_1$ state and destabilizes this state relative to the $^2A_2$ state. Second, we wanted to describe the changes associated with the interaction of both states with alkyl substituents; thus the energy separation had to be large enough to resolve them. In the parent compound (aniline **5**), the splitting of the $^2A_2$ and $^2B_1$ negative ion states is *ca* 0.6 eV,[22] which is sufficient to resolve the corresponding resonances. Finally, the amino substituent was chosen because, although it causes a strong electronic perturbation on one of the benzene $e_{2u}$ orbitals, it does not significantly change the geometry of the six-membered ring relative to benzene.[23] Thus variations in the EAs of **5–9** should primarily be a result of the structural and electronic effects of alkyl substitution and not of structural changes due to amino substitution.



The ET spectra for **5–9** are displayed in Fig. 1 and the corresponding electron affinities are given in Table 1. It is readily seen that a methyl substituent stabilizes

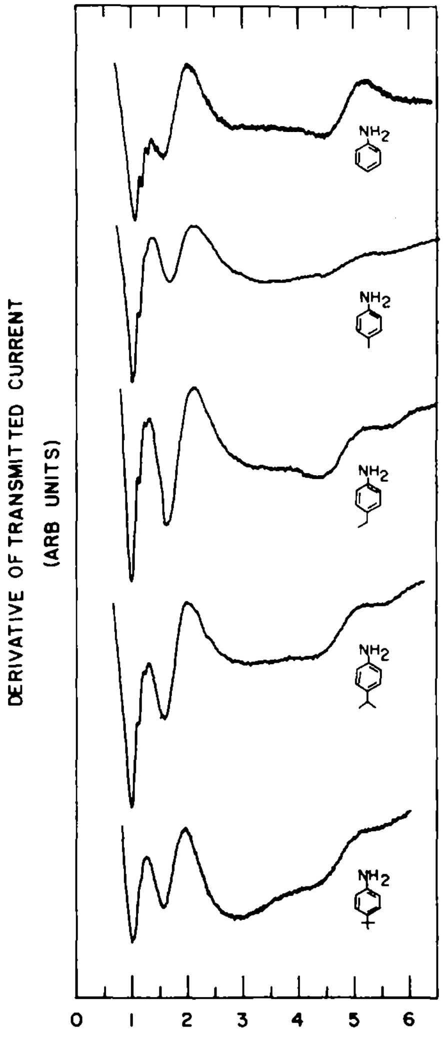


Fig. 1. Electron transmission spectra of **5–9** obtained under low-rejection conditions.

Table 1. Electron affinities and attachment energies of aniline and its *p*-alkyl derivatives[a]

A. High-rejection conditions[b]

| Compound | $AE_1(\pi^*(2a_2))$ | $AE_2(\pi^*(3b_1))$[c] | $AE_3$ |
|---|---|---|---|
| Aniline (5) | 1.25 | 1.77 | 4.92 |
| | | | 5.07[d] |
| | 1.21[e] | 1.79[e] | 4.95[e] |
| *p*-Methylaniline (6) | 1.18 | 1.88 | 4.91 |
| *p*-Ethylaniline (7) | 1.15 | 1.82 | 4.82 |
| *p*-i-Propylaniline (8) | 1.17 | 1.71 | 4.84 |
| *p*-t-Butylaniline (9) | 1.14 | 1.65 | 4.70 |

B. Low-rejection conditions[b]

| Compound | $AE_a(\pi^*(2a_2))$[f] | $AE_1(\pi^*(2a_2))$ | $AE_2(\pi^*(3b_1))$ |
|---|---|---|---|
| Aniline (5) | 1.11 | 1.20 | 1.80 |
| | 1.13[d] | | 1.85[c] |
| *p*-Methylaniline (6) | 1.06 | 1.12 | 1.85 |
| *p*-Ethylaniline (7) | 1.04 | 1.10 | 1.82 |
| *p*-i-Propylaniline (8) | 1.04 | 1.10 | 1.77 |
| *p*-t-Butylaniline (9) | 1.05 | 1.08 | 1.72 |

[a] All energies are in eV and the singly occupied orbital is given in parentheses : $AE_1$ (center of resonance) and $AE_a$ (first vibrational feature), ±0.05 eV ; $AE_2$ and $AE_3$, ±0.1 eV.

[b] See text.

[c] The second resonance is barely discernible.

[d] Ref. 22*a* ; only the energy of the first vibrational feature was reported for the first resonance.

[e] Ref. 22*b*.

[f] Vibrational spacings were 0.10–0.12 eV.

the $^2A_2$ state by 0.08 eV and destabilizes the $^2B_1$ state by 0.05 eV (Fig. 2). These results immediately lead to the conclusion that *the* $^2A_2$ *state is the ground state of the toluene negative ion in the gas phase*. Furthermore, we can now understand the decrease in the AE of toluene relative to benzene as resulting from some (as yet unspecified) stabilization of the $^2A_2$ state and possibly also from a decreased $^2B_1$ contribution to the ground state.

### $^2B_1$ *State*

Substitution of Me groups onto the Me carbon of **6** leads to a nearly uniform stabilization of the $^2B_1$ state by *ca* 0.04 eV per Me group. In order to understand this trend, which arises from a greater stabilization of $\pi^*$ negative ion states by C–C hyperconjugation relative to C–H hyperconjugation, we performed *ab initio* molecular orbital calculations on **5** and **6**, on 4–21 geometry-optimized benzene and toluene in two different conformations (**10** and **11**),[24] and on benzene with ring geometries corresponding to the foregoing toluene structures (Table 2). The latter two calculations allow us to factor out the $\pi^*$ orbital energy changes due to structural distortions of the six-membered ring. Note that conformations **10** and **11** are equal in energy to within a few cal mol$^{-1}$.[25]

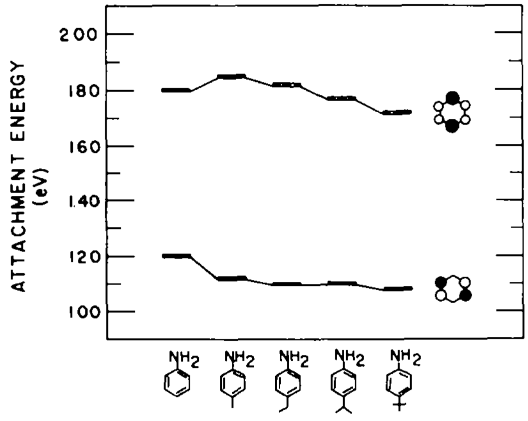
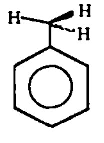
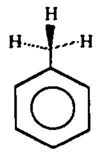


Fig. 2. Correlation diagram for the $\pi^*$ orbitals of **5**–**9**. The energies of the higher energy $3b_1$ orbitals are somewhat less certain due to overlap of the $^2B_1$ and $^2A_2$ resonances.

From Table 2 we immediately see that the $\pi^*(2a_2)$ and $\pi^*(3b_1)$ orbitals of toluene are calculated in the wrong order at the STO-3G level. This same order had previously been obtained by INDO SCF-MO calculations on toluene radical anions of unspecified geometry,[9b] as well as on restricted Hartree–Fock (HF) STO-3G calculations on optimized structures of the radical anions of benzene substituted with a standard Me group, although unrestricted HF calculations gave the correct order.[9a] The incorrect orders can be attributed to limited basis sets since the correct order ($2a_2$ under $3b_1$) is obtained at the 6-31G level. Note that distortion of benzene into the geometry of the phenyl ring of toluene places $\pi^*(2a_2)$ *above* $\pi^*(3b_1)$, so this is not the origin of the observed order in toluene.



**10**



**11**

Table 2. *Ab Initio* HF-SCF molecular orbital energies for benzene and various derivatives

| | Energy (eV) | | | |
|---|---|---|---|---|
| | STO-3G | | 6-31G | |
| | $\pi^*(2a_2)$ | $\pi^*(3b_1)$ | $\pi^*(2a_2)$ | $\pi^*(3b_1)$ |
| Benzene[a] | 7.371 | | 4.057 | |
| Distorted Benzene (**10**)[b] | 7.336 | 7.401 | 4.084 | 4.028 |
| Toluene (**10**)[a] | 7.469 | 7.396 | 4.028 | 4.222 |
| Distorted benzene (**11**)[b] | 7.396 | 7.342 | 4.080 | 4.032 |
| Toluene (**11**) | 7.451 | 7.413 | 4.070 | 4.170 |
| Aniline (**5**)[c] | 7.398 | 7.746 | 3.983 | 4.521 |
| *p*-Methylaniline (**6**)[d] | 7.424 | 7.791 | 3.945 | 4.634 |
| *p*-Methylaniline (**6**)[e] | 7.430 | 7.784 | | |
| *p*-Methylaniline (**6**)[f] | 7.432 | 7.782 | | |

[a] 4-21-optimized geometry; ref. 24.

[b] Benzene with the six-membered ring of toluene in conformation **10** or **11**.

[c] Microwave geometry; ref. 23.

[d] Toluene (**10**) substituted with the amino group of aniline.

[e] Aniline substituted with the methyl group of toluene (**10**).

[f] Aniline substituted with the methyl group of toluene (**11**).

The 6-31G order in Table 2 is due to several causes, the origins of which can be illustrated by reference to Fig. 3. Hyperconjugation results from mixing of a π or π* orbital with pseudo-π bonding ($\sigma_\pi$) and antibonding ($\sigma_\pi^*$) orbitals of the substituent group, where $\sigma_\pi^*$ mixes into π or π* in a bonding manner (A) while $\sigma_\pi$ adds in an antibonding manner (B). For higher-lying occupied π orbitals, the latter interaction predominates and π is invariably destabilized. However, the situation is more complex in the case of π* since interactions A and B in Fig. 3 are nearly balanced.

Modelli *et al.*[26] and Giordan[27] have attributed the greater stabilization of π* by t-Bu relative to Me to the lower energy of $\sigma_\pi^*$ in t-Bu relative to Me. That is, interaction A in Fig. 3 is greater for t-Bu than for Me. While this might at first seem to provide a reasonable explanation, it ignores the fact that $\sigma_\pi$ for t-Bu is higher than that for Me and that interaction B in Fig. 3 will therefore also be greater for t-Bu. We also note that $AE_3$, which is thought to correspond (at least in part) to the configuration involving temporary occupation of the $\pi^*(4b_1)$ orbital,[22] is decreased to about the same extent as $AE_2$ (Table 1A), *even though* $\pi^*(4b_1)$ *is* 3 eV *higher in energy than* $\pi^*(3b_1)$. This is clearly not consistent with the above explanation.

Giordan has also suggested the possibility of (unspecified) "stabilizing through-space interactions between the t-Bu group and the π system" in order to

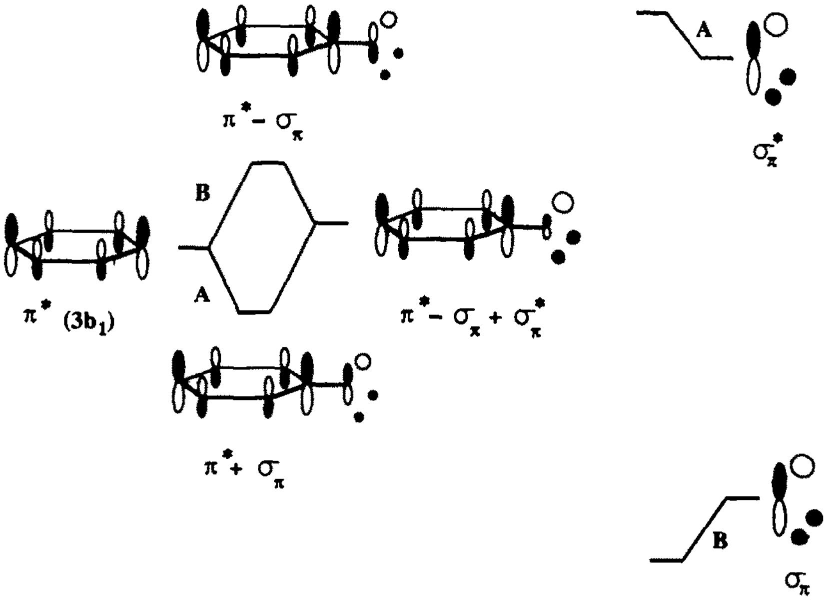


Fig. 3. Interaction diagram for the mixing of the $\pi^*(3b_1)$ orbital of benzene with the pseudo-π Me C—H antibonding ($\sigma_\pi^*$) and bonding ($\sigma_\pi$) orbitals, with interaction energies of A and B, respectively.

rationalize the smaller AE of t-butylethylene relative to propene.[27] We have performed STO-3G and 6-31G calculations on ethylene, propene,[28] and partially geometry-optimized t-butylethylene, all with the double bond length of propene (1.342 Å), and have reached *just the opposite conclusions*. Our results show the $\pi^*$ orbital of t-butylethylene to be below that of propene at both levels of calculation, but more so at the 6-31G level. The latter difference (0.3 eV) is close to the experimental value.[27] Of particular interest is the observation that the $\sigma_x^*$ orbitals of both compounds are *destabilized* relative to $\pi^*$ of ethylene on going from STO-3G to 6-31G. Since longer range through-space interactions are more important in larger basis set calculations, it is clear that such interactions are *destabilizing* in t-butylethylene, and even more so in propene.

Since both of the previous explanations have been shown to be invalid, how are we to understand the stabilization of the $^2B_1$ state of t-butylbenzene relative to that of toluene? The magnitude of interactions A and B in Fig. 3 will depend not only on the energy difference between $\pi^*$ and $\sigma_x$ or $\sigma_x^*$ but also on the overlap between these component orbitals. According to second-order perturbation theory, the change in energy ($\Delta\varepsilon$) of $\pi^*$ due to interaction with a second orbital (e.g. $\sigma_x^*$) is given by Eq. (3) where $\pi^*$ and $\sigma_x^*$ are the unperturbed basis orbitals of energy $\varepsilon_{\pi^*}$ and $\varepsilon_{\sigma_x^*}$, respectively, and $\mathscr{H}'$ is the interaction Hamiltonian

$$\Delta\varepsilon = \frac{\langle \pi^* | \mathscr{H}' | \sigma_x^* \rangle^2}{\varepsilon_{\pi^*} - \varepsilon_{\sigma_x^*}}. \qquad (3)$$

Interaction B is small in toluene since $\pi^*(3b_1)$ and $\sigma_x$ are energetically very different (i.e. the denominator of Eq. (3) is large). On the other hand, even though $\pi^*$ and $\sigma_x^*$ are much closer in energy, interaction A is even smaller. This results from the stabilizing interaction between $C_1(2p_x)$ and $C_7(2p_x)$ in $\pi^* + \sigma_x^*$ (Fig. 3) being partially cancelled by the long-range destabilizing interactions between the $C_1(2p_x)$ and the Me H(1s) orbitals (i.e. the numerator of Eq. (3) is smaller for $\pi^* + \sigma_x^*$ than for $\pi^* - \sigma_x$), and can be clearly seen by reference to the final 6-31G wavefunction ($\pi^* - \sigma_x + \sigma_x^*$) in Fig. 3. *This analysis demonstrates that the overlap term in Eq.* (3) *is more important than the energy term for methyl hyperconjugation in the* $\pi^*(3b_1)$ *orbital of toluene*.

In our view, the key difference between Me and t-Bu is the fact that the C—C bond in the latter is *ca* 50% longer (1.54 Å) than the C—H bond in Me (1.08 Å). Furthermore, the $\pi^*(3b_1)$ Me $C(2p_x)$ coefficients in t-butylbenzene are reduced relative to the corresponding Me H(1s) coefficients in toluene. Thus the long-range $C_1(2p_x) \cdots$ Me $C(2p_x)$ interactions in t-butylbenzene and t-butylethylene should be reduced relative to the $C_1(2p_x) \cdots$ Me H(1s) interactions in toluene and propene, particularly in the more diffuse $\sigma_x^*$ orbitals (interaction A). This would lead to a *reduction in the antibonding component* of the (overall bonding) $\pi^* + \sigma_x^*$ interaction and therefore to a net stabilization of $\pi^*$ by C–C hyperconjugation in t-butylbenzene.

We believe that this proposal also has a bearing on the recent observation that the total spin population ($\rho_H$) for a proton hyperconjugated with a delocalized radical anion is almost twice as large as $\rho_C$ for a similarly oriented Me group.[29] We plan to explore these ideas further.

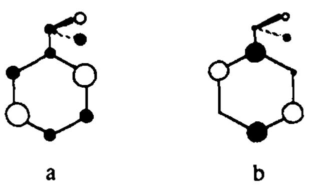


Fig. 4. Representation of the two lowest 6-31G $\pi^*$ wavefunctions for toluene in conformation **10**. Orbital a is predominantly $2a_2$ whereas orbital b is predominantly $3b_1$.

It is worth noting at this point that the above discussion follows in a general way the simple perturbation explanations of alkyl effects on gas phase acidities of alcohols and amines.[30] However, our analysis of orbital energies and overlap effects extends these arguments in important ways. The effects which we have observed might also be attributed to a greater polarizability of t-Bu relative to Me. However, as Janousek and Brauman have pointed out,[30c] the computation of the polarizability involves a summation over all excited states of appropriate symmetry. Thus, computing the polarizability is equivalent semiclassically to taking into account all the $\pi^*$ orbitals.

### $^2A_2$ *State*

The $^2A_2$ state of aniline is stabilized by 0.08 eV on addition of a methyl group at the *para* position to form **6**. This change might at first seem surprising since the *para* carbon lies in a nodal plane of the $\pi^*(2a_2)$ orbital. It is interesting to note in Table 2 that the experimental trend is not reproduced at the STO-3G level; i.e. the calculations indicate a destabilization of $\pi^*(2a_2)$ by a *para* Me group in both conformations **10** and **11**. However, a stabilization (relative to benzene) of $\pi^*(2a_2)$ in conformation **10** (but not in conformation **11**) is calculated at the more diffuse 6-31G level (Table 2). Note that in conformation **10** the $\pi^*(2a_2)$ and $\pi^*(3b_1)$ orbitals of distorted benzene are strongly mixed by interaction with the unsymmetrically disposed H(1s) orbitals of the Me group (Fig. 4). We therefore refer to them as "$2a_2$" and "$3b_1$", where these are the major components.

These calculations, along with two additional considerations, lead us to conclude that the stabilization of the $^2A_2$ state in toluene relative to benzene results from a stabilizing (in phase) overlap in the $\pi^*$("$2a_2$") orbital of the Me H(1s) orbital with the $C(2p_x)$ orbital

Table 3. Electron affinities and attachment energies of benzene and its alkyl derivatives

| Compound | $AE_a$[a] | $AE_a$[b] |
|---|---|---|
| Benzene | 1.15 | 1.13 |
| Toluene | 1.11 | 1.11 |
| Ethylbenzene | | 1.09 |
| i-Propylbenzene | 1.08 | 1.06 |
| t-Butylbenzene | 1.06 | 1.04 |

[a] Refs 3 and 10*c*; first vibrational feature obtained under low-rejection conditions (see text); ±0.05 eV.

[b] This work; center of resonance obtained under high-rejection conditions (see text); ±0.05 eV.

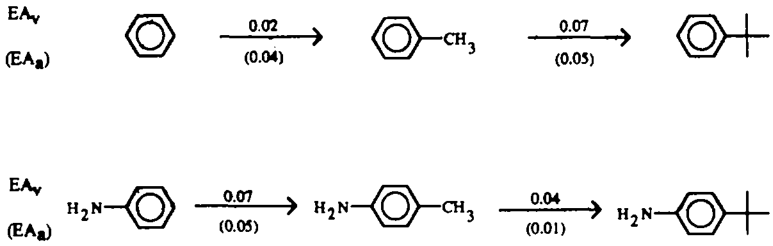


Fig. 5. Changes in the "vertical" and adiabatic electron affinities ($\Delta AE_v$ and $\Delta AE_a$, respectively) of benzene and aniline on alkyl substitution, calculated from high- and low-rejection data, respectively (Tables 1 and 3).

on the *ortho* C atom. First, as noted above, our calculations are expected to be most reliable at the 6-31G level. Second, the fact that stabilization of the $\pi^*$("$2a_2$") orbital in **10** (relative to benzene) is calculated at the 6-31G level but not at the less diffuse STO-3G level indicates that it is the longer-range orbital interactions that cause the additional stabilization in the larger basis set. As seen in Fig. 4, the Me H(1s)$\cdots$C$_2$(2p$_\pi$) interactions are the only ones which can possibly play this role.

### *Substituent effects on the attachment energies*

The AEs obtained for benzene and its alkyl derivatives under high-rejection conditions are given in Table 3. Recall that spectra obtained under these conditions reflect the total electron-scattering cross-section and therefore do not resolve overlapping resonances as well as do low-rejection spectra. We discuss these spectra at this point because ET spectra are normally obtained under these conditions.

Note that AE$_v$ (the center of the first resonance) is increased more on going from aniline to *p*-methylaniline (0.07 eV, Table 1A) than from benzene to toluene (0.02 eV), but is increased less on going from *p*-methylaniline to *p*-t-butylaniline (0.04 eV) than from toluene to t-butylbenzene (0.07 eV) (Fig. 5). We reach the same conclusions on comparing the AE$_a$ values of Jordan *et al.*,[3] which were obtained under low-rejection conditions, with our data for **5**, **6**, and **9** obtained under the same conditions.

We suggest that these substituent effects differ somewhat because the data for toluene and t-butylbenzene reflect a strong overlapping of the $^2A_2$ and the $^2B_1$ resonances. Since addition of Me destabilizes the $^2B_1$ resonance, the decrease in AE on going from benzene to toluene is attenuated. Conversely, since t-Bu stabilizes the $^2B_1$ resonance (relative to Me), the decrease in AE on going from toluene to t-butylbenzene is enhanced. In fact, we cannot exclude the possibility that the $^2B_1$ state lies below the $^2A_2$ state in the latter compound.

## CONCLUSIONS

This study has led to some important conclusions regarding the negative ion states of alkylbenzenes.

(1) The $^2A_2$ state is below the $^2B_1$ state in toluene. These states would appear to be nearly isoenergetic in t-butylbenzene if the data for the p-alkylanilines are referenced to benzene, but it is possible that these states are mixed with each other in benzene and the alkylbenzenes.

(2) The $^2B_1$ state of toluene is destabilized relative to benzene primarily by antibonding interactions between the C$_1$(2p$_\pi$) and the Me H(1s) orbitals (see $\pi^*-\sigma_\pi+\sigma_\pi^*$ in Fig. 3). We also propose that, contrary to previous statements, the $^2B_1$ state of t-butylbenzene is lower than that of toluene not because of a decrease in the energy term of Eq. (3) but because of an increase in the overlap term. That is, the antibonding interactions mentioned above are reduced in the analogous C$_1$(2p$_\pi$)$\cdots$Me C(2p$_\pi$) interaction in t-butylbenzene, primarily owing to the greater distance between the latter orbitals. This idea requires further investigation.

(3) The $^2A_2$ state of toluene is stabilized relative to benzene by bonding interactions between the *ortho* C (2p$_\pi$) and Me H(1s) orbitals in the singly occupied ($\pi^*$) molecular orbital.

(4) The first attachment energy of t-butylbenzene appears to be decreased relative to toluene either because of a greater mixing between the corresponding states or possibly because the $^2B_1$ state actually lies at a lower energy than the $^2A_2$ state in t-butylbenzene.

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