A Theoretical Approach to the Birch Reduction. Structures and Stabilities of the Radical Anions of Substituted Benzenes

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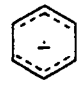
Abstract: Ab initio molecular orbital calculations at the RHF/STO-3G and UHF/STO-3G levels have been carried out for the radical anions of a number of substituted benzenes ($C_6H_5X^{-\cdot}$: X = H, CH_3, COO^-, CF_3, CN, $CH{=}CH_2$, COOH, NO_2, CHO, F, OCH_3, OH, and NH_2). For π-donor substituents the ground state is ^2A while for π acceptors it is ^2B. The benzene radical anion is stabilized by π-accepting and σ-accepting substituents. Calculated molecular electrostatic potentials suggest that the kinetically favored sites of protonation for the radical anions are ortho or meta for π-donor substituents and ipso or para for π-acceptor substituents.

Introduction

The effect of addition of an electron to benzene or to substituted benzenes has attracted considerable theoretical and experimental attention. From a theoretical point of view, addition of an electron to benzene itself is of interest as a typical Jahn-Teller situation. Examination of the π molecular orbitals of benzene (Figure 1) shows that the added electron can be accommodated in either one of the pair of degenerate e_{2u} orbitals. If D_{6h} symmetry is maintained, this leads to a degenerate $^2E_{2u}$ electronic state for the benzene radical anion (Bz^-). According to the Jahn-Teller theorem,[1] the system distorts under such circumstances and there have been numerous studies[2,3] of such distortions. The $^2E_{2u}$ state splits into ^2A_u and $^2B_{1u}$ components for which minimum-energy structures can be determined. These have D_{2h} symmetry. In a recent paper,[3] we found that the best ^2A_u and $^2B_{1u}$ structures, represented schematically as **1** and **2**, have very similar energies, the latter being favored by less than 1 kJ mol^{-1} (CI/STO-3G). **1** and **2** correspond to stationary points on the Jahn-Teller surface[2d,4] and are connected by a monotonic energy path. Hence structures **1** and **2** can interconvert relatively freely, a result which is consistent with the observation[5] of six equivalent hydrogen atoms in the ESR spectrum of Bz^-.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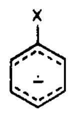
For the radical anion of a substituted benzene (denoted SBz^-) structures **1** and **2** each give rise to two distinct structures of different energy. **1** gives rise to **3** and **5** while **2** leads to **4** and **6**. Note that by symmetry only **3** and **4** are required to be stationary points. **5** and **6**, and their mirror images, are arbitrary points on the perturbed Jahn-Teller surface and may or may not correspond to minimum (or maximum) energy structures.



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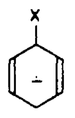

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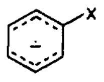

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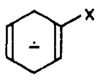

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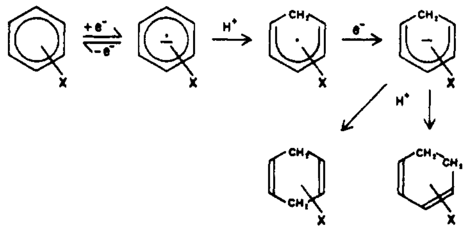
The radical anions of benzene and substituted benzenes are of particular interest to experimental organic chemists because of their involvement in the first stage of the Birch reduction[6] of substituted benzenes by alkali metals and alcohols in liquid ammonia or similar solvents (eq 1). This paper represents part of a continuing study[3] of the theory of the Birch reduction. The rate of the reduction is probably controlled by two factors: the concentration of the initially formed radical anion and its relatively slow protonation by the alcohol which needs to be present for consummation of the reduction process. Information relating to the first of these factors is examined here.



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We use ab initio molecular orbital theory to examine radical anions, $C_6H_5X^{-\cdot}$, of a set of substituted benzenes with substituents X = H, CH_3, COO^-, CF_3, CN, $CH{=}CH_2$, COOH, NO_2, CHO, F, OH, NH_2, OCH_3. Three particular aspects are examined in detail. In the first place, we determine for each substituent whether the favored geometric structure is **3**, **4**, **5**, or **6** and whether this corresponds to a ^2A_u-like state (labeled loosely as ^2A) or a $^2B_{1u}$-like state (labeled ^2B). Such a classification is only strictly applicable to structures **3** and **4**, which have a symmetry plane passing through X (perpendicular to the molecular plane); for structures **5** and **6**, we obtain estimates of the degree of ^2A and ^2B character in the ground state. Secondly, we examine the effect of the substituent on the stability of Bz^- compared with its effect in benzene, i.e., the relative electron affinities of benzene and substituted benzenes. Finally, we use our wave functions for the various SBz^-'s to predict the preferred sites of proton addition.

Where possible, we compare our results with available experimental data. These include data from electron-attachment experiments in the gas phase, ESR spectra in solution, and metal/ammonia reductions in solution. We should stress at the outset that our calculations refer, in principle, to isolated vibrationless ions in the gas phase. In practice, many of the SBz^-'s are very short-lived species in the gas phase, being able to readily eject an electron. The use of a limited basis set prevents this from happening in our treatment, which may therefore reflect behavior in noninteracting solvents. In other solvents, the behavior of these systems may be substantially modified through specific interaction with the solvent and by

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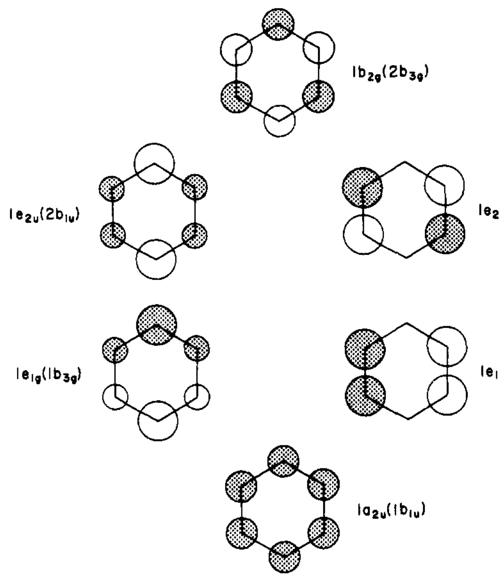


Figure 1. Symmetry classifications of Hückel π-type molecular orbitals of benzene. Symmetries refer to point groups D_{6h} (D_{2h}).

possible association with the counterion. Experimental studies of the Birch reduction are in progress using cryptands to eliminate the effect of counterions.[7] These will be more directly comparable to our theoretical work and the results will therefore be of particular interest. There is also the possibility in the case of electron-stabilizing substituents (e.g., -COOH) that the Birch reduction proceeds via protonation of the dianion $C_6H_5X^{2-}$, rather than the monoanion. Finally, we note that for several of the substituents which we have selected (e.g., F, OH, CH=CH$_2$, CHO, NO$_2$), the reduction process results in alternative fates for the substituted benzene. We point out, however, that, whereas OH and CHO might behave very differently from OCH$_3$ and COR, respectively, in the experimental situation, their theoretical behavior is very similar and they therefore serve as useful (and computationally less expensive) models for the latter pair of substituents for which experimental information is available. Moreover, it is useful to examine a large selection of substituents so that a general picture of the effect of substituents might emerge. An understanding of the behavior of the isolated systems is desirable as a first step in investigating perturbations due to factors such as solvation and counterion association.

Method

Ab initio self-consistent-field (SCF) molecular orbital calculations were carried out using the restricted[8] (RHF) and, in a few specified cases, the unrestricted[9] (UHF) Hartree-Fock procedures. They were performed with a modified version[10] of the GAUSSIAN 70 system of programs,[11] the minimal STO-3G[12] basis set being used throughout.

The ring geometries used in the calculations on the radical anions of the substituted benzenes (**3–6**) were based on the optimized geometries **1** and **2** obtained in our previous study[3] and reproduced in Figure 2. Unless otherwise noted, standard values[13] of bond lengths and bond angles were used for the substituents.

For the COO$^-$ group, values (C–O = 1.26 Å, OCO = 130.0°) were taken from STO-3G optimized geometries[14] of formate and acetate anions. Except for the radical anions of anisole and aniline, no structural optimizations were carried out.

For anisole radical anion, the COC angle (α) was optimized in the conformation with COCH trans leading to α = 118.6 (**3**), 116.9 (**4**), 117.2 (**5**), and 118.0° (**6**). These values compare with α = 118.0° from similar calculations on neutral anisole.[15]

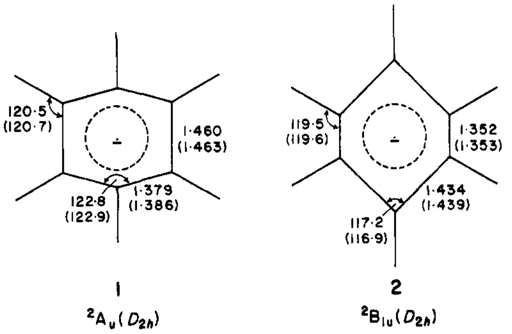


Figure 2. Optimized RHF/STO-3G and UHF/STO-3G (in parentheses) structures for Bz$^-$. Bond lengths in angstroms, bond angles in degrees, all C–H lengths assumed equal to 1.082 Å (1.080 Å UHF).

For aniline radical anion, calculations were performed both on planar structures and on structures in which the three angles (β) around nitrogen (assumed equal) were optimized leading to β = 109.4° (**3**) compared with β = 112.1° (STO-3G) in aniline itself.[15] The conformations for the other substituents follow: CH$_3$ and CF$_3$, CCCZ (Z = H or F) orthogonal; COOH, planar with CCOH trans; CHCH$_2$, OH, COO$^-$, CHO, NO$_2$, all planar. These correspond to the minimum energy conformations determined from the similar calculations for the neutral substituted benzenes except for the CF$_3$ group, for which there is almost no energy difference between cis and orthogonal forms.[15]

The protonation sites of SBz$^-$ were studied with the aid of molecular electrostatic potentials (MEPs), the theory of which is well summarized in a recent review.[16] The MEP calculations were carried out with a program based on the GAUSSIAN 70 system.[11]

Results and Discussion

Favored States. Table I lists the total RHF/STO-3G energies for the ground electronic states of structures **3–6**. In a few cases we have also examined a higher electronic state and these results are also included in Table I.[17] In previous work,[3] on the parent Bz$^-$, we found that RHF/STO-3G calculations predict a $^2B_{1u}$ ground state for **1**, favored by 6.7 kJ mol^{-1} over a ^2A_u ground state for **2**. Better calculations at the CI/STO-3G level predict an energy difference of only 0.3 kJ mol^{-1}. It is likely that a comparable bias toward the $^2B_{1u}$ state will also be present in the STO-3G calculations for **3–6**. Although the magnitude of this correlation correction may vary from system to system, we have used the result for Bz$^-$ to provide an empirical correction of 6.4 kJ mol^{-1} to the energies of **3** and **5**, yielding the corrected relative energies shown in Table II. We feel that applying such a correction is better than not doing so. It is certainly necessary for the unsubstituted case and is likely to be a good approximation for substituents (e.g., CH$_3$) which perturb the Jahn–Teller surface only slightly. For substituents with a stronger effect, such a small correction makes little difference to the relative energies. Only in the case of π-donor substituents are the energy orderings modified: without the correction, the asymmetrical structure **6** is favored.

Also of interest is the degree, $D_{B_{1u}}$, of $^2B_{1u}$ character in the wave functions of **3–6**. The $D_{B_{1u}}$ values are estimated by projecting out the ^2A_u and $^2B_{1u}$ components present in the singly occupied molecular orbital (SOMO), using the Hückel 1e$_{2u}$ orbital coefficients (Figure 1):

$$D_{B_{1u}} = \frac{1}{\sqrt{12}}(2c_1 - c_2 - c_3 + 2c_4 - c_5 - c_6)$$

$$D_{A_u} = \tfrac{1}{2}(c_2 - c_3 + c_5 - c_6) \qquad (2)$$

(where c_i are the molecular orbital coefficients, numbered starting from the carbon atom adjacent to the substituent) and normalizing so that $D_{B_{1u}}{}^2 + D_{A_u}{}^2 = 1$. This procedure is only

Table I. Calculated Total Energies (E, RHF/STO-3G, hartrees) and State Descriptions ($D_{\mathrm{B_{1u}}}$)[a] for Structures of the Radical Anions ($C_6H_5X^{-\cdot}$) of Substituted Benzenes

substituent	3		4		5		6	
(X)	E	$D_{\mathrm{B_{1u}}}$	E	$D_{\mathrm{B_{1u}}}$	E	$D_{\mathrm{B_{1u}}}$	E	$D_{\mathrm{B_{1u}}}$
H	−227.656 79	0	−227.659 36	1	−227.656 79	0.866	−227.659 36	0.500
CH_3	−226.239 34	0	−266.243 15	1	−266.240 29	0.859	−266.242 20	0.491
COO^-	−411.832 31	0	−411.840 71	1	−411.836 89	0.875	−411.836 03	0.503
CF_3	−558.637 82	0	−558.653 08	1	−558.648 33	0.926	−558.644 87	0.588
CN	−318.230 13 −318.237 65	1 0	−318.269 04	1	−318.262 86	0.958	−318.253 44	0.678
$CH{=}CH_2$	−303.597 95	0.997	−303.629 20	1.000	−303.623 45[b]	0.966	−303.609 64[c]	0.698
COOH	−412.758 57	0.999	−412.790 59	1.000	−412.784 80[d]	0.973	−412.772 80[e]	0.739
NO_2	−428.385 31 −428.419 67	0 1	−428.436 54	1	−428.432 73	0.989	−428.422 76	0.983
CHO	−338.913 80	1.000	−338.936 02	1.000	−338.931 04[f]	0.995	−338.918 52[g]	0.989
F	−325.126 24	0	−325.120 37	1	−325.121 21	0.732	−325.127 44	0.440
F[h]	−325.126 32	0	−325.120 45	1				
OCH_3	−340.073 91	0.007	−340.066 76	1.000	−340.070 02[i]	0.678	−340.075 77[j]	0.419
OH	−301.500 49	0.013	−301.489 56	1.000	−301.494 05[k]	0.657	−301.501 60[l]	0.420
NH_2[m]	−281.966 59	0	−281.951 21	1	−281.958 70	0.599	−281.966 99	0.398
NH_2[n]	−281.975 38	0						

[a] See text. [b] C=C—C$\overset{\cdots}{-}$C trans. [c] C=C—C=C trans. [d] HO—C—C$\overset{\cdots}{-}$C trans. [e] HO—C—C=C cis. [f] O=C—C$\overset{\cdots}{-}$C cis. [g] O=C—C=C trans. [h] D_{2h} ring geometry was optimized for **3** and **4** (^{2}A and ^{2}B states, respectively). From ref 3. [i] C—O—C$\overset{\cdots}{-}$C cis. [j] C—O—C=C trans. [k] H—O—C$\overset{\cdots}{-}$C trans. [l] H—O—C=C trans. [m] Planar N. [n] Pyramidal N.

approximate, in that eq 2 refers to D_{6h} orbitals with zero overlap between atomic orbitals, and we are neglecting the coefficients on the substituent. The lower symmetry of SBz^- in fact allows symmetry components other than A_u or B_{1u} to mix in. Nevertheless, the $D_{\mathrm{B_{1u}}}$ values, quoted in Table I, are useful in providing an approximate measure of the B_{1u} and A_u character of the individual wave functions induced by the substituent.

Examination of Table I shows that for π-donating substituents (X = F, OH, NH_2, OCH_3) structure **3** with a ^{2}A ground state ($D_{\mathrm{B_{1u}}}$ = 0) is uniformly preferred while π-accepting substituents (X = CH_3, COO^-, CF_3, CN, $CH{=}CH_2$, COOH, NO_2, CHO) all prefer structure **4** with a ^{2}B ground state ($D_{\mathrm{B_{1u}}}$ = 1). These results are readily rationalized in terms of the nodal properties (Figure 1) of the SOMO in the ^{2}A and ^{2}B states. In the former, the SOMO has a node, and hence zero electron density, on the carbon adjacent to the substituent and is therefore favored by π electron donor substituents. The SOMO of the ^{2}B state, on the other hand, has a large coefficient at the ipso carbon, thus allowing charge transfer to π-electron acceptors.

In the same way, the relative energy orderings in Table II for structures **3–6** are explained. The energies decrease with increasing SOMO coefficient for the π acceptors and increase for the π donors.

The strongest π acceptors ($CH{=}CH_2$, COOH, NO_2, CHO) all prefer the ^{2}B state, even in **3**. It should be pointed out, however, that the energy ordering of structures **3–6** for these substituents, although identical with that for the other π acceptors, is dependent on the suitability of the various geometries to accommodate the ^{2}B state.

Relative π-donor/acceptor strengths are reflected in the $D_{\mathrm{B_{1u}}}$ values for structures **5** and **6**, and are reasonably consistent with the ordering derived from substituent π charges in both SBz^- and SBz.[15] The closer the $D_{\mathrm{B_{1u}}}$ values are to 1, the stronger the π electron accepting ability of the substituent, while the closer they are to zero, the stronger is the π-donor strength. The "reference" or unsubstituted Bz^- values for **5** and **6** (X = H) are $\sqrt{3}/2$ and $1/2$, respectively.

We have carried out UHF/STO-3G calculations only for a subset (X = H, CH_3, CN, NO_2, F, OH, NH_2) of the substituents and only for structures **3** and **4**. Calculated total and corrected relative energies are shown in Table III. For the unsubstituted benzene radical anion, the ^2A_u state is now favored over $^2B_{1u}$ by 6.9 kJ mol^{-1}. We therefore apply a correction of 7.2 kJ mol^{-1} to the energy differences between **3** and **4**. This leads to favored states and relative energies in reasonable agreement with the corresponding corrected RHF results (Table II).

Table II. Corrected Relative Energies (ΔE, RHF/STO-3G, kJ mol^{-1}) for Structures of Radical Anions of Substituted Benzenes

substituent (X)	3	4	5	6
H	0.3	0	0.3	0
CH_3	3.6	0	1.1	2.5
COO^-	15.7	0	3.6	12.3
CF_3	33.7	0	6.1	21.6
CN	76.0	0	9.8	62.7
$CH{=}CH_2$	82.0	0	8.7	51.4
COOH	84.1	0	8.8	46.7
NO_2	44.3	0	3.6	36.2
CHO	58.3	0	6.7	45.9
F	0	21.8	13.2	3.2
OCH_3	0	25.2	10.2	1.5
OH	0	35.1	16.9	3.5
NH_2[a]	0	46.8	20.7	5.4

[a] Planar N.

Comparison with ESR Data. Except for the toluene radical anion, the preferred states (Table II) agree with the available experimental ESR data (specifically $C_6H_5NO_2^{-\cdot}$,[18,19] $C_6H_5CN^{-\cdot}$,[20] $C_6H_5CHO^{-\cdot}$,[20] $C_6H_5OCH_3^{-\cdot}$,[20,21] $C_6H_5COOH^{-\cdot}$,[22] and $C_6H_5COO^{-\cdot 2-}$[22]). Our results for $C_6H_5OH^{-\cdot}$, $C_6H_5CH_3^{-\cdot}$ and $C_6H_5CN^{-\cdot}$ are also in agreement with those of a recent INDO MO study and have been rationalized using a one-electron MO model.[23] ESR experimental studies[20,24] indicate that the preferred state of the toluene radical anion *in solution* is ^{2}A, whereas our calculations suggest the ^{2}B state, and that there is actually a negative charge on the CH_3 group. Jordan et al.[25] have previously questioned whether the ordering of states observed in solution is the same as in the gas phase and have noted that the toluene radical anion may provide another example of the reversal of the methyl substituent effect in solution.[26] Indeed, our calculations are consistent with the hyperconjugative electron acceptance by a methyl group observed[27] in other anionic species.

On the other hand, we note that, as with the benzene radical anion, the relative energies of the different structures (**3–6**) for toluene$^{-\cdot}$ are relatively close, and vibronic coupling should

Table III. Calculated Total Energies (E, UHF/STO-3G, hartrees) and Corrected Relative Energies (ΔE, kJ mol^{-1}) for Structures of the Radical Anions of Substituted Benzenes

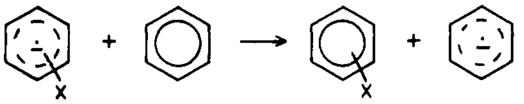
substituent	3		4	
(X)	E	ΔE	E	ΔE
H	−227.676 18	0.3	−227.673 57	0
CH_3	−266.258 82	3.1	−266.257 25	0
CN	−318.265 42	75.2	−318.291 33	0
NO_2	−428.454 49	33.5	−428.464 51	0
F	−325.145 82	0	−325.135 22	20.6
OH	−301.520 14	0	−301.505 51	31.2
NH_2[a]	−281.986 26	0	−281.968 46	39.5

[a] Planar N.

be important. This has experimentally been found to be a general feature of alkylbenzene radical anions, and is also borne out by calculations which have taken vibronic coupling into account.[20,24]

Stabilization Energies. According to most experimental studies,[25,28,29] the electron affinities of benzene and many substituted benzenes are negative. Our calculations indeed predict a higher energy for the benzene radical anion than for neutral benzene but, as noted in a previous paper,[3] *absolute* electron affinities calculated at this level of theory are not really meaningful.

On the other hand, the *relative* electron affinities, i.e., electron affinities relative to benzene, of substituted benzenes should be more reliable. This is because there is some prospect of cancellation of errors associated with the limitations of the basis set. These relative electron affinities are given by the energy changes (ΔE) for the formal reaction



We refer to these quantities also as stabilization energies (SE) because they provide a measure of the stabilizing effect of a substituent in the benzene radical anion compared with its effect in neutral benzene. A positive value implies a greater stabilization in the anion.

Calculated values, based on the theoretical ground states, are presented in Table IV. Included in the table are relevant experimental electron affinities. We note that these are vertical electron affinities, whereas our calculations refer to adiabatic values. We have only used the results of one group of workers for X = CH_3 and the π donors,[25,28] and one group for the strong π acceptors,[30] in order that our comparisons are consistent. There are many other literature values available,[29] but these are not suitable for comparison purposes since large variations are observed between results obtained from different experimental techniques.[29b]

Table IV. Stabilization Energies[a] (SE, eV)[b] for Radical Anions ($C_6H_5X^{-\cdot}$) of Substituted Benzenes

substituent	SE		
	calcd		
(X)	RHF	UHF	exptl[c]
H	0	0	0
CH_3	0.00	0.00	0.04[d]
COO^-	−4.04		
CF_3	0.79		
CN	1.54	1.76	1.40[f]
$CH{=}CH_2$	0.96		0.90[e]
COOH	1.30		
NO_2	2.29	2.66	2.34[g]
CHO	1.40		1.57[f]
F	0.27	0.28	0.26[d]
OCH_3	0.08		0.06[e]
OH	0.14	0.14	0.14[e]
NH_2	−0.01[h]	−0.12[i]	0.02[e]

[a] Energy changes for the formal reaction $C_6H_5X^{-\cdot} + C_6H_6 \rightarrow C_6H_5X + C_6H_6^{-\cdot}$, i.e., electron affinities of substituted benzenes relative to benzene. Lowest energy ^2A or ^2B state (**3** or **4**) used for $C_6H_5X^{-\cdot}$; ^2A states corrected by subtraction of 6.4 kJ mol^{-1} for RHF and addition of 7.2 kJ mol^{-1} for UHF. [b] 1 eV = 96.49 kJ mol^{-1}. [c] The experimental electron affinity of benzene is taken as −1.15 eV, from ref 28b. [d] Reference 28b. [e] Reference 28a. [f] Reference 30b. [g] Reference 30a. [h] Pyramidal N. [i] Planar N.

Table V. Splittings (RHF/STO-3G, eV) between the First and Second Anion States of Substituted Benzenes (C_6H_5X)

substituent (X)	vertical	Koopmans	exptl
F	0.24	0.23	
OCH_3	0.34	0.37	0.63
OH	0.40	0.40	0.72
NH_2	0.37	0.39	0.72

Although we do not have sufficient comparisons with experiment to assess adequately the calculated stabilization energies, the agreement appears generally to be reasonable and similar at both the RHF and UHF levels. The calculated values may be rationalized in terms of both σ- and π-electron effects.[28b] Largest stabilizing interactions are observed for substituents (e.g., NO_2, CN, COOH, CHO) which are strong σ-electron acceptors and π-electron acceptors. For the NH_2, OH, and F substituents, there appears to be competition between *stabilizing* σ-electron withdrawal (F > OH > NH_2) and *destabilizing* π-electron donation (NH_2 > OH > F) in the anion, with the latter reinforced by stabilizing π-electron donation in the neutral benzene, with the result that the fluoro substituent is slightly stabilizing and the amino substituent slightly destabilizing. We note, however, that the amino group is found experimentally to be very slightly (by 0.02 eV) stabilizing. Furthermore, our stabilization energies for X = COOH, OCH_3, CH_3, and NH_2 are in the same order as experimentally measured rates of reduction[33] for COONa, OCH_3, CH_3, and NH_2, consistent with a dependence of the reduction rates on the concentration of the radical anion.

For a methyl substituent, the calculations predict a near-zero stabilization energy. Experimental results are in conflict on this point. ESR equilibrium studies in solution,[31] polarographic half-wave potential measurements,[32] and rate determinations for metal-ammonia reductions of benzene and alkylbenzenes[33,34] all indicate a destabilizing effect of the alkyl substituent in the anion. On the other hand, gas-phase electron attachment experiments[25] indicate a stabilizing effect of the methyl group in the toluene radical anion. It may well be that the destabilization observed in solution is a solvent effect. The reversal of direction of alkyl substituent effects in solution has been observed in other systems.[26]

Vertical Energy Splittings. Jordan et al.[28b] have also obtained values for the second electron affinities of some SBz$^-$'s. These correspond to electron capture into the next-to-lowest unoccupied molecular orbital in the neutral benzene. We can obtain approximate experimental values of the vertical ^2A–^2B energy splittings by using the first and second electron affinities quoted by Jordan et al.

In order to calculate vertical splittings, we use the geometries of ref 15 for neutral substituted benzenes and compute the total energy differences for an additional electron in the two lowest unoccupied orbitals. We also use Koopmans' theorem,[35] applied to the neutral benzenes, to calculate the splittings (Table V); the values found for $C_6H_5F^{-\cdot}$ and $C_6H_5OH^{-\cdot}$ are similar to those calculated by Jordan.[28b] There are insufficient experimental data available to assess fully the adequacy of the theoretical approaches in estimating the energy splittings,

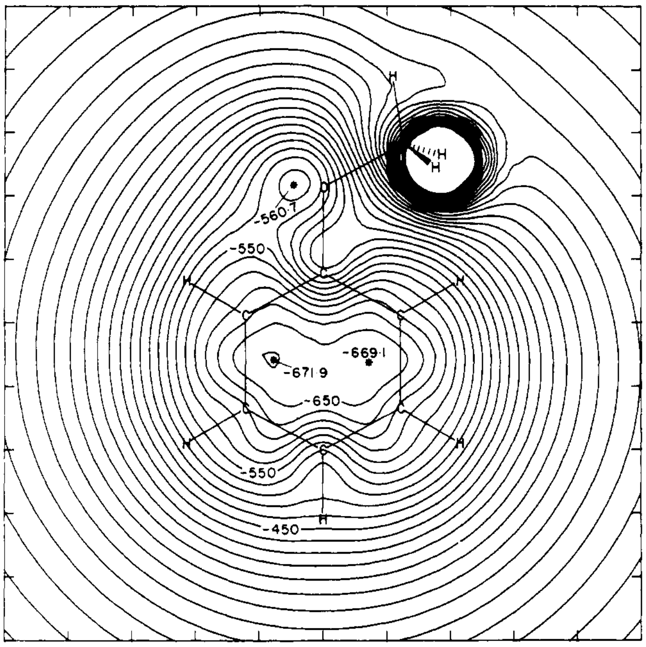


Figure 3. MEP map of anisole radical anion 1.2 Å above, and parallel to, the ring plane. Contours are at 20 kJ mol^{-1} intervals. Border scale in 1.0 Å units.

although it is apparent that the splittings in these few cases are underestimated by ~0.3 eV.

Protonation Sites. The experimentally determined mechanisms for the Birch reduction indicate reversible electron addition coupled with irreversible proton addition.[6,33,36–42] For this reason, we use the molecular electrostatic potential (MEP) to determine the most likely paths for protonation. Such an approach has proved successful in previous studies of protonation reactions[16,43,44] and, in particular, we have shown that the MEP predictions succeed in cases where considerations based on simpler parameters (e.g., calculated charges and HOMO coefficients) fail.[43,45]

We hope in this way to add light to the work of Burnham[36] and Zimmerman,[37] who use calculated transition-state energies and π-electron charges, respectively, but predict different favored protonation positions (meta and ortho, respectively) for the Birch reduction of anisole. Other previous calculations,[38] on the other hand, using Hückel molecular orbital theory, applied to polycyclic aromatic hydrocarbons (reduction of biphenyl, terphenyl, and some polyacenes),[38,41a,41b] have been very successful in predicting the experimentally observed protonation sites. These predictions were based only on the magnitudes of the HOMO coefficients.

The MEP is the first-order interaction energy between a proton and the unperturbed molecule. It is the dominant energy term at intermediate to large distances, and hence is only valid for the initial approach of the proton. It can thus be used to determine the favored approach channels, which, for irreversible reactions, will lead to the favored products. At small distances, however, polarization, charge-transfer, and exchange terms become significant, and the MEP is no longer strictly appropriate.

There are some shortcomings in using MEPs to predict the favored sites of protonation in our SBz$^-$ study. These are (1) our calculations are for isolated gas-phase ions and do not take into account any effects of the solvent; (2) there is evidence that the counterion (Li$^+$, Na$^+$, K$^+$, etc.) is associated with the anion to various extents;[6,33,41a,41c,46] (3) there is some dispute as to whether the radical anion (SBz$^-$) or dianion (SBz^{2-}) is the intermediate which is protonated,[6,38,41a,41c,46] though the latter does not seem likely except for polycyclic aromatics[47] or benzenes with stabilizing groups (e.g., COOH).[42]

Accounting for solvent effects would be difficult, but we expect that the average effect it has on SBz$^-$ would be a distortion on its MEP such that relative differences are maintained and that the preferred protonation sites would remain preferred.

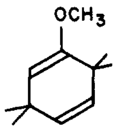
We do not attempt to attack the problems associated with (2) and (3) above at this stage, though in principle we could (and hope to) do calculations on the SBz$^-$M$^+$ aggregate.[48] In contrast, it would be of little value to perform MEP calculations on the dianion, as the addition of another electron to SBz$^-$ should not significantly alter the MEP, since this extra electron would go into the same orbital as the unpaired electron.

In some previous work,[41a,c] it has been assumed that the metal ion sits near the most negative site in the radical anion. Protonation may therefore be hindered at this site and may therefore take place at the next most negative site. Such considerations may be applicable to NH$_4^+$ as protonating agent but are likely to be less so for alcohols which can coordinate with the metal. The amount of M$^+$ association, and hence the product distribution, depends upon the experimental conditions as well as the metal. The metal ion may also be located near the substituent, leaving the ring relatively unaffected.

The results of our calculations show that the SBz$^-$ anions are characterized by a tubular region of negative MEP situated about 1.1–1.2 Å above the molecular plane. This tube is oriented either between atoms C(1) and C(4) or at right angles to this between the bonds C(2)–C(3) and C(5)–C(6), depending upon whether the favored state is ^{2}B or ^{2}A, respectively, i.e., depending on whether the substituent is a π-electron acceptor or a π-electron donor, respectively. C(1), of course, is the ring carbon to which the substituent is attached. One or two minima are located within this tubular region.

On the basis of the orientation of this tube, the MEP clearly distinguishes between ortho/meta protonation (when the ^{2}A state is preferred, i.e., for π-donor substituents) and ipso/para protonation (^{2}B state, π acceptors). The further distinction between ortho and meta or between ipso and para should depend upon the relative proximity of the MEP minima to the two positions.

Figure 3 is an example of the MEP for the anisole radical anion. It is a slice taken 1.2 Å above, and parallel to, the molecular plane. In this case there are two essentially equivalent minima near the C(2)–C(3) and C(5)–C(6) bonds. Close examination of the MEP reveals that the exact minima lie about 1.15 Å above the plane and are marginally closer to the ortho carbons.[49] We thus predict that first protonation would occur extensively at both ortho and meta positions, with perhaps a slight preference for the ortho positions. Assuming that the second protonation occurs at the 3 position in the subsequently formed cyclohexadienyl anion (see below), this result is consistent with the observed product (7) for anisole reduction,[6a]



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but indicates that both reaction pathways, as given by Burnham,[36] are likely to be important.

Figures 4 and 5 are MEP plots for Bz$^-$ with the π-accepting substituents NO$_2$ and COO$^-$ (1.2 Å above the molecular plane for NO$_2$ and 1.0 Å for COO$^-$ to show up the tubular region more clearly). C$_6$H$_5$NO$_2^{-\cdot}$ has one minimum near the para carbon, while C$_6$H$_5$COO$^{2-\cdot}$ has one near the ipso carbon. Hence we expect initial protonation at the para and ipso positions, respectively. This situation could be reversed by the presence of counterions. Counterions could also be associated with the negative region around the oxygen atoms in all of these molecules.

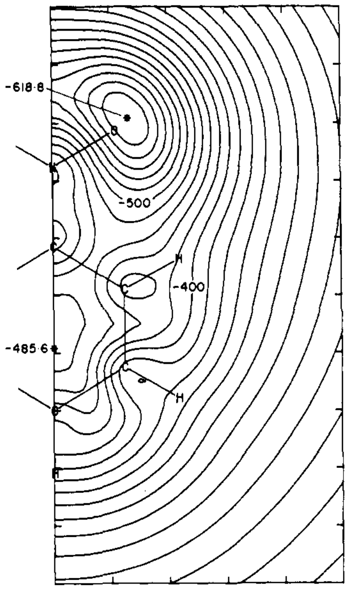


Figure 4. MEP map of nitrobenzene radical anion, 1.2 Å above molecular plane.

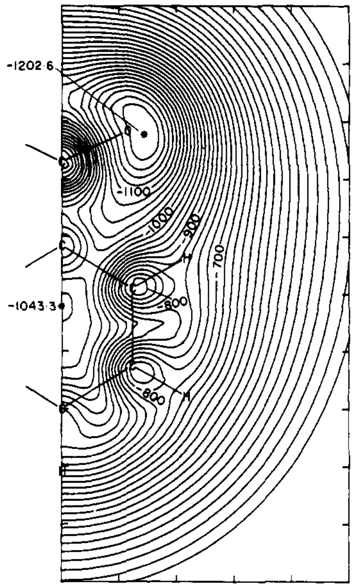
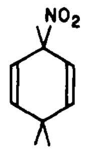


Figure 5. MEP map of benzoate radical dianion, 1.0 Å above molecular plane.

In any case, assuming again second protonation at the 3 position in the substituted cyclohexadienyl anion, the (kinetically controlled) products would be **8** and **9**, respectively, **9**



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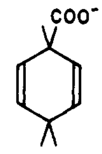

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being consistent with the experimental results[39,42,50] for irreversible protonations.

Of the remaining SBz⁻'s, $C_6H_5CN^{-\cdot}$ and $C_6H_5COOH^{-\cdot}$ have two almost equal minima near both the ipso and the para carbons, with a slight preference for the ipso carbon, while the π-donor substituents (F, OH, and NH_2) all create MEPs very similar to that of $C_6H_5OCH_3^{-\cdot}$, with minima always marginally closer to the ortho carbons. The MEP for $C_6H_5OH^{-\cdot}$ is practically identical with that for $C_6H_5OCH_3^{-\cdot}$.

The results for NO_2, CN, F, and OH are of no practical use in the study of the Birch reduction, since the substituents, NO_2 and CN, are themselves preferentially reduced;[6c] i.e., protonation takes place on the substituent rather than the ring, while fluorine is cleaved from the ring during reduction.[51] Phenolic compounds are not usually reduced owing to the formation of phenolic salts[6a,52] although in amine solvents phenol is reducible to cyclohexanone.[53]

We conclude by presenting the π-electron charges of the SBz⁻'s in Figure 6 for comparison with the electrostatic potential. Qualitatively, they generally predict the same protonation sites as the MEP.

Calculations are currently in progress on substituted cyclohexadienyl radicals ($C_6H_6X^{\cdot}$) which will give information concerning the thermodynamically preferred initial site of protonation and on substituted cyclohexadienyl anions ($C_6H_6X^-$) using molecular electrostatic potentials to study the second protonation step. Preliminary calculations on the latter suggest that the second protonation takes place at the 3 position of the substituted cyclohexadienyl anion, regardless of the substituent. Full details will be published in due course.

Conclusions

Several important points emerge from this theoretical study of the radical anions (SBz⁻) of substituted benzenes.

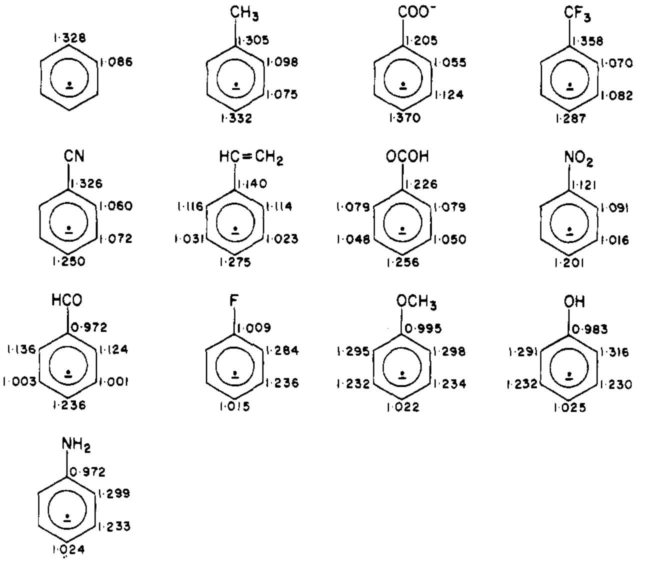

Figure 6. π-Electron distributions (RHF/STO-3G) for the ground-state structures of radical anions of substituted benzenes (pyramidal NH_2 in $C_6H_5NH_2^{-\cdot}$).

(1) Whereas the ^2A_u and $^2B_{1u}$ states of Bz⁻ have very similar energies, corresponding ^2A and ^2B states of the SBz⁻'s often have quite different energies.

(2) The ^2A state is favored by π electron donor substituents (e.g., NH_2, OH, OCH_3, F) while the ^2B state is favored (generally more strongly) by π electron acceptor substituents (e.g., CH_3, CF_3, $CH{=}CH_2$, NO_2, CN, COOH, COO^-), results which can readily be rationalized in terms of the molecular orbital coefficients of the (highest) singly occupied orbital in the corresponding states of Bz⁻.

(3) The benzene radical anion is generally substantially stabilized by substituents which are both π-electron acceptors and σ-electron acceptors. The effect of π electron donor substituents is much smaller reflecting opposing σ stabilization (strongest for F) and π destabilization (strongest for NH_2).

(4) The stabilization energies are in qualitative agreement with available data on the relative rates of Birch reduction of substituted benzenes.

(5) The calculated molecular electrostatic potentials are used to indicate kinetically preferred sites of protonation in the SBz⁻'s. Two classes may be distinguished: (i) For a π-electron

donor substituent, protonation occurs at the ortho or meta positions. For the systems examined, the results do not indicate a strong preference for one or the other of these sites. (ii) For a π-electron acceptor substituent, protonation occurs at the ipso or para positions. The former is preferred for CN, COOH, and COO^- substituents while the latter is preferred for NO_2.

Acknowledgments. We thank Dr. Mark Vincent for the use of his restricted SCF program and Professor G. Subba Rao for helpful discussions.

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