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A Theoretical Approach to the Birch Reduction. Structures and Stabilities of Cyclohexadienyl Radicals[1]

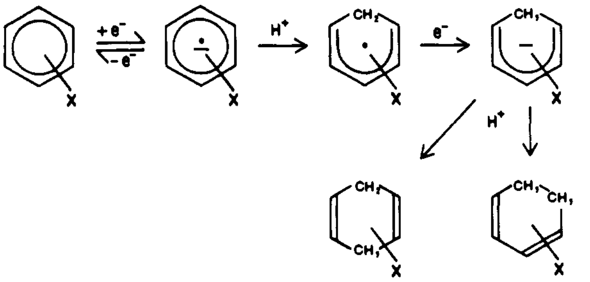
Arthur J. Birch, Alan L. Hinde, and Leo Radom*

Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia. *Received October 15, 1979*

Abstract: Ab initio molecular orbital calculations with the minimal STO-3G basis set and restricted (RHF) and unrestricted (UHF) Hartree-Fock procedures have been carried out for a series of substituted cyclohexadienyl radicals (SCHD$^{\cdot}$). The structure of the unsubstituted cyclohexadienyl radical has been fully optimized and substituents (CH_3, CN, COOH, NO_2, COO^-, F, OCH_3, OH, and NH_2) have been sited in the 1, 2, 3, or 6 positions. The calculations indicate that the thermodynamically preferred site of protonation of a substituted benzene radical anion (corresponding to the most stable SCHD$^{\cdot}$ isomer) is para to the substituent, except for the strong π donors (OH, OCH_3, and NH_2) and CH_3, where ortho protonation is favored. The thermodynamic predictions are compared with predictions of kinetically controlled protonation based on calculated molecular electrostatic potentials.

Introduction

The Birch reduction of substituted benzenes by alkali metals and alcohols in liquid ammonia is a reaction of widespread synthetic utility[2] (1). As part of a continuing study[1] of the theory of the Birch reduction, we have previously examined in detail the reversible electron addition to substituted benzenes (SBz) yielding substituted benzene radical anions (SBz$^-$), and the subsequent irreversible protonation of the SBz$^-$ systems. In this paper, we examine products of the first protonation step in the reaction sequence (1), namely, the substituted cyclohexadienyl radicals (SCHD$^{\cdot}$). Relative energies of isomeric SCHD$^{\cdot}$'s reflect the thermodynamically preferred protonation sites of the SBz$^-$'s. Although, under usual reaction conditions, this first protonation step is thought to be irreversible and hence subject to kinetic control,[3] a study of the thermodynamically preferred products allows a useful comparison with the kinetically preferred products as well as providing relative stabilities of the various SCHD$^{\cdot}$ isomers.



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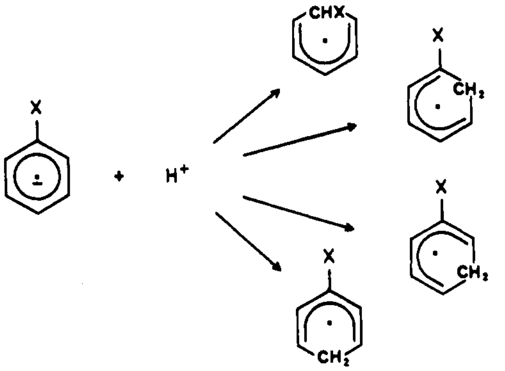
The protonation reaction (2) has several possible isomeric outcomes depending on whether the proton adds ipso, ortho, meta, or para to the substituent X. We have previously argued[1b] that, under kinetic control, the preferred protonation sites are largely determined by electrostatic considerations, as reflected in minima of molecular electrostatic potential (MEP) maps.[1b,4] Relative rates, under such conditions, are determined by the relative activation energies of protonation, and the activation energies in turn can be expected to be paralleled by the depths of the MEP minima. In contrast, under reversible conditions, the preferred protonation site is simply the thermodynamically most stable SCHD$^{\cdot}$ isomer.



(2)

The main aims of this study are then to determine the thermodynamically preferred protonation sites of SBz$^-$ and compare them with the MEP-controlled (kinetically controlled) sites on the one hand, and, on the other, to present and compare the energetics of the protonation reaction (2) with the depths of the MEP minima. The SCHD$^{\cdot}$'s are also of interest in their own right and comparisons of our findings are made with available experimental (ESR spectral and thermochemical) data.

Previous calculations[5-8] on CHD$^{\cdot}$ have been aimed at producing spin densities and hyperfine coupling constants and vary in sophistication from simple valence bond to semiempirical procedures. The most sophisticated is an INDO semiempirical study[7] in which a complete geometry optimization of CHD$^{\cdot}$ was carried out, and calculations on several fluoro-substituted derivatives were performed using the optimized structure. The motivation for these calculations was mainly a desire to interpret and confirm the ESR spectra of cyclohexadienyl rad-

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icals, which can be produced experimentally with a variety of techniques.[7-17] In these ESR experiments, the splitting constants are not significantly modified by the presence of substituents.

This paper presents ab initio molecular orbital calculations on CHD$^\cdot$ and a number of SCHD$^\cdot$'s with substituents X = H, CH_3, CN, NO_2, COOH, COO^-, F, OCH_3, OH, and NH_2. CN and NO_2 are taken as representative of π acceptors and F, OCH_3, OH, and NH_2 of π donors. OCH_3 was included because anisole is one of the few π-donor substituted benzenes for which experimental Birch reduction data are available, but, as it turns out, OCH_3 and OH substituted CHD$^\cdot$'s give very similar theoretical results. Calculations on some isomers of SCHD$^\cdot$, with the substitutents COOH and COO^-, were also carried out, again because Birch-reduction data are available.

In relating our calculations to Birch-reduction data in solution, we stress that the calculations refer, in principle, to isolated (gas-phase) reactions in which there are no solvent effects. 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, there may be specific interactions of the anionic intermediates with solvent molecules and with the counterions, and this would undoubtedly influence the preferred sites of protonation. In addition, we note that for several of the substituents which we have selected (e.g., F, $CH{=}CH_2$, CHO, NO_2), the reduction process may result in alternative fates for the substituted benzenes (e.g., cleavage for F, reduction on the substituent for $CH{=}CH_2$, CHO, and NO_2). However, we include these substituents as models for particular electronic behavior. In any case, we believe that an understanding of these systems in the absence of solvent is an important first step to the understanding of the more complex situation in solution.

Method

Standard ab initio SCF-MO calculations were performed with a modified version[18a] of the GAUSSIAN 70 system of programs.[18b] Most calculations were carried out with a restricted Hartree-Fock (RHF)[19] procedure but some results with an unrestricted (UHF) procedure[20] are reported as well. The minimal STO-3G basis set[21] was used throughout, except for single-point 4-31G[22] calculations on the optimized RHF/STO-3G and UHF/STO-3G structures of CHD$^\cdot$.[23]

CHD$^\cdot$ was fully optimized under a C_{2v} constraint, leading to the structure shown in Figure 1. The restriction to C_{2v} geometry, with its planar ring, seems resonable in view of the optimized INDO geometry[7] and the experimental temperature dependence of the ESR spectrum.[8] It is apparent from the INDO calculations, however, that the planar structure is at a shallow energy minimum and requires little energy for the methylene group to distort from planarity.

For the substituted CHD$^\cdot$'s, the optimized structure (Figure 1) was used in conjunction with standard values[24] of bond lengths and bond angles for the substituents. The conformations adopted for the substituents are included together with total and relative energies in Table I. Where appropriate, several conformations were considered. For the OCH_3 group, the COC angle (α) was optimized leading to α = 112.9° (6 position), α = 117.7° (1 position), α = 117.6° (2 position), and α = 118.2° (3 position).

The use of a planar ring should be satisfactory for substituents at the 1, 2, and 3 positions since the plane of symmetry is maintained, but substituents at the 6 position destroy this symmetry and distortion of the ring from planarity can be expected. This has been found for 6-fluoro-CHD$^\cdot$[7] and 6-silyl-CHD$^\cdot$ (CNDO/2 calculation),[8] for which the methylene group is ~10° out of plane (F equatorial) and 4° out of plane (SiH_3 axial), respectively. Nevertheless, a planar ring has been used throughout the present study.

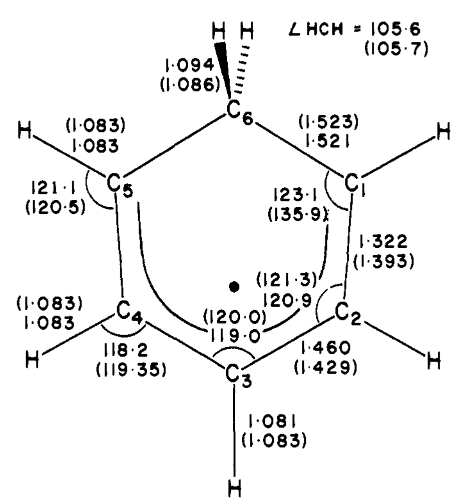
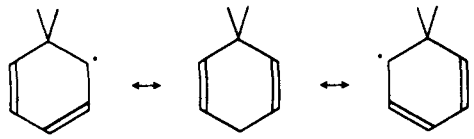


Figure 1. Optimized RHF/STO-3G and UHF/STO-3G (in parentheses) structural parameters for CHD$^\cdot$: bond lengths in ångstroms, bond angles in degrees.

Results and Discussion

A. Optimized Structure for CHD$^\cdot$. The optimized (RHF and UHF) geometric parameters for CHD$^\cdot$ are displayed in Figure 1. Both RHF and UHF results reflect contributions from valence structures of the type



The UHF/STO-3G geometric parameters, which are quite similar to UHF/INDO values reported previously,[7] show some distinct differences (notably the C_1-C_2 bond length) from the RHF values. These differences may be rationalized in terms of higher multiplet contamination of the UHF wave function, a result more readily apparent after we discuss the electronic structure of CHD$^\cdot$ in more detail.

The ground state corresponds to the unpaired electron occupying a π-type b_1 orbital (classified according to C_{2v})[25] and is therefore a $^2B_1$ state. The singly occupied molecular orbital (SOMO) is shown in Figure 2. It is symmetric with respect to the plane perpendicular to the ring plane, which passes through C(3)-C(6), and resembles the $2b_{1u}$ orbital of Bz$^-$. The largest coefficients of the SOMO appear on atoms 1, 3, and 5 and on the methylene 1s-hydrogen orbitals, which create a pseudo-π orbital, while atoms 6, 2, and 4 have small coefficients. This is consistent with the observed ESR spectrum of CHD$^\cdot$.[7-10,12-15,17,26,27] Figure 2 also shows the lowest unoccupied molecular orbital (LUMO) (a_2 in C_{2v}) which is antisymmetric and is comparable to the $1a_u$ orbital of Bz$^-$. A qualitative picture of these orbitals may be constructed by considering the interaction of the SOMO of a pentadienyl fragment with the π_{CH_2} and $\pi^*_{CH_2}$ orbitals of a methylene group.

Comparison of the UHF and RHF optimized structural parameters shows that, in the UHF structure, the C(1)-C(2) bond was increased markedly, the C(2)-C(3) bond length has slightly decreased, and C(1)-C(6) is unaltered. The increased C(1)-C(2) length may be attributed to contamination by a low-lying $^4B_1$ state, which arises from the promotion of an electron from the highest doubly occupied molecular orbital (a_2) to the LUMO. This has the effect of decreasing the

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

substituent	6 position	1 position	2 position	3 position
		RHF/STO-3G		
H	−228.420 32 (0)	−228.420 32 (0)	−228.420 32 (0)	−228.420 32 (0)
CH_3	−266.999 41 (16.6)	−267.005 73[b] (0)	−267.004 55[b] (3.1)	−267.005 24 (1.3)
	[HCC(6)H trans]	[HCC(1)C(2) cis]	[HCC(2)C(1) cis]	[HCCC cis]
CN	−318.962 5(41.6)	−318.975 58 (7.3)	−318.972 92 (14.3)	−318.978 36 (0)
COOH				−413.508 82
				[planar, HOCO cis]
NO_2	−429.113 83[c] (11.4)	−429.116 85 (3.5)	−429.113 14 (13.2)	−429.118 18 (0)
	[ONC(6)H cis]	[planar]	[planar]	[planar]
COO^-		−412.747 77 (9.5)		412.751 41 (0)
[planar]				
F	−325.867 03 (37.9)	−325.881 27 (0.5)	−325.878 18 (8.6)	−325.881 46 (0)
OCH_3	−340.827 32 (27.5)	−340.837 79 (0)	−340.833 53[d] (11.2)	−340.835 58 (5.8)
[HCOC trans]	[COC(6)H trans]	[COC(1)C(2) cis]	[COC(2)C(1) cis]	[COCC cis]
OH	−302.246 10 (39.9)	−302.261 28[e](0)	−302.257 32[e] (10.4)	−302.259 87 (3.7)
	[HOC(6)H trans]	[HOC(1)C(2) cis]	[HOC(2)C(1) cis]	[HOCC cis]
NH_2	−282.727 55[f](22.1)	−282.735 97 (0)	−282.731 36 (12.1)	−282.735 02 (2.5)
	[:NC(6)H 60°]	[planar]	[planar]	[planar]
		UHF/STO-3G		
H	−228.470 80 (0)	−228.470 80 (0)	−228.470 80 (0)	−228.470 80 (0)
CH_3	−267.049 67 (16.0)	−267.055 75 (0)	−267.054 00[g] (4.6)	−267.005 24 (3.4)
	[HCC(6)H trans]	[HCC(1)C(2) cis]	[HCC(2)C(1) cis]	[HCCC cis]
CN	−319.013 38 (53.0)	−319.033 61 (0)	−319.029 29 (11.4)	−319.032 07 (4.0)
NO_2	−429.229 16 (12.1)	−429.233 76 (0)	−429.230 93 (7.4)	−429.164 73 (181.2)
	[ONC(6)H cis]	[planar]	[planar]	[planar]
F	−325.917 67 (33.9)	−325.930 59 (0)	−325.928 16 (6.4)	−325.929 10 (3.9)
OH	−302.296 48 (31.8)	−302.308 59 (0)	−302.305 76[h] (7.4)	−302.306 70 (5.0)
	[HOC(6)H trans]	[HOC(1)C(2) cis]	[HOC(2)C(1) cis]	[HOCC cis]
NH_2	−282.777 82[i] (12.0)	−282.782 40 (0)	−282.779 73 (7.0)	−282.780 86 (4.0)
	[:NC(6)H 60°]	[planar]	[planar]	[planar]

[a] Energies relative to the lowest energy isomer for the particular substituent. [b] Total (and relative) energies for other conformations: −267.003 17 (6.7) HCC(1)C(2) trans (1-position); −267.002 46 (8.6) HCC(2)C(1) trans (2-position). [c] Total (and relative) energy for ONC(6)H orthogonal: −429.112 83 (14.1). [d] Total (and relative) energy for COC(2)C(1) trans ($\alpha = 118.8$): −340.829 88 (20.8). [e] Total (and relative) energies for trans conformations: −302.259 09 (5.7) 1 position; −302.255 76 (14.5) 2 position. [f] Total (and relative) energies for other :NCH dihedral angles: −282.722 05 (36.5) cis; −282.722 11 (36.4) 120°; −282.724 81 (29.3) trans. [g] Total (and relative) energy for HCC(2)C(1) trans: −267.053 52 (5.8). [h] Total (and relative) energy for HOC(2)C(1) trans: −302.305 60 (7.8). [i] Total (and relative) energy for :NC(6)H trans: −282.775 40 (18.4).

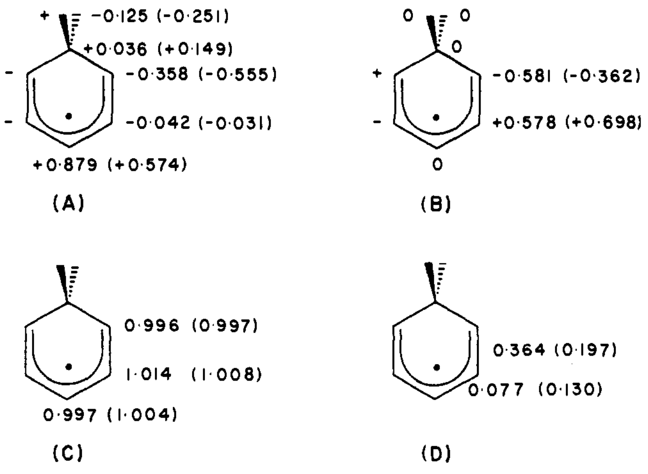


Figure 2. Calculated electronic properties of the cyclohexadienyl radical (RHF values, UHF values in parentheses): (A) SOMO coefficients (b_1 symmetry); (B) LUMO coefficients (a_2 symmetry); (C) π-electron populations; (D) π-overlap populations.

bonding interaction between C(1) and C(2) and increasing the antibonding interaction. The amount of spin contamination from higher multiplet states is large, as shown by $\hat{S}^2 = 1.495$.

B. Relative Energies of SCHD· Isomers. Total and relative RHF and UHF energies for the isomeric cyclohexadienyl radicals are listed in Table I. We note that in all cases the SOMO is similar to the SOMO of the unsubstituted cyclohexadienyl radical (Figure 2). This again is consistent with ESR spectra of SCHD·'s[7,8,13-16,28] (specifically, for example, substituents OH,[13-16] COOH,[15] CH_3,[13,28] NH_2,[13] and F[7]).

The relative (RHF) energies of Table I predict directly the *thermodynamically* preferred protonation sites of SBz^-. It can be seen that the π acceptors (CN, NO_2) all favor protonation para to the substituent, forming a 3-substituted CHD·, while most of the π donors (OCH_3, OH, NH_2) and CH_3 give preference to ortho protonation (resulting in the 1-substituted isomer). The fluorine substituent shows a slight preference for para protonation, but this must be considered inconclusive in view of the small ortho/para difference for this substituent. The COO^- group is found to be a very weak π donor when attached to a cyclohexadienyl radical framework and the 3-substituted isomer lies significantly lower in energy than the 1 isomer.

The energy differences between the 1- and 3-substituted isomers, irrespective of the substituent, are quite small (less than 10 kJ mol^{-1}), so it would be expected that significant amounts of both isomers would form under equilibrium conditions.

The 6-substituted CHD·'s all have quite high relative energies and this may be partly due to greater inaccuracies in the assumed geometries—both neglect of the possibility of methylene-group puckering and of XCH angle distortion from the value in the unsubstituted system. However, it should be noted that the 10° methylene distortion previously calculated

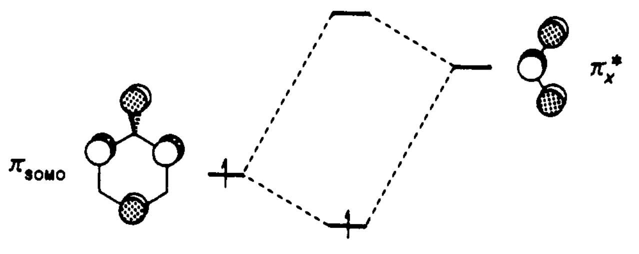


Figure 3. Orbital interaction diagram for the perturbation of the CHD$^{\cdot}$ SOMO by the π^* orbital of a typical π-acceptor substituent (e.g., NO_2).

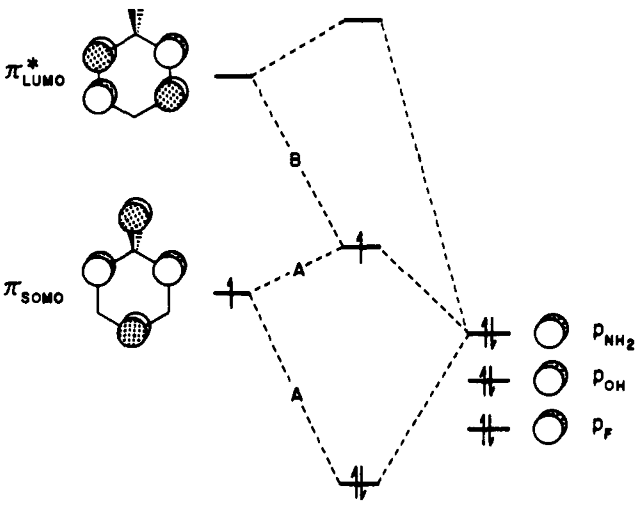


Figure 4. Orbital interaction diagram for the perturbation of CHD$^{\cdot}$ orbitals by a π-donor substituent at C(1) or C(2).

Table II. Relative Proton Affinities (RHF/STO-3G, kJ mol^{-1}) for Radical Anions of Substituted Benzenes[a]

substituent (SBz$^-$ state)	6 position	1 position	2 position	3 position
H ($^2B_{1u}$)	0	0	0	0
(^2A_u)	+0.35	+0.35	+0.35	+0.35
CH_3 (^2B)	−12.4	+4.2	+1.1	+2.9
CN (^2B)	−177.2	−142.9	−149.9	−135.6
COOH (^2B)				−112.2
NO_2 (^2B)	−219.7	−211.8	−221.5	−208.3
COO^- (^2B)		+383.6		+393.1
F (^2A)	−59.4	−22.0	−30.1	−21.5
OCH_3 (^2A)	−26.2	+1.2	−9.9	−4.5
OH (^2A)	−46.7	−6.9	−17.3	−10.6
NH_2 (^2A)	−6.4	+15.7	+3.6	+13.2

[a] Calculated as energy changes in reaction 3 using data for SBz$^-$'s from ref 1b. All ^2A SBz$^-$ energies have been corrected by subtraction of 6.4 kJ mol^{-1}.

for 6-F-CHD$^{\cdot}$ afforded less than 3 kJ mol^{-1} energy lowering over the planar structure, so that further geometry optimization is unlikely to alter the energy orderings of Table I for most substituents. In fact, the higher relative energies of 6-substituted cyclohexadienyl radicals undoubtedly reflects the more favorable interaction of π-donor and π-acceptor substituents with unsaturated or radical centers compared to a saturated carbon.[29]

The relative stabilities of the SCHD$^{\cdot}$ isomers, as discussed above, can be rationalized in terms of orbital interactions between the substituent and the CHD$^{\cdot}$ SOMO and LUMO, using perturbation molecular orbital (PMO) theory.[30] Such arguments have been successfully applied previously to radical systems.[31]

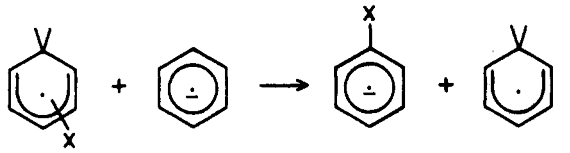
π-Acceptor substituents are characterized by a low-lying antibonding LUMO (π^*_X) which can interact with the SOMO of CHD$^{\cdot}$ yielding the one-electron stabilization indicated in Figure 3. The interaction is strongest at the carbon atom with the largest SOMO coefficient; hence stabilization is greatest at C(3) and is almost zero at C(2) (see Figure 2 for SOMO and LUMO coefficients). C(1) is intermediate. The relative energies of the isomers decrease in the order 2 position > 1 position > 3 position in accordance with these PMO arguments.

Substituents which are π donors, such as F, OH, and NH_2, are characterized by a high-energy doubly occupied p orbital which can interact with the SOMO to give a stabilizing three-electron interaction (A, Figure 4). In contrast to the π acceptors, however, the resultant SOMO can further interact favorably (B) with the antisymmetric CHD$^{\cdot}$ LUMO, provided that the substituent is at the 1 or 2 position. Interaction B is precluded by symmetry for substituents at C(3). Greatest stabilization can be expected at the carbon atom with largest SOMO and LUMO coefficients, i.e., at C(1). The stabilization is also large at C(3), due to the large SOMO coefficient (giving rise to a favorable interaction A), but is minimal at C(2) since the SOMO coefficient is nearly zero.

The pattern observed in the calculations for the isomers of the π-donor substituted CHD$^{\cdot}$'s is consistent with the above arguments, except for F and COO^-. F, however, being the most electronegative of the π-donor substituents, has the lowest lying p orbital in the sequence NH_2, OH, F, and is therefore sufficiently below the LUMO that the interaction reverts to SOMO control. COO^- also lacks a suitable high-lying occupied orbital: the highest occupied orbital has a node at the carbon atom which prevents significant overlap with the ring.

The relative energies as predicted by the UHF calculations (Table I) are generally similar to the RHF values except for a relative favoring of the 1-substituted isomer. Indeed, the 1-substituted isomer is the lowest energy isomer in all (UHF) cases. This may be due to the larger C(1) coefficient and smaller C(3) coefficient for the UHF SOMO as compared with the RHF SOMO (see Figure 2).

C. Proton Affinities Stabilization Energies. The proton affinity (PA) of a SBz$^-$ is defined as the negative of the energy change for the appropriate reaction (2). Because of inadequacies in the SBz$^-$ calculations,[1b] raw theoretical values of proton affinities are likely not to be meaningful. Proton affinities relative to that for Bz$^-$ are likely to be more reliable. These are given by energy changes in reaction 3, and the calculated values[32] are listed in Table II. A positive value implies a preference for protonation of SBz$^-$ compared to Bz$^-$. Alternatively, a positive value implies that the substituent stabilizes CHD$^{\cdot}$ more than Bz$^-$. The PAs are very nearly related by a change of sign to stabilization energies (SEs) for the SBz$^-$'s calculated relative to substituted benzenes, i.e., energies of reaction 4.[1b] This suggests that the PAs are dominated by the substituent effect in SBz$^-$.



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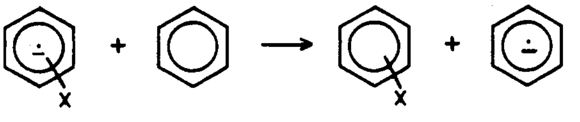

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A more useful probe for the effect of a substituent in CHD is to use neutral benzene as the reference system. The SE so calculated is the energy change for reaction 5. SEs defined in

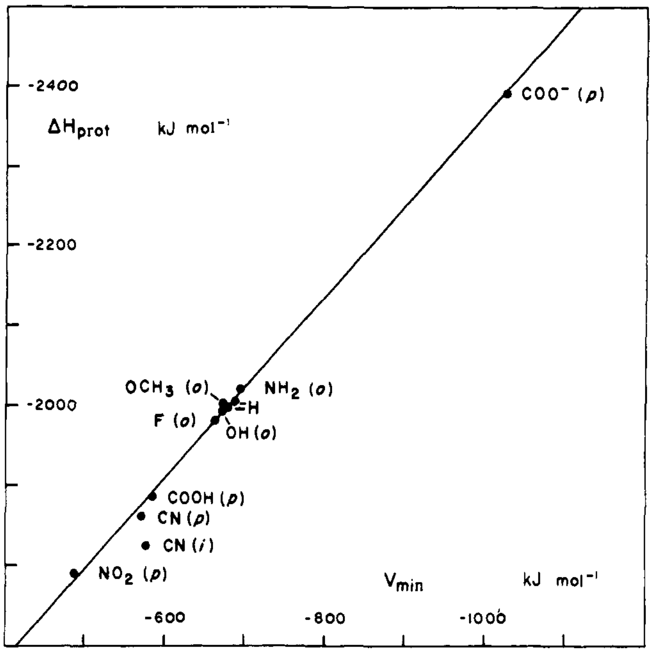
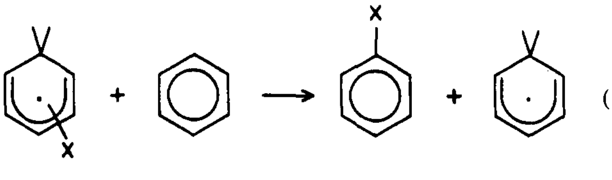


Figure 5. Correlation of heats of protonation (ΔH_{prot}) with values of MEP minima (V_{min}) for various sites (indicated as *i, o, m,* or *p* in parentheses) of SBz^-.

Table III. Stabilization Energies (RHF/STO-3G, kJ mol^{-1}) of Substituted Cyclohexadienyl Radicals[a] (or Relative Hydrogen Atom Affinities of Substituted Benzenes)

substituent	6 position	1 position	2 position	3 position
H	0	0	0	0
CH_3	−12.3	4.3	1.2	3.0
CN	−29.0	5.3	−1.7	12.6
COOH				13.4
NO_2	0.9	8.8	−0.9	12.3
COO^-		−6.0		3.6
F	−33.1	4.2	−3.8	4.8
OCH_3	−19.0	8.5	−2.7	2.7
OH	−33.5	6.3	−4.1	2.6
NH_2	−19.1	3.0	−9.1	0.5

[a] Calculated as energy changes in reaction 5 using data for SBz's from W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 1496 (1972).



(5)

this way are listed in Table III. They may alternatively be considered as relative hydrogen atom affinities of substituted benzenes. The main patterns that emerge from inspection of this table are that substituents generally stabilize the radical at positions 1 and 3 and destablize it at positions 6 and 2, and that π acceptors are generally more stabilizing than π donors.

D. Comparison of Thermodynamically and Kinetically Preferred Sites of Protonation of SBz^-. There is generally a close parallel between the MEP preferred protonation sites and the thermodynamically preferred protonation sites of SBz^-. Thus, the π donors (OCH_3, OH, NH_2) have their MEP minima closest to the ortho carbons of SBz^- and this is also the thermodynamically favored protonation site. The π acceptors (CN, COOH, NO_2) have MEP minima at the para carbon paralleling the thermodynamic results.

On the other hand, there are differences which should be noted. For the π acceptors, there is often a second minimum at the ipso carbon which is deeper than at the para carbon, and this does not correspond to a preferred SCHD· structure. For the π donors, the MEP minimum is only marginally closer to ortho than to meta whereas it is the ortho and para isomers of SCHD· that are close in energy.

In summary, our results suggest that π acceptors induce ipso and/or para protonation under irreversible conditions and a mixture of ortho- and para-protonated products under equilibrium conditions, while π donors favor irreversible ortho and/or meta protonation and thermodymamically controlled ortho and para protonation. We suggest, however, that for π donors ortho protonation might be dominant under irreversible conditions in view of the slight MEP ortho preference, coupled with the thermodynamic favoring of ortho over meta which would become increasingly important as the proton approaches.

The close paralleling of the MEP minima and the minimum energy SCHD·'s suggests that the MEP reflects well the total interaction energy of a proton with SBz^-. It would therefore be interesting to see how well the values of the MEP minima, V_{min}, correlate with the protonation energies, ΔH_{prot}, for protonation at the site closest to the minimum. A good correlation would indicate that polarization and other terms are relatively constant or imitate the behavior of the MEP terms. Good correlations have been reported previously.[33]

Values of ΔH_{prot} are plotted against V_{min} in Figure 5. The point corresponding to the ipso position of $C_6H_5CN^{-\cdot}$ is clearly anomalous being due, as suggested above, to the poorer 6-substituted geometries, or possibly to the significantly different electronic environment at C(6) suggesting a different regression equation. This point was excluded from the correlation coefficient, which is 0.9990, showing that an almost perfect linear relationship exists between ΔH_{prot} and V_{min}. The regression line has the equation $\Delta H_{\text{prot}} = 1.131 V_{\text{min}} - 1232.6$ (kJ mol^{-1}).

The order of points in Figure 5 shows diagrammatically the relative PAs of SBz^-, with the lowest PA at the bottom left and the highest at the top right. The uncharged π donors, and H, are clustered together, while COO^-, with its extra charge, is far removed to the top right.

E. Relative Reaction Rates. With the theoretical data presented so far, it is now feasible to comment on relative Birch reduction rates. The proposed rate law[34] gives a rate constant for the reaction as $k = K_{\text{eq}}k_1$, where K_{eq} is the equilibrium constant for the first electron addition and k_1 is the forward rate constant for the irreversible first protonation step.

Rate theory tells us that, for a reaction with a reversible followed by an irreversible step, the logarithm of the rate, ln (k), is linearly related to the sum of the total energy change, ΔE^{e}, for the equilibrium reaction and the activation energy, ΔE^{a}, for the irreversible reaction. This is pictured diagrammatically in Figure 6.

The theoretical calculations do not provide ΔE^{a} values; indeed theoretically $\Delta E^{\text{a}} = 0$. As pointed out above, however, the depths of the MEP minima, V_{min}, should correlate with the activation energies. Furthermore, by virtue of the excellent correlation of V_{min} with the total protonation energies, ΔH_{prot}, it can be expected that ΔH_{prot}, indirectly via V_{min}, will itself parallel the activation energies. Hence the theoretical model for qualitatively predicting the relative rates of reduction of substituted benzenes consists of using the sum of the electron-addition and proton-addition energies, i.e., the total hydrogen atom addition energy changes ΔE^{H} (Figure 7). Note again the absence of any activation barrier in these hypothetical gas-phase calculations.

Relative ΔE^{H} values were presented in Table III as stabilization energies. The more positive the SE, the faster would

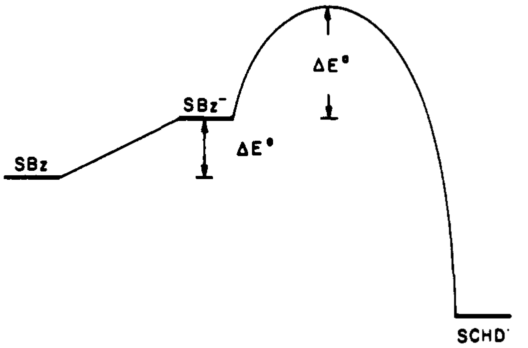


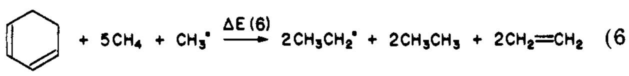
Figure 6. Reaction profile for initial electron addition and proton addition steps in the Birch reduction of a substituted benzene.

be expected the reduction relative to benzene. Assuming that protonation takes place at the para position for π acceptors and at the ortho position for π donors, the data in Table III suggest greatest rates for π acceptors (e.g., CN, NO_2), and intermediate rate enhancement for π donors (e.g., OCH_3). These results are in qualitative agreement with the experimentally observed rates.[34] For CH_3, the interpretation of the results is complicated by the fact that the methyl substituent effect in solution is the reverse of that found in the gas phase (or theoretically).[1b,35]

The experimental reduction of benzoic acid is very rapid.[34] Because of metal-ion association, and solvent effects, it is unclear as to whether the substituent COOH, or COO^-, best models the experimental situation for benzoic acid. Since the ion pair, $C_6H_5COO^-M^+$, is most likely to be present in solution, it would seem that calculations should incorporate the substituent COOLi or COONa. Failing this, the substituent COOH should more closely resemble COOLi (or COONa) than COO^-. If this is accepted, the theoretical results (i.e., for COOH) are in qualitative agreement with experiment.

We have noted previously[1b] that the SEs of some SBz^-'s alone gave the relative rates in the order observed experimentally. It may therefore be reasonable to assume that the first protonation step is quite fast, requiring an activation energy that is small and that does not vary greatly with substituent, and that the relative rates are therefore largely determined by K_{eq} and can be modeled by the SEs of the SBz^-'s.

F. The Heat of Formation of CHD·. We have used two procedures to estimate the heat of formation of the cyclohexadienyl radical. In the first, we begin with the bond separation reaction[36] for CHD· (6). The energy changes for reactions of



$$+ 5CH_4 + CH_3^{\cdot} \xrightarrow{\Delta E(6)} 2CH_3CH_2^{\cdot} + 2CH_3CH_3 + 2CH_2{=}CH_2 \quad (6)$$

this type (which have been termed isodesmic[36]) are known to be calculated quite accurately at the STO-3G and 4-31G levels, because all bond types are conserved in the reaction. In this way, a good estimate for the heat of formation, ΔH_f, for CHD can be found, by utilizing good experimental $\Delta H_f{}^\circ$ data for the smaller species.

Using the RHF/STO-3G and RHF/4-31G total energies of CHD· at the RHF/STO-3G optimized geometry, and the published total energies,[37] at the same ab initio level, of the other molecules involved in eq 6 yields $\Delta E(6)$ = 128.7 (STO-3G) or 128.3 (4-31G) kJ mol^{-1}. Combining these values with experimental heats of formation for the remaining species in reaction 6[38] gives $\Delta H_f{}^\circ$ for CHD· as 276.3 (STO-3G) or 276.6 kJ mol^{-1}.

An independent estimate for ΔH_f(CHD·) can be found using the simple reaction

$$C_6H_7^{\cdot} \xrightarrow{\Delta E(7)} C_6H_6 + H^{\cdot} \quad (7)$$

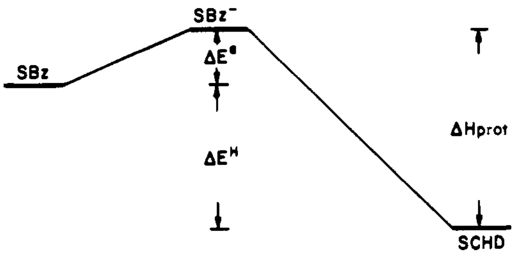


Figure 7. Energy profile pertaining to the ab initio molecular orbital (or gas phase) description of the initial electron addition and proton addition steps in the Birch reduction of a substituted benzene.

for which[37,39] $\Delta E(7)$ = 89.4 (STO-3G) and 33.7 (4-31G) kJ mol^{-1}. Since reaction 7 is nonisodesmic, it is not unexpected that the STO-3G and 4-31G values of the energy change are not in close agreement. Taking the more reliable 4-31G value yields[38] ΔH_f(CHD·) = 267.2 kJ mol^{-1}. This is in very good agreement with the values calculated above from reaction 6.

Our calculations thus suggest a heat of formation for the cyclohexadienyl radical of ~270 kJ mol^{-1}. This compares with indirect experimental estimates[40] of 206.7, 184, and 189.5 kJ mol^{-1}.

Conclusions

(1) Our calculations suggest that π acceptors induce ipso and/or para protonation of substituted benzene radical anions (SBz^-) under irreversible conditions and a mixture of ortho- and para-protonated products under equilibrium conditions, while π donors favor irreversible ortho and/or meta protonation and thermodynamically controlled ortho and para protonation. The thermodynamic preference is for para protonation for all substituents except the strong π donors (OH, OCH_3, and NH_2) and CH_3.

(2) An excellent correlation exists between values of minima in molecular electrostatic potential (MEP) maps for SBz^-'s and the protonation energies at the carbon atoms closest to the MEP minima.

(3) The stabilization energies of substituted cyclohexadienyl radicals (compared with substituted benzenes) are in qualitative agreement with relative rates of reduction of substituted benzenes.

(4) The singly occupied molecular orbital of the cyclohexadienyl radical is a b_1 π orbital and is only slightly perturbed by substituents. This is consistent with the observed ESR spectra.

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Structure and Singlet–Triplet Separation in Simple Germylenes GeH_2, GeF_2, and $Ge(CH_3)_2$

Jean-Claude Barthelat,[1a] Bruno Saint Roch,[1b] Georges Trinquier,*[1a] and Jacques Satgé[1b]

Contribution from the Laboratoire de Physique Quantique (E.R.A. 821) and Laboratoire de Chimie des Organominéraux (E.R.A. 829), Université Paul Sabatier, 31077 Toulouse Cedex, France. Received November 19, 1979

Abstract: Ab initio valence-only calculations were performed on the three first states of GeH_2, GeF_2, and $GeMe_2$ with double ζ plus polarization basis sets. The three compounds are predicted to have singlet ground states. SCF singlet-triplet (S–T) energy gaps are 10 kcal/mol for GeH_2, 64 kcal/mol for GeF_2, and 14 kcal/mol for $GeMe_2$. SCF ground state equilibrium geometries correspond to GeH = 1.60 Å, ∠HGeH = 93°, GeF = 1.76 Å, ∠FGeF = 97°, CGe = 2.02 Å, and ∠CGeC = 98°. Extended CI increases the S–T gap to 19 kcal/mol for GeH_2 and to 74 kcal/mol for GeF_2. Full sets of force constants and vibrational frequencies were calculated and compare well with available IR and UV data.

I. Introduction

Divalent species of the group 4B elements are of considerable interest in organic and organometallic chemistry. Mainly this is due to the high reactivity of these unstable intermediates.

Recently, an excellent review describing their electronic structure and reactivity has been published by Nefedov et al.;[2] the evolution of the main features of these carbene-like molecules on going from carbon to lead is discussed in detail from the available experimental data.

In recent years, there have been a large number of theoretical studies to examine the low-lying electronic states of methylene,[3] halogenated carbenes,[4] and unsaturated carbenes.[5] The major aim of these works is to ascertain the nature of the ground state and to calculate the singlet–triplet ($^1A_1$–$^3B_1$) separation in comparison with the results of experimental works. Similar studies are also reported on the simplest silylene (SiH_2)[6-8] and silicon difluoride.[9,10] However, despite the important contribution of germylenes as starting products or intermediates in organometallic chemistry,[11] up to now the electronic structure of the simplest germylene (GeH_2) has not been subjected to any theoretical investigations.

The question as to whether the ground state of substituted germylenes is a singlet or a triplet is of interest in this context. The purpose of the present research is to answer this question for some simple germylenes, especially for the organic derivatives which are practically unexplored.

To this end, ab initio valence-only calculations have been carried out for the three lowest states of GeH_2, GeF_2, and $Ge(CH_3)_2$. Moreover, vibrational frequencies are calculated and compared with experimental values, when available, for all the states studied.

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