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A Theoretical Approach to the Birch Reduction. Structures and Stabilities of Cyclohexadienyl Anions

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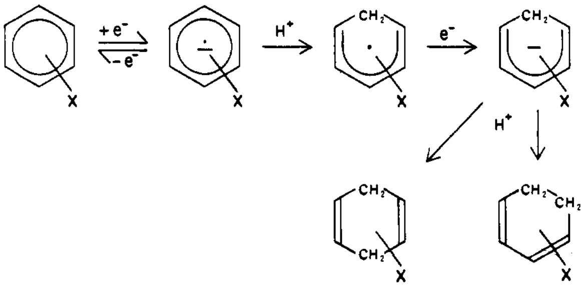
Abstract: Ab initio molecular orbital calculations with the minimal STO-3G basis set have been carried out for the cyclohexadienyl anion (CHD$^-$), the homocyclopentadienyl anion (HCPD$^-$), and a series of substituted cyclohexadienyl anions (SCHD$^-$) with substituents CH_3, CN, COOH, NO_2, COO$^-$, F, OCH_3, OH, and NH_2. Optimized structures have been obtained for CHD$^-$ and HCPD$^-$. The former has a planar ring while the latter has a substantially folded (121.7°) structure. CHD$^-$ lies 186 kJ mol^{-1} lower in energy than HCPD$^-$ (4-31G//STO-3G). Relative isomer energies of 1-, 2- and 3-substituted cyclohexadienyl anions are ordered in accordance with expectations based on the coefficients of the highest occupied molecular orbital of CHD$^-$. Molecular electrostatic potential plots of substituted cyclohexadienyl anions predict that kinetic protonation takes place preferentially at the carbon atom *para* to the first protonation site (i.e., at C(3)). This is so regardless of substituent or substituent position. Rates of nucleophilic substitution reactions of substituted benzenes correlate well with the calculated stabilities (relative to corresponding substituted benzenes) of the substituted cyclohexadienyl anion intermediates involved in an S_N addition/elimination mechanism.

Introduction

In recent papers,[1-3] we have examined theoretically the benzene radical anion ($Bz^{-\cdot}$),[1] substituted benzene radical anions ($SBz^{-\cdot}$),[2] and substituted cyclohexadienyl radicals ($SCHD^{\cdot}$),[3] species involved in the first two steps of the Birch reduction of substituted benzenes by alkali metals and alcohols in liquid ammonia[4] (eq 1).



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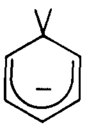
In this paper, we examine substituted cyclohexadienyl anions (SCHD$^-$) which are the products of the penultimate step in the reaction sequence 1. These anions are stable in solution as salts involving the alkali metal cation,[5,6] and under certain conditions in liquid ammonia can be stored for several days.[7] The structures and stabilities of these anions are clearly of importance in obtaining a full understanding of the mechanism of the Birch reduction. As a cautionary remark, we note that our calculations refer, in principle, to isolated species in the gas phase. Under normal reaction conditions, both solvent and counterion undoubtedly play important roles. In addition, reactions for some of the substituents follow a course different from that of the normal Birch reduction. For example, groups such as NO_2, F, and CN are reducible preferentially to the ring while OH normally exists as phenolate anion. However, they are included for completeness and in order to establish general principles. Results for OH provide useful models for those of alkoxy substituents.

The second protonation step in the Birch reduction (i.e., protonation of the SCHD^{-1}'s) is known experimentally to occur predominantly para to the first protonation (i.e., at C(3)) under irreversible conditions. It is of interest to examine whether this result is consistent with predictions based on molecular electrostatic potentials (MEP's) of the SCHD$^-$'s.

The cyclohexadienyl anion is of special interest in its own right because of the possibility that it is a homoaromatic species, the homocyclopentadienyl anion (HCPD$^-$), corresponding to the nonplanar structure **2** rather than the planar **1**. However, both theory[7,8] and experiment[7,9] suggest that this is not the case. Initial MINDO/3 calculations with full optimization of the geometry of CHD$^-$ indicated a planar nonhomoaromatic anion (**1**).[7] Subsequent MINDO/3 calculations[8] yielded a secondary local minimum in the surface corresponding to the homocyclopentadienyl anion (**2**) and lying approximately 150 kJ mol^{-1} higher in energy than **1**. Structure **1** is found to lie in a very flat region of the MINDO/3 surface with only 2.5 kJ mol^{-1} being required for a 10° puckering of the methylene group, or 9.2 kJ mol^{-1} for a 20° puckering.[7] Because the MINDO/3 calculations predict such a flat minimum, it is desirable to examine whether the prediction of a planar structure is supported at the ab initio level.



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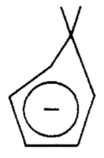

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Finally, the substituted cyclohexadienyl anions are of interest through their role as intermediates in aromatic nucleophilic substitution reactions[10-15] In particular, the dependence of such

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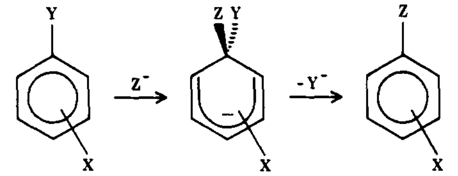


(2)

reactions on the nature and position of X is of interest.

Method

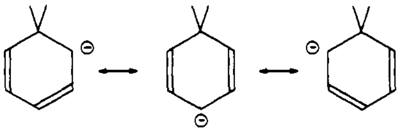
Standard self-consistent-field molecular orbital calculations were carried out using a modified version[16a] of the GAUSSIAN 70 system of programs.[16b] The parent cyclohexadienyl anion (**1**) was fully optimized under a C_{2v} symmetry constraint (i.e., a planar ring) with the STO-3G basis set.[17] In addition, CHD^- was examined in a nonplanar structure in which the methylene group was deflected 2° from the ring plane [C(6)C(1)C(5)C(4) dihedral angle of 2°] and C(1)–H(1) and C(5)–H(5) bonds bent below the plane so as to maintain planarity at C(1) and C(5). The optimized structural parameters of the planar structure were used for this distorted structure. Finally, optimization of a homocyclopentadienyl structure (**2**) was carried out assuming C_s symmetry. For this structure the methylene group and the C(1)–H(1) and C(5)–H(5) bonds were allowed to distort out of the plane as in the 2° structure and the rest of the molecule was kept planar. The C–H bond lengths, other than C(6)–H, were not reoptimized. Subject to these constraints, the remaining lengths and angles were fully optimized. Single calculations with the split-valence 4-31G basis set[18] were carried out on the optimized structures of **1** and **2** to provide improved energy comparisons.

For the substituted cyclohexadienyl anions, the STO-3G optimized parameters for C_{2v} CHD^- were used for the ring and standard bond lengths and angles[19] for the substituents except that the COC angle (α) of the methoxy substituent was optimized in each case to avoid steric problems. This yielded α = 112.1° (6 position), 118.1° (1 position), 118.5° (2 position), and 116.9° (3 position).

Examination of the kinetically preferred sites of protonation of the $SCHD^-$'s was carried out with the aid of molecular electrostatic potentials (MEP's), the theory of which is well summarized in recent reviews.[20,21] The MEP calculations were carried out with a program based on the GAUSSIAN 70 system.[16,22,23]

Results and Discussion

A. Geometric Structures of the Cyclohexadienyl Anion (CHD^-, 1) and Homocyclopentadienyl Anion ($HCPD^-$, 2). The optimized C_{2v} structure for CHD^- is shown in Figure 1. The theoretical bond lengths reflect contributions from valence structures of the type **3**. Comparison with the STO-3G optimized structure for the cyclohexadienyl radical[3] shows that the two structures are quite similar, a result which is not surprising since the highest occupied molecular orbitals (HOMO's) of both species are essentially nonbonding. More detailed examination shows an increase in the C(1)–C(2) bond length and a decrease in the C(2)–C(3) length in moving from CHD· to CHD^-.



3a **3b** **3c**

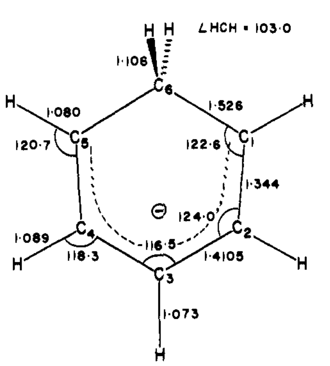


Figure 1. STO-3G optimized structure of the cyclohexadienyl anion (CHD^-, **1**).

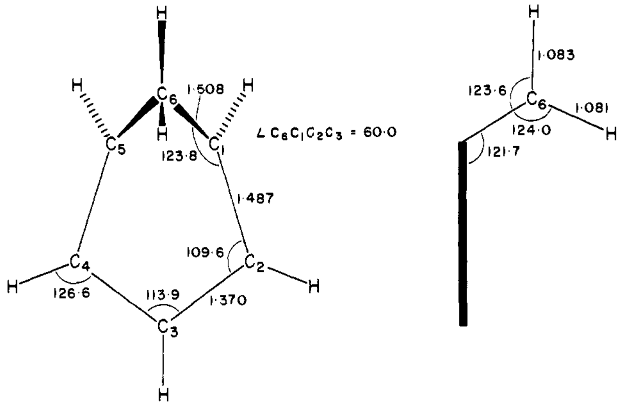


Figure 2. STO-3G optimized structure of the homocyclopentadienyl anion ($HCPD^-$, **2**).

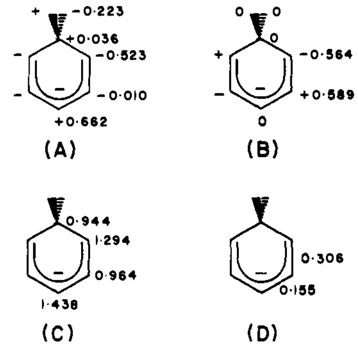


Figure 3. Calculated electronic properties of the cyclohexadienyl anion: (A) HOMO coefficients (b_1 symmetry); (B) LUMO coefficients (a_2 symmetry); (C) π-electron populations; (D) π-overlap populations.

The calculated energy of the 2° puckered CHD^- structure is 0.2 kJ mol^{-1} higher than that of the C_{2v} form. It is likely then that the CHD^- ring is planar although, in view of the small energy difference, further optimization would be necessary to confirm this conclusion.

Figure 2 shows the STO-3G optimized structure of $HCPD^-$ (**2**: total energy −228.20722 (STO-3G), −230.77162 (4-31G)). This structure corresponds to a local energy minimum lying 142.5 kJ mol^{-1} (STO-3G) or 186.1 kJ mol^{-1} (4-31G) above **1**. A similar value (151 kJ mol^{-1}) was calculated at the MINDO/3 level.[8] We find the CH_2 group puckered 121.7° out of the plane (C(6)-C(1)C(5)C(4) angle) while the C(1)–C(5) length is shortened to 1.609 Å.

B. Electronic Structure of CHD^-. The coefficients of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for CHD^- are given in Figure 3. These two orbitals and the remainder of the π MO's can be satisfactorily constructed by considering the interaction of the

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Table I. Calculated Total Energies (hartrees) and Relative Energies[a] (kJ mol^{-1}) in Parentheses for Conformations of Substituted Cyclohexadienyl Anions

substituent	6 position	1 position	2 position	3 position
H	−228.26148[b] (0)	−228.26148[b] (0)	−228.26148[b] (0)	−228.26148[b] (0)
CH_3	−266.84323 (8.9) [HCC(6)H trans]	−266.84663[c] (0) [HCC(1)C(2) cis]	−266.84460[d] (5.3) [HCC(2)C(1) cis]	−266.84389 (7.2) [HCC(3)C(2) cis]
CN	−318.83532 (94.5)	−318.86265 (22.7)	−318.84122 (79.0)	−318.87130 (0)
COOH	-	-	-	−413.39068 [planar, HOCO cis]
NO_2	−429.00411[e] (71.9) [ONC(6)H cis]	−429.02280 (22.8) [planar]	−428.98797 (114.3) [planar]	−429.03151 (0) [planar]
COO^- [planar]	-	−412.44157 (0)	-	−412.44105 (1.4)
F	−325.73184 (0)	−325.72478 (18.5)	−325.73144 (1.0)	−325.71830 (35.5)
OCH_3 [HCOC trans]	−340.69218 (0) [COC(6)H trans]	−340.67095 (55.7) [COC(1)C(2) cis]	−340.67953 (33.2) [COC(2)C(1) trans]	−340.66382 (74.5) [COCC cis]
OH	−302.10894 (0) [HOC(6)H trans]	−302.09498[f] (36.7) [HOC(1)C(2) cis]	−302.10631[g] (6.9) [HOC(2)C(1) trans]	−302.08589 (60.5) [HOCC cis]
NH_2	−282.58203[h] (0) [:NC(6)H 60°]	−282.55785 (63.5) [planar]	−282.57240 (25.3) [planar]	−282.54597 (94.7) [planar]

[a] Energies relative to the lowest energy isomer for the particular substituent. [b] 4-31G energy: −230.84249. [c] Total (and relative) energies for HCC(1)C(2) trans are −266.84305 (9.4). [d] Total (and relative) energies for HCC(2)C(1) trans are −266.84347 (8.3). [e] Total (and relative) energies for ONC(6)H orthogonal are −429.00093 (80.3). [f] Total (and relative) energies for HOC(1)C(2) trans are −302.09453 (37.8). [g] Total (and relative) energies for HOC(2)C(1) cis are −302.10591 (7.9). [h] Total (and relative) energies for other :NCH dihedral angles are as follows: −282.57936 (7.0) cis, −282.57576 (16.5) trans, −282.57434 (20.2) 120°.

Hückel orbitals of a pentadienyl fragment with the π_{CH_2} and $\pi^*_{CH_2}$ orbitals of a methylene group. The interaction diagram of Figure 4 shows the combined orbitals, along with the 4-31G calculated orbital energies (eV). Orbital energies for $\mathrm{CHD}\cdot$ appear in parentheses for comparison.

It can be seen from Figure 4 that the HOMO of the pentadienyl fragment interacts by nearly equal amounts with the π and π^* methylene orbitals resulting in a HOMO of nearly the same energy as the pentadienyl HOMO. The two methylene orbitals combine with a resultant nearly zero C(6) p-orbital coefficient. This result has been used previously to explain the nonhomoaromaticity of CHD^-: the molecule would not benefit from puckering because the coefficient of the p orbital at C(6) in near-planar structures is too small to allow significant overlap with the pentadienyl orbitals.[7]

The large coefficients on C(1), C(3), and C(5) of the CHD^- HOMO are reflected in the large π-atomic charges on these atoms (Figure 3) and are consistent with the resonance structures **3a**, **3b**, and **3c**. The total π charge, summed over these atoms, is, in fact, 4.026, implying that the negative charge is concentrated on C(1), C(3), and C(5). The greatest HOMO coefficient, and π-charge, is at C(3); the latter conclusion has previously been reached from NMR studies.[7,9c,24]

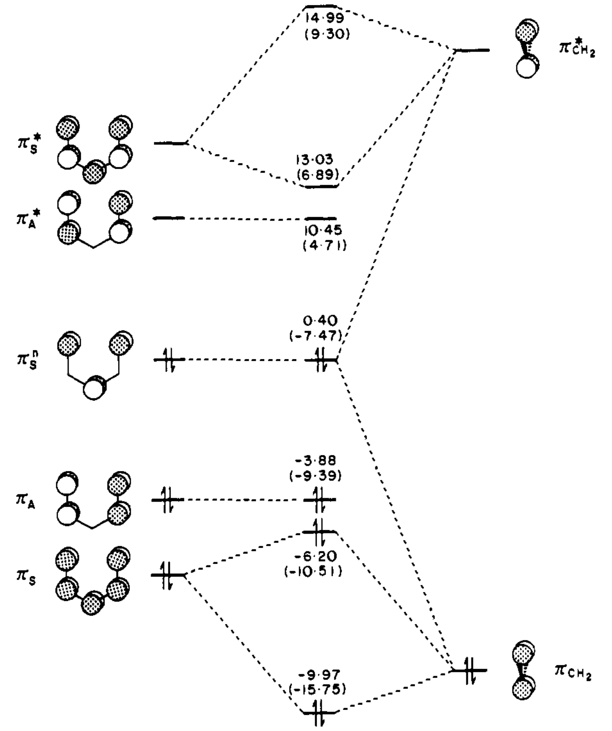

Figure 4. Schematic orbital interaction diagram for the π-molecular orbitals of CHD^-. Calculated orbital energies of CHD^- (4-31G) and $\mathrm{CHD}\cdot$ (RHF/4-31G, in parentheses) are also shown.

The orbital energies of CHD^- have all shifted 5 to 10 eV above those of $\mathrm{CHD}\cdot$ (Figure 4). This is generally expected for anions compared to neutral parent molecules. It might therefore be expected that the stabilizing or destabilizing influence of a substituent will be dominated by interaction with the HOMO, at least for positions 1 to 5. Greatest stabilization should occur for π acceptors at C(3), followed by C(1), C(5). Conversely, greatest destabilization for π donors will occur at C(3), followed by C(1), C(5). The effect of substitution at the saturated 6 position is likely to be relatively insensitive to the π-electron properties of the substituent, but rather will be dominated by σ effects which should stabilize the anion for an electron-withdrawing substituent.

C. Relative Energies and Electronic Properties of SCHD^- Isomers. The STO-3G total energies and relative energies for SCHD^- isomers are presented in Table I. As expected, the π donors (F, OCH_3, OH, NH_2) all prefer the 6-substituted isomer and the π acceptors (CN, NO_2) the 3-substituted isomer. Previous calculations[15] and our own unpublished data indicate that the predicted preference for 6-fluoro CHD^- is enhanced when the C–F length is optimized and a more flexible basis set is used in the theoretical treatment. The energy ordering for positions C(2), C(1), and C(3) for the π donors is opposite to that for the π acceptors and corresponds to increasing destabilization for the π donors and increasing stabilization for the π acceptors, at these three positions, as the HOMO coefficient increases.

Some information regarding the relative isomer stabilities comes from experiments[6] in which the SCHD^- anions are produced from the 2,5- or 1,4-dihydrobenzenes by the action of strong base, notably KNH_2–NH_3. These results show that in 2,5-dihydroanisole, the proton in the 2 position rather than that in the 5 position is selectively removed while in the 1,4-dihydrobenzoate salt the 1- rather than the 4-proton is removed. Although the experimental situation is undoubtedly influenced by ion-pairing and solvation, a detailed discussion of which is beyond the scope of this paper, the experimental results are nevertheless consistent with the theoretical predictions (Table I) that the 2-methoxy CHD^- is lower in energy than 1-methoxy CHD^- and that 3-nitro

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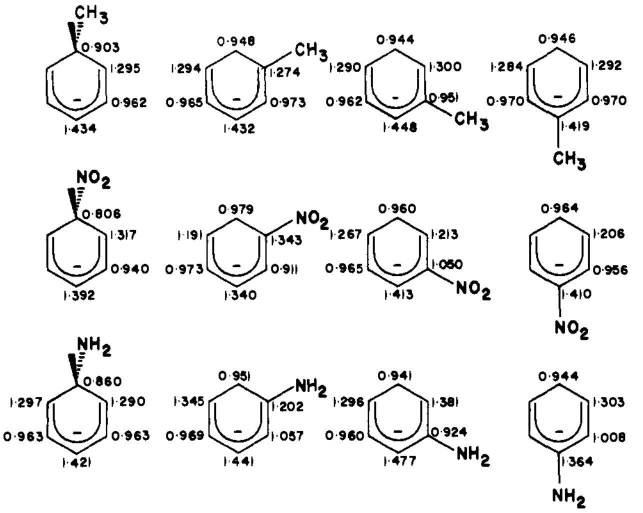


Figure 5. Mulliken atomic π populations for representative substituted cyclohexadienyl anions.

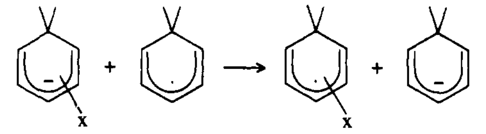
CHD$^-$ is lower in energy than 6-nitro CHD$^-$ (using NO_2 as a model π-accepting substituent).

It is important to note that the SCHD$^-$ intermediate involved in the Birch reduction of substituted benzenes is decided by the product of the first *irreversible*[25] protonation step (i.e., SBz$^-$ $\rightarrow$ SCHD$^\cdot$) and is not necessarily the most stable SCHD$^-$ isomer. This is indeed the case for π-donor substituents for which we predict[2,3] that the SCHD$^-$ intermediate involved in the Birch reduction is the 1- or 2-substituted isomer even though the 6-substituted isomer lies lowest in energy. We are unaware of any evidence for equilibration of the 6- and 1- or 2-substituted anions under the normal experimental conditions.

Atomic π-electron populations for representative substituted cyclohexadienyl anions are displayed in Figure 5. These are consistent with contributions from the expected classical valence structures.

D. Stabilities of SCHD$^-$ Isomers. Relative Electron Affinities of SCHD$^\cdot$. CHD$^-$ is similar to the benzene radical anion in that both have higher calculated energies than the parent neutral molecules; i.e., both benzene and CHD$^\cdot$ have negative electron affinities (EA's) at the 4-31G level of theory. However, absolute values of electron affinities at this level of theory are unreliable. Relative values are likely to be more meaningful. From this point of view, we note that the calculated EA of CHD$^\cdot$ is about 2 eV (200 kJ mol^{-1}) less negative than that of benzene (−3.30 eV vs. −1.27 eV); no gas-phase data are available to indicate whether CHD$^-$ is a resonance state or a stable anion.

Relative electron affinities of SCHD$^\cdot$ or stabilization energies of SCHD$^-$ relative to SCHD$^\cdot$ [SE(SCHD$^-$/SCHD$^\cdot$)] may be defined as energy changes for reactions of type 3. These sta-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bilization energies are presented in Table II. They give a measure of the stabilizing effect of a substituent in CHD$^-$ compared with its effect in CHD$^\cdot$, positive values implying a greater stability in the anion.

For a given type of substituent, the SE's of the four isomers follow the same pattern. The π donors stabilize CHD$^-$ in the order 6 position >2 position >1 position >3 position, and this is due to opposite effects in the energy orderings of SCHD$^-$ vs. SCHD$^\cdot$: the lower energy SCHD$^-$'s tend to correspond to the higher energy SCHD$^\cdot$ isomers, leading to a reinforcement of energy changes in (3). This arises because large SOMO coefficients in SCHD$^\cdot$ produce favorable interactions whereas, in SCHD$^-$, large HOMO coefficients lead to destabilization. All the 6-substituted and most of the 2-substituted isomers are stabilized (SE > 0), while all the 3- and most of the 1-substituted isomers are destabilized (SE < 0).

The SE's for the π acceptors (NO_2, CN) are nearly in the opposite order, i.e., 3 position > 1 position > 6 position > 2 position. In contrast to the π donors, the qualitative orderings of the SCHD$^-$ isomer energies are identical with those for the SCHD$^\cdot$ isomers implying similar stabilizing interactions for the SCHD$^-$'s and the SCHD$^\cdot$'s: large HOMO coefficients lead to stabilization in both SCHD$^-$ and SCHD$^\cdot$ for π acceptors. The actual values of the SE's, Table II, are, however, largely dominated by the SCHD$^-$ relative isomer energies. The π acceptors (which are also σ acceptors) stabilize all CHD$^-$ positions (SE > 0).

The SE's for the CH_3 group are dominated by the energies of the radical and, except for the 6 position, indicate a slight destabilization.

For the various substituents, at any given position, the SE's are consistently in the order:

$$NO_2 > CN > COOH > F > OH > NH_2 > COO^-$$

and this corresponds to the order found[2] for SBz$^-$ suggesting that similar σ- and π-electron effects are operative for both systems. The relative position of CH_3 within the sequence varies from site to site and this is characteristic of the more polarizable nature of the methyl group which is more pliable to its environment than the other substituents. Note that the OCH_3 and OH SE's are quite close. The ordering of SE's is also consistent with stabilities of the anions as reflected in their ease of decomposition through aromatization by loss of hydride ion.[5] A series of decreasing stability determined in this manner is COOH > OMe > H > alkyl.

E. Sites of Protonation in Substituted Cyclohexadienyl Anions. The molecular electrostatic potential (MEP) for CHD$^-$ was examined in a series of slices taken parallel to the molecular plane at distances of 0.0, 0.75, 1.0, 1.25, and 1.5 Å from the plane. In the section coinciding with the molecular plane (Figure 6), MEP minima occur about 1.5 Å away from each bond, the deepest occurring for C(2)–C(3). These minima get deeper above the plane, as the π system is entered, and persist to at least 0.75 Å. At 1.0 Å, the MEP is dominated by the π-electron system, although the effect of the positive nuclei is still apparent in the MEP maxima above the carbon atoms. At 1.25 Å we reach the deep minimum (−696.3 kJ mol^{-1}) due to the π electrons which is positioned close to C(3), i.e., *para* to the methylene carbon. A rough interpolation using planes at 1.0, 1.25, and 1.50 Å places the global minimum at ~1.15 Å above (and below) the molecular plane. All subsequent plots, for SCHD$^-$, are therefore taken in the 1.2 Å plane, which should be sufficiently close to the exact minimum for qualitative and semiquantitative purposes.

The MEP at 1.2 Å (also included in Figure 6) shows that the deep negative region extends from C(3) to C(1) and C(5), with secondary minima near C(1) and C(5), but C(2) and C(4) are in comparison more positive by over 100 kJ mol^{-1}. This clearly indicates that *kinetically controlled protonation takes place preferentially at the carbon atom para to the first proton*, agreeing with experimental results. Protonation at C(1) is not excluded but should occur far less rapidly given the ~60 kJ mol^{-1} difference in the MEP values above C(1) and C(3) (as seen by examining the contours). This compares favorably with rate data for the protonation of CHD$^-$, indicating that protonation occurs eight times faster at C(3) than at C(1).[26]

The effect of a π-acceptor substituent such as NO_2 or CN on the MEP of CHD$^-$ is an overall reduction in its depth as seen in Figure 7 for the four isomers of NO_2-substituted CHD$^-$. This is due to the withdrawal of both π and σ electrons from the ring. The shallowest minima are found to occur for the strongest electron acceptor, NO_2, and the deepest for CN, the weakest acceptor. The

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[25] See, for example, Birch, A. J.; Johnson, W. M. P. *Aust. J. Chem.* **1976**, *29*, 1631.

[26] Bates, R. B.; Carnighan, R. H.; Staples, C. E. *J. Am. Chem. Soc.* **1963**, *85*, 3032.

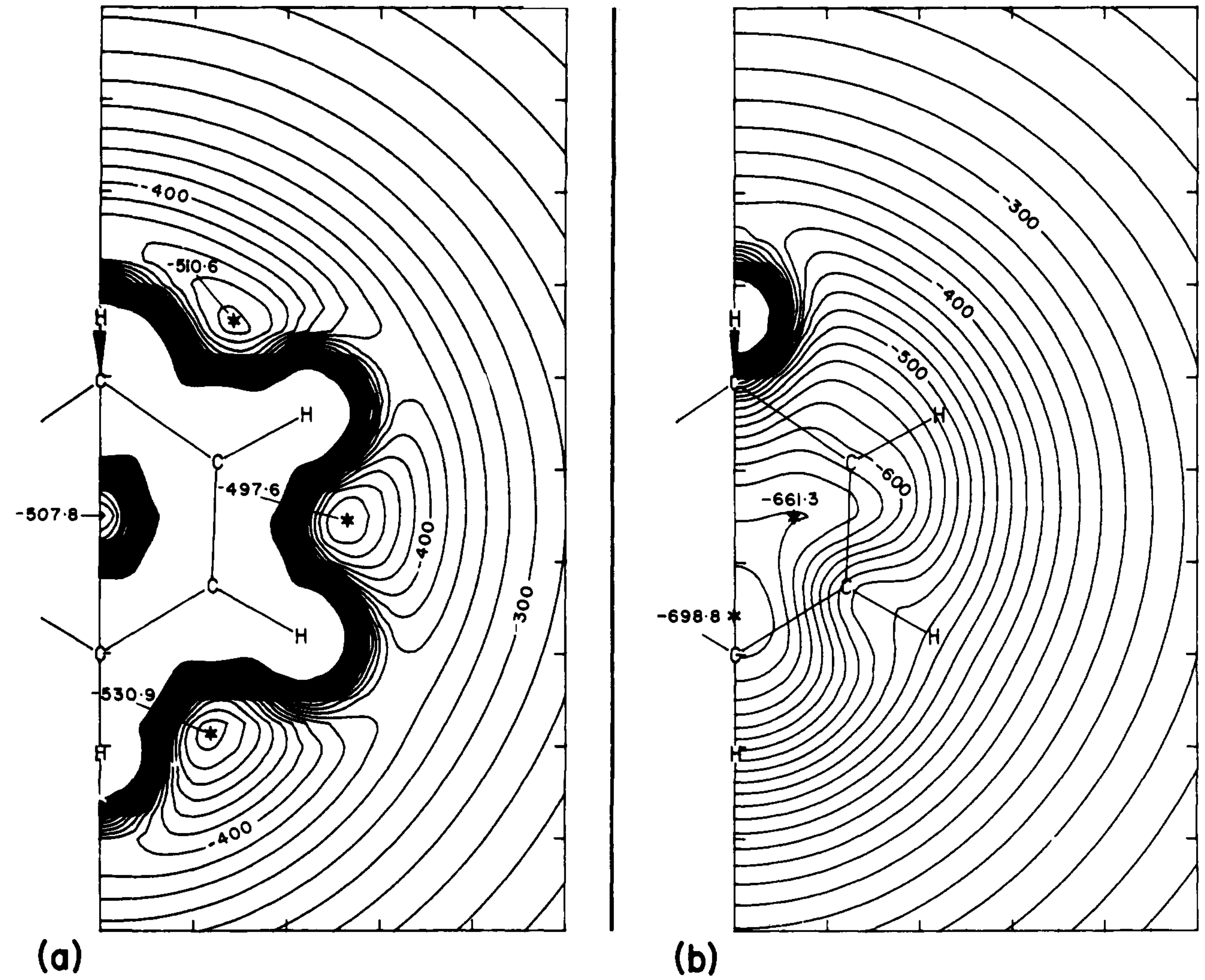


Figure 6. MEP maps of cyclohexadienyl anion (a) in the molecular plane, and (b) 1.2 Å above the molecular plane.

Table II. Stabilization Energies of Substituted Cyclohexadienyl Anions [SE($SCHD^-$/SCHD·)] or Relative Electron Affinities of Substituted Cyclohexadienyl Radicals (kJ mol^{-1})[a]

	position			
substituent	6	1	2	3
H	0	0	0	0
CH_3	7.0	-3.4	-0.4	-6.6
CN	83.1	120.5	71.3	136.0
COOH				106.9
NO_2	129.0	170.1	88.4	189.5
COO^-		-386.9		-397.8
F	62.1	6.2	31.8	-11.3
OCH_3	62.2	-21.0	22.3	-33.9
OH	56.9	-19.6	20.6	-39.7
NH_2	35.0	-50.6	-0.3	-79.3

[a] As defined by reaction 3.

Table III. Stabilization Energies of Substituted Cyclohexadienyl Anions [SE($SCHD^-$/SBz)] or Relative Hydride Ion Affinities of Substituted Benzenes (kJ mol^{-1})[a,b]

	position			
substituent	6	1	2	3
H	0	0	0	0
CH_3	-5.3	-5.7	-4.6	-3.5
CN	54.1	125.8	69.6	148.6
COOH				120.2
NO_2	129.9	178.9	87.5	201.8
COO^-		-392.9		-394.2
F	29.0	10.4	27.9	-6.6
OCH_3	43.3	-12.5	10.0	-31.2
OH	23.4	-13.3	16.5	-37.1
NH_2	15.8	-47.6	-9.5	-78.8

[a] As defined by reaction 5. [b] Calculated using data for substituted benzenes from: Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972,** *94,* 1496.

depths of the MEP, for the isomers of $SCHD^-$, reflect the varying amount of π-electron withdrawal with substituent position. Thus the MEP becomes shallower as the substituent goes from positions 6, 2, 1, to 3. The shape of the potential, for the π acceptors, is very similar to that of the unsubstituted species; i.e., the deepest minimum occurs near C(3). Distinct additional minima also occur near C(1) and C(5) for the 6- and 3-substituted isomers. The greatest deviation from the symmetrical MEP of CHD^- occurs when the substituent is at C(2): the MEP is shifted away from C(1) making the latter less suitable for protonation.

MEP plots for the π-donor substituent, OH, are given in Figure 8. This substituent appears to contribute an increase in the depth of the MEP because of π-electron donation and a decrease because of σ-electron acceptance with the latter effect predominating. The shapes of the MEP's are again very similar to that of CHD^-, additional minima occuring at C(1) and/or C(5) for all isomers. The greatest asymmetry occurs in the 1-substituted isomer for which the MEP is distorted away from C(1) in a similar manner to that of π acceptors at the 2 position. The electrons are less delocalized and contribute to a deeper MEP at C(5).

In summary, the MEP results for the $SCHD^-$'s show an overwhelming preference for kinetically controlled protonation *para* to the first protonation site, i.e., at C(3), regardless of substituent or of substituent position. Protonation at C(1) and/or C(5) is

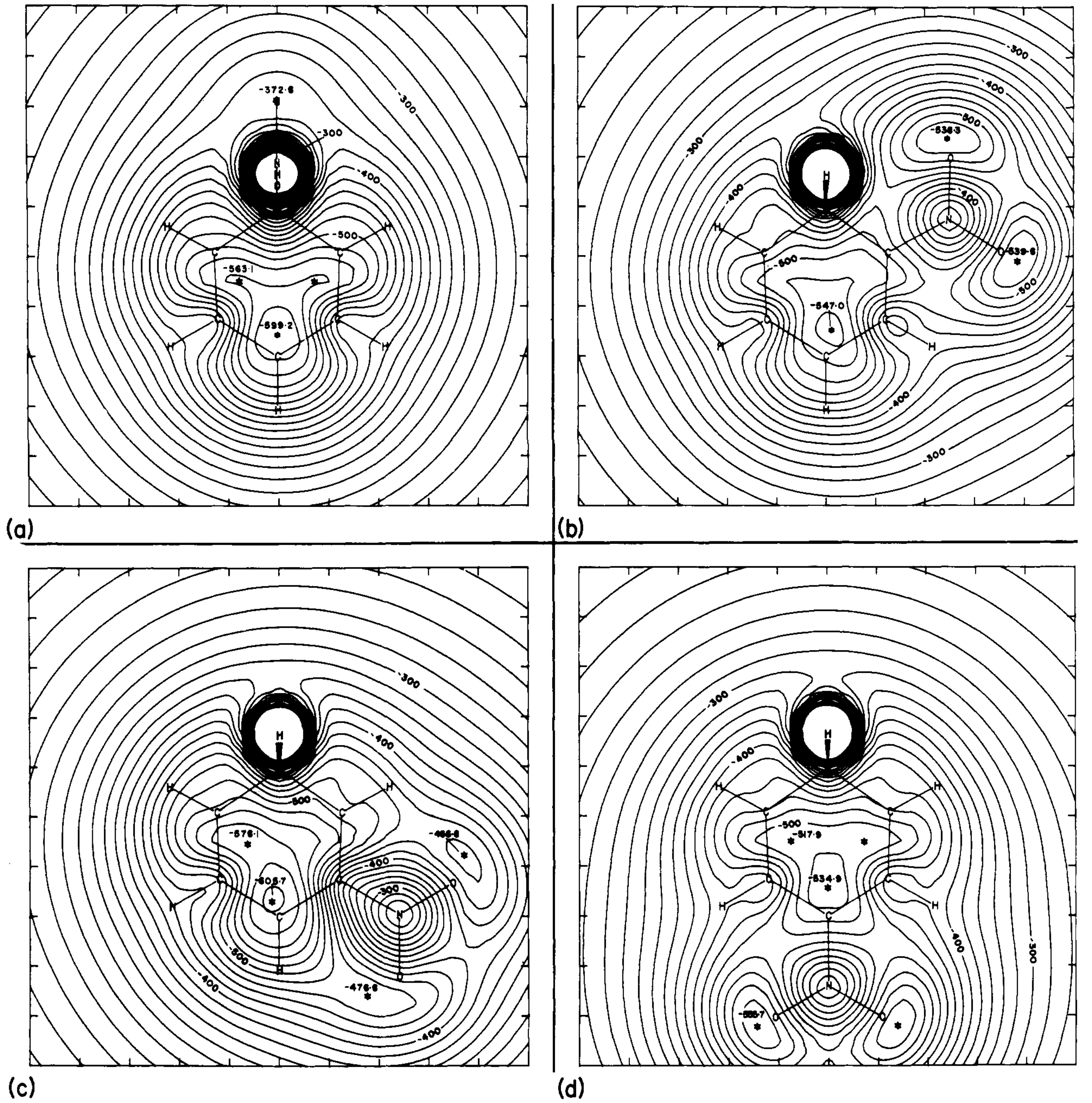


Figure 7. MEP maps of nitrocyclohexadienyl anion isomers 1.2 Å above the molecular plane: (a) 6-substituted isomer, (b) 1-substituted isomer, (c) 2-substituted isomer, (d) 3-substituted isomer.

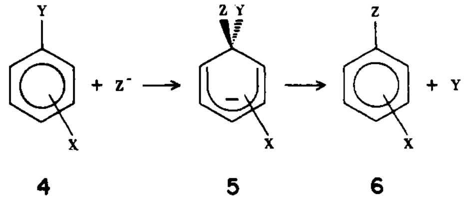
possible for all isomers, although the C(1)/C(3) MEP difference is generally 10 to 40 kJ mol^{-1}. Furthermore, 2-substitution of a π acceptor or 1-substitution of a π donor makes protonation unlikely at C(1). Because of the reduced depths of the MEP upon substitution with an electronegative group, the rate of second protonation should be reduced for such substituted CHD$^-$'s relative to unsubstituted CHD$^-$.

It is interesting that for the protonation of the SCHD$^-$'s both electrostatic and frontier orbital considerations[27] lead to similar conclusions. In particular, examination of the coefficients within the SCHD$^-$ HOMO's shows consistently higher values at C(3) than at the other positions, consistent with kinetically controlled protonation *para* to the first protonation site.

It should be recognized that our theoretical results set a base line from which perturbations can be rationally examined. For example, in the reduction of anisole, *t*-BuOH gives virtually pure 2,5-dihydro derivative as predicted. MeOH gives evidence of about 30% 2,3-dihydro derivative.[28] The causes of such effects need further elucidation.

F. Aromatic Nucleophilic Substitution. Although aromatic nucleophilic substitution reactions generally require quite vigorous conditions, they are important industrially. For example, phenol and aniline are commonly made by such procedures.[10]

The accepted addition/elimination mechanism for aromatic S$_N$ reactions, in which the leaving group, Y, is replaced by a nucleophile, Z$^-$, involved the formation of a stable cyclohexadienyl anion intermediate (**5**). The rate of substitution is determined



(4)

4 **5** **6**

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(27) See, for example, Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976.

(28) Birch, A. J.; Smith, M. unpublished data.

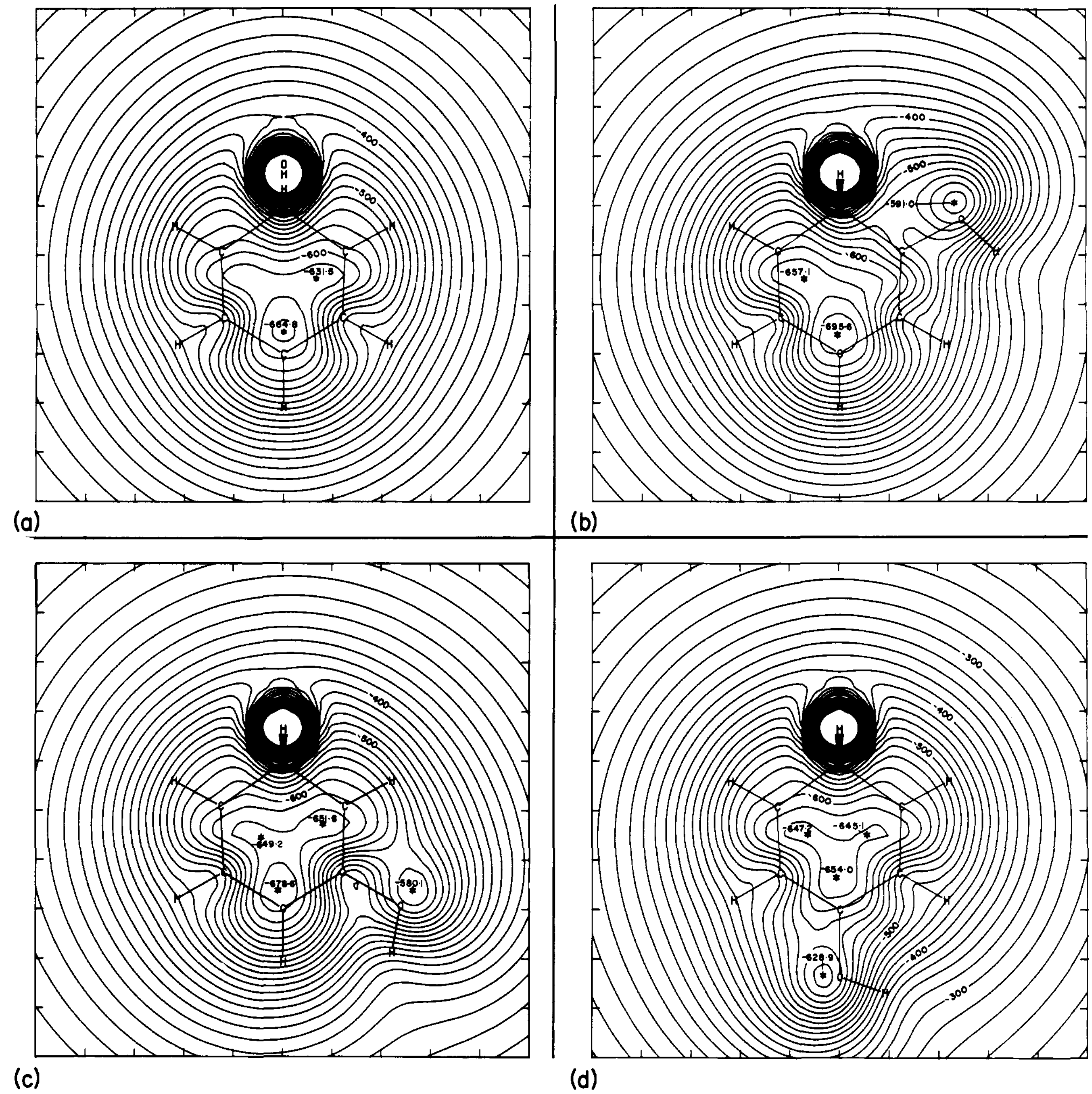
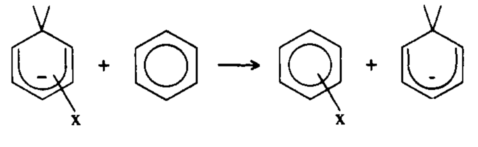


Figure 8. MEP maps of hydroxycyclohexadienyl anion isomers 1.2 Å above the molecular plane: (a) 6-substituted isomer, (b) 1-substituted isomer, (c) 2-substituted isomer, (d) 3-substituted isomer.

by the energy of the rate-limiting transition state for the two reaction steps. These transition states are energetically more similar to **5** than to either **4** or **6** and hence the rate is reflected indirectly in the stability of **5** itself. Rate data, for the nucleophilic substitution of aromatic compounds, have been successfully interpreted by a consideration of the effect of the substituents on the stability of the anionic intermediate.[11,13,15] In contrast, the use of frontier molecular orbital theory to study the interaction between the substrate and the incoming nucleophile has been less successful, although there is some controversy on this point.[12,13]

Our results for the energies of the SCHD$^-$'s can be used, on this basis, to predict relative reactivities of substituted benzenes to nucleophilic substitution. Stabilization energies of the SCHD$^-$'s relative to substituted benzenes [SE(SCHD$^-$/SBz)] may be defined as energy changes for reactions of the type in eq 5. These



(5)

SE's give the hydride ion affinity of a substituted benzene relative to that of benzene itself. In relation to nucleophilic substitution, a positive SE indicates a greater stability of the substituted anion compared to the unsubstituted anion and hence a rate enhancement, and vice versa. Our results, or course, refer to an S_N reaction in which both the nucleophile (Z^-) and leaving group (Y^-) are H^-. We use this as a model for S_N reactions involving other nucleophiles and leaving groups although, for larger nucleophiles, steric effects may contribute to the observed reactivities.

Table III lists the calculated SE's defined in (5). The values are qualitatively in very good agreement with rate data reported for aromatic S_N reactions, generally with Y = halogen and Z = OMe$^-$ or piperidine.[10] Thus, strongly electron-withdrawing groups (X), such as NO_2 and CN, which greatly activate the ring toward nucleophilic attack, lead to large calculated stabilization energies. NO_2 is more stabilizing than CN in accord with experiment. Substituent position increases the rate in the order *meta* << *ortho* < *para* and this is reflected in our SE's.

The results for the π-donor substituents are made less clear-cut by opposing π donation and σ withdrawal, but are in agreement with experiment. For a given ring position, the SE's increase in the order $NH_2 < OH < F$ as expected on the basis of both the unfavorable π-donating ($NH_2 > OH > F$) and favorable σ-accepting ($NH_2 < OH < F$) properties of this set of substituents. For a given substituent, the SE's increase in the order *para* < *ortho* < *meta*. Furthermore, the difference in SE's for *ortho* and *para* substitution increases in the order $F < OH < NH_2$. These results are all consistent with observed rate data.[10] Calculations on the fluoro-substituted system have recently been reported[15] which also predict a stability order of *para* < *ortho* < *meta*.

The results for methyl group are least satisfactory when compared with experiment. This is not unexpected with such a weakly perturbing substituent since other factors such as solvation, leaving group, and nucleophile can be expected to play a more dominant role in determining the rate of reaction.

Conclusions

(1) The equilibrium structure of the cyclohexadienyl anion has a planar ring, and is therefore nonhomoaromatic at the STO-3G level. This agrees with most experimental and previous theoretical data. The homocyclopentadienyl anion is nevertheless predicted to correspond to a local minimum in the $C_6H_7^-$ energy surface.

(2) The relative isomer energies and stabilization energies of 1-, 2- and 3-substituted cyclohexadienyl anions are ordered in accordance with the coefficients of the highest occupied molecular orbital of CHD^-. Greatest stabilization for the π acceptors, or destabilization for the π donors, occurs when the substituent is attached to C(3) (i.e., *para* to the methylene group), and least stabilization/destabilization occurs at C(1). 6-Substituted isomers are stabilized by σ-electron-withdrawing substituents.

(3) Molecular electrostatic potential plots of substituted cyclohexadienyl anions predict that kinetic protonation takes place preferentially at the carbon atom *para* to the first protonation site (i.e., at C(3)). This is so regardless of substituent or of substituent position. Protonation can occur at the *ortho* carbons also, but at a slower rate. When a π donor is substituted at C(1), or a π acceptor at C(2), protonation at the C(1) carbon is impeded.

(4) Rates of nucleophilic substitution reactions of substituted benzenes correlate well with the calculated stabilities (relative to corresponding substituted benzenes) of the substituted cyclohexadienyl anion intermediates involved in the addition/elimination mechanism.

A Triple Bond between Osmium Atoms. Preparation and Structure of Dichlorotetrakis(2-hydroxypyridinato)diosmium(III)

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Abstract: The reaction of osmium(III) chloride with 2-hydroxypyridine (α-pyridone) in ethanol gives the dark red to red-purple $Os_2(hp)_4Cl_2$, where hp = 2-hydroxypyridine anion. This air-stable substance has been obtained in crystalline form as the monoetherate, **1**, and as the bisacetonitrile solvate, **2**, and X-ray crystal structure analysis has been performed on both. **1** forms orthorhombic crystals with $a = 10.036$ (1) Å, $b = 12.114$ (1) Å, and $c = 11.003$ (1) Å, and refinement to $R_1 = 0.037$ and $R_2 = 0.047$ was carried out in space group *Pmmn* by using a disordered model, based on molecules of D_2 symmetry with an internal twist angle of 17.5°. **2** forms monoclinic crystals with $a = 9.416$ (1) Å, $b = 17.304(3)$ Å, $c = 17.331$ (2) Å, $\beta = 90.70$ (1)°, and refinement in space group $P2_1/n$ was convergent with $R_1 = 0.040$ and $R_2 = 0.043$. In this compound also the virtual molecular symmetry was D_2 but the twist angle was 5.5°. The Os–Os distances were 2.344 (2) and 2.357 (1) Å in **1** and **2**, respectively. The difference in twist angles is presumably caused by different intermolecular forces.

Introduction

In the developing chemistry of compounds containing multiple bonds between atoms of the transition metals[1,2] the discovery of entirely new M–M multiple bonds is still possible and is, indeed, one of the most important goals. In view of the extensive chemistry of both triple and quadruple bonds between rhenium atoms and the existence of some multiple bonds between ruthenium atoms[3] we considered osmium an excellent candidate for the formation of new multiple M–M bonds. Our thinking took the following concrete form, leading rationally to the results reported here.

While the electronic population would be right for the existence of a quadruple bond between two Os^{IV} ions, it has long been recognized[4] that M–M bonds, especially multiple ones, are favored by lower oxidation numbers and indeed no triple or quadruple bond is yet known between metal atoms in oxidation states as high as +4. Hence, we turned our attention to the possibility of an $Os^{III}{\equiv}Os^{III}$ triple bond. This would have to be of the same electronic type as those between Re^{II} atoms, where the central electron configuration is formally $\sigma^2\pi^4\delta^2\delta^{*2}$. The bond order of 3 is due to the six electrons occupying the σ and π orbitals, since the δ bonding is cancelled by the presence of two δ^* electrons. Since many triple bonds of the simple $\sigma^2\pi^4$ type exist between M^{III} atoms,[2] including the recently described $[Mo_2(HPO_4)_4]^{2-}$ species,[5] a compound containing an $Os^{III}{\equiv}Os^{III}$ bond seemed a plausible objective.

The question of what ligands to use admitted of several viable answers. A set of three-atom bridging ligands seemed most attractive and of the various possibilities[6] we selected the 2-hydroxypyridine anion, hp, as an initial candidate. Considering then the recent isolation and structural characterization[7] of

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