the preferred orientation of the reactions. We calculated relative contributions at 298 K to the rate constants for Saytzeff elimination to but-2-ene and Hofmann elimination to but-1-ene. The force constants for 2-chlorobutane were as specified by the model force field[4] and those for the antiperiplanar transition states were obtained by the methods described above: the bond orders of the making and breaking bonds and the parameters for the reaction-coordinate mode were exactly as those for the reaction of chloroethane with hydroxide ion. A relative rate constant k(Saytzeff)/k(Hoffman) of 1.087 was obtained,[14] confirming the view that the generally much larger ratios observed experimentally are related to various potential energetic considerations.[2,15]

Further work with a wider range of E2 transition-state models, including solvation shells, is evidently required and is in hand.

Acknowledgment. We thank the S.R.C. for support.

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

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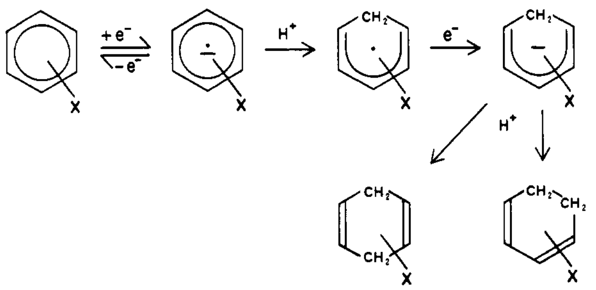
Abstract: Ab initio molecular orbital calculations have been carried out on 1,3-cyclohexadiene (1,3-CHD), 1,4-cyclohexadiene (1,4-CHD), and substituted systems with substituents CH_3, CN, NO_2, F, OH, and NH_2. 1,3-CHD is indicated to be nonplanar with C_2 symmetry while 1,4-CHD is planar with D_{2h} symmetry. The energy difference between 1,3-CHD and 1,4-CHD is small. For substituted cyclohexadienes, the favored isomer is always the 1-substituted 1,3-CHD. Comparison of the energy data for the cyclohexadienes with previously calculated molecular electrostatic potentials for substituted cyclohexadienyl anions suggests that the thermodynamically favored and kinetically favored sites of protonation in the cyclohexadienyl anions frequently differ.

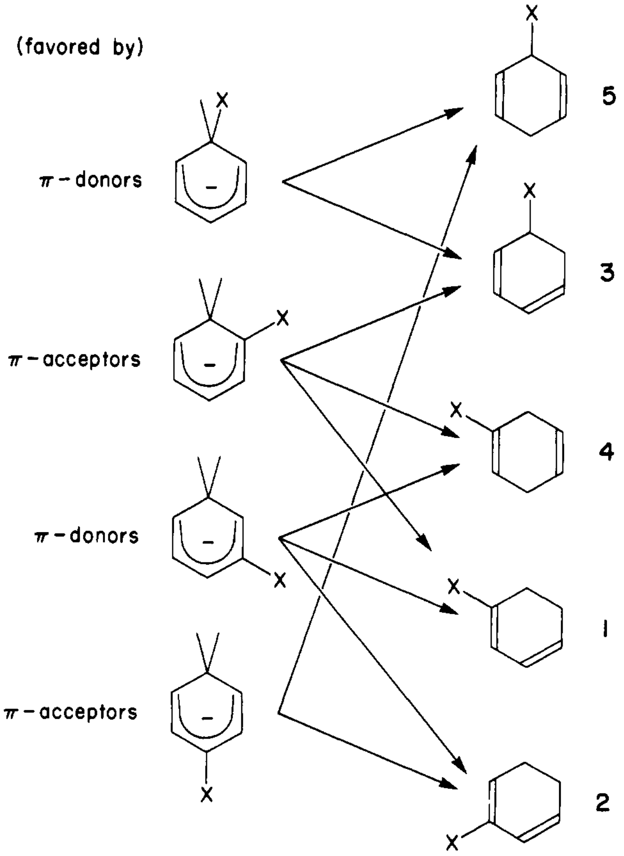
Introduction

A reaction of widespread synthetic utility is the Birch reduction of substituted benzenes by alkali metals and alcohols in liquid ammonia (eq 1).[1] In recent papers,[2-5] we have examined species involved in the first three steps of the reaction sequence (1). In this paper, we examine the final step of the reaction sequence, namely, the protonation of the cyclohexadienyl anions (CHD$^-$'s) to yield a 1,3-cyclohexadiene (1,3-CHD, structures **1**-**3**) or a 1,4-cyclohexadiene (1,4-CHD, structures **4**, **5**). 1,4-CHD's are formed under irreversible Birch reduction conditions (such as in the presence of an alcohol and with use of, for example, NH_4Cl to quench the reaction) by protonation of the CHD$^-$ at the 3-position (i.e., para to the first protonation site). We have examined this previously[5] with the aid of theoretical molecular electrostatic potentials. 1,3-CHD is a conjugated diene and is thermodynam-



(1)

Scheme I



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ically slightly more stable than 1,4-CHD and eventually forms under equilibrium conditions (e.g., when a strong base such as NH_2^- is added). A number of isomers are possible for substituted cyclohexadienes (SCHD's), and, under reversible conditions, the product distribution will equilibrate in favor of the thermodynamically more stable isomers, although such an equilibration may be hindered by the ease with which protons can be abstracted from the initially formed SCHD's. This depends in turn upon the stability or instability of the cyclohexadienyl anion conjugate to the cyclohexadiene.

The formation of 1,3-CHD's, as pointed out previously,[5] is not excluded under irreversible conditions, although protonation of CHD^- at the 1-position usually is much slower that at the 3-position.[6] Similarly, 1,4-CHD's may be present under equilibrium conditions but normally in smaller concentrations than the 1,3-CHD isomers.

Summarized in Scheme I are the five possible 1,3-CHD and 1,4-CHD isomers and the paths by which they can be formed by initial (irreversible) protonation of the four $SCHD^-$ isomers. Those isomers of $SCHD^-$ that are favored by π donors and those favored by π acceptors, as determined in our previous calculations,[5] are also indicated.

There have been a number of experimental studies on the isomerization of 1,4-CHD's to 1,3-CHD's both in solution[7-18] and in the gas phase.[19-23] These studies identify the most stable isomers and sometimes give the equilibrium isomeric ratios. Early experimental work using potassium amide in ammonia suggested that the thermodynamically preferred isomers were the 2,3-dihydrobenzene (or 1-substituted 1,3-CHD) (**1**) for π donors, e.g., $X = OCH_3$,[8] and the 3,4-dihydrobenzene (or 2-substituted 1,3-CHD) (**2**) for π acceptors, e.g., $X = COOH$.[9] Very recent studies[18] with $(CH_3CN)_3Cr(CO)_3$ as catalyst suggest, however, that for π-acceptor substituents, e.g., $COOCH_3$, the 2,3-dihydrobenzene is in fact the thermodynamically preferred isomer and the previous results[9] may therefore reflect incomplete equilibrium (see below).

Equilibration ratios of 1,4-CHD:1,3-CHD = 30–35%:70–65%[10,18] and 2,5-dihydroanisole:2,3-dihydroanisole = ~16%:~84%[12,13] have been found under various conditions in solution. For the $COOCH_3$ substituent, the equilibrium ratios determined by using the chromium catalyst are[18] 2,3-dihydro:3,4-dihydro:2,5-dihydro = ~65%:18%:17%.

The gas-phase studies would perhaps be expected to give more reliable equilibrium ratios, but gaseous 1,3-CHD and 1,4-CHD generally do not isomerize at high temperature; they preferentially dehydrogenate to benzene.[23] Gas-phase isomerizations have, however, been carried out on CH_3-1,3-CHD's, and the observed equilibrium ratios are 5-CH_3-1,3-CHD (1,2-dihydrotoluene):1-CH_3-1,3-CHD (2,3-dihydrotoluene):2-CH_3-1,3-CHD (3,4-dihydrotoluene) = 13%:57%:30%.[19]

Some of the experimental studies, both gas phase and in solution, as well as hydrogenation experiments,[25-28] also yielded useful energy data. A significant finding is the small energy difference between 1,4-CHD and 1,3-CHD found in all these studies. The most accurate estimate appears to be 1.1 kJ mol^{-1} in favor of 1,3-CHD determined from measurements in acetic acid.[25]

Apart from their involvement in the Birch reduction, 1,4-CHD and 1,3-CHD are also of interest from the point of view of their equilibrium structures. 1,4-CHD was thought to be either planar or boat shaped, and a recent article[29] reviews the evidence, both experimental and theoretical, for these forms. The weight of evidence currently favors a planar structure. Previous ab initio calculations,[30] carried out at a level comparable with the extended 4-31G basis set, but without geometry optimization, also suggest that 1,4-CHD is planar.

1,4-CHD has received attention because of the orbital interactions arising from the two, nonconjugated double bonds.[31] The orbital interactions resulting from the pseudo-π-orbitals of the intervening methylene groups, termed *through-bond* interactions, reverse the order of the π orbitals arising from pure *through-space* interactions.

1,3-CHD is an example of a conjugated diene in which the two ethylene moieties are not in the same plane. 1,3-CHD has been included in a number of computational studies on conjugated dienes which examine the equilibrium conformations and the relationship between the C═C—C═C dihedral angle with properties such as electronic spectra,[32] chirality and rotatory strengths,[33] heats of formation,[34] and potential energy surfaces.[35] These calculations were all at the semiempirical or molecular mechanics levels.

The nonplanarity of 1,3-CHD is thought to be due to angle strain at the saturated carbons, which would prefer to be tetrahedrally bonded, and steric interaction between the eclipsed methylene hydrogens. These factors appear to outweigh π conjugation, which is maximized in a planar configuration. The C═C—C═C dihedral angle, obtained computationally[32,35-38] and experimentally[39-42] ranges from 8 to 20° and from 17 to 18°, respectively. The surface in the vicinity of the minimum energy conformation is apparently quite flat,[35] with little energy (8.4 kJ mol^{-1},[36] 4.6–5.0 kJ mol^{-1} [34]) required to invert the structure. In most of the structural determinations, each ethylene group was assumed to be planar (C—C═C—C dihedral angle = 0°), but those calculations which investigated the deviation from a zero dihedral angle found only 1 to <5° distortion.[35,37,38]

In the present study, ab initio calculations have been performed on 1,4-CHD, 1,3-CHD, and substituted systems with substituents CH_3, CN, NO_2, F, OH, and NH_2. Optimized structures have been obtained for 1,4-CHD and 1,3-CHD, and these have been

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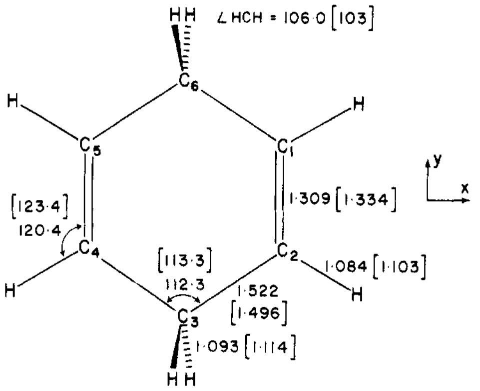

Figure 1. Optimized STO-3G (and experimental[47] in brackets) structural parameters for 1,4-cyclohexadiene.

used in subsequent calculations for the substituted systems. Experimental data with which the calculations are compared include isomerization data, ionization potentials, electron affinities, and heats of formation. In addition, comparisons are made of thermodynamically favored sites of protonation of substituted cyclohexadienyl anions (SCHD$^-$) (as indicated by the relative isomer stabilities of the appropriate cyclohexadienes) and the kinetically favored sites of protonation (as examined previously[5] with the aid of calculated molecular electrostatic potentials).

Method

Standard ab initio SCF–MO calculations were carried out by using a modified version[43a] of the Gaussian 70 system of programs.[43b] Calculations were performed at the STO-3G level[44] except for single calculations with the 4-31G basis set[45] on the STO-3G optimized structures of 1,3-CHD and 1,4-CHD. The geometry of 1,4-CHD was fully optimized under a D_{2h} symmetry constraint while for 1,3-CHD, C_2 symmetry was assumed with the additional approximation of planarity at the ethylenic carbon atoms (as suggested by previous theoretical and experimental results).

For the substituted cyclohexadienes, the optimized structures of 1,3-CHD and 1,4-CHD were used in conjunction with standard values[46] of bond lengths and angles for the substituents. Because of the two inequivalent methylene hydrogens in 1,3-CHD, there are two distinct substituent positions at C(5). These are labeled 5a and 5e for a substituent replacing the axial hydrogen, H_a, and equatorial hydrogen, H_e, respectively, as indicated in Figure 2 (see below).

Our calculations refer, of course, to isolated molecules in the gas phase. The results provide a base line from which the perturbing effect of solvent and counterion (for the anions) can be rationally examined.

Results and Discussion

A. Optimized Structures of 1,4-CHD and 1,3-CHD. (i) 1,4-Cyclohexadiene. The theoretical structure for planar D_{2h} 1,4-CHD is compared with an electron diffraction structure[47] in Figure 1. Both theory and experiment indicate that the C—C, C═C, and C—H bond lengths are almost identical with corresponding (theoretical[48] or experimental[49]) values for propene.

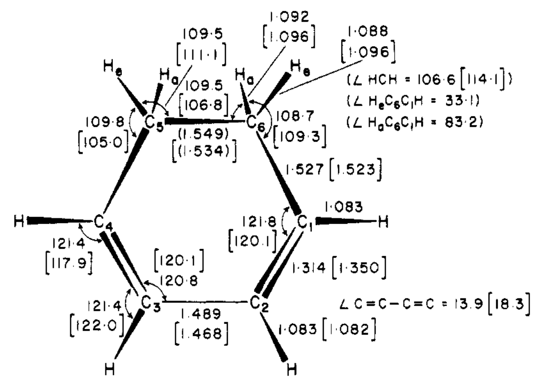

Figure 2. Optimized STO-3G (and experimental[42] in brackets) structural parameters for 1,3-cyclohexadiene.

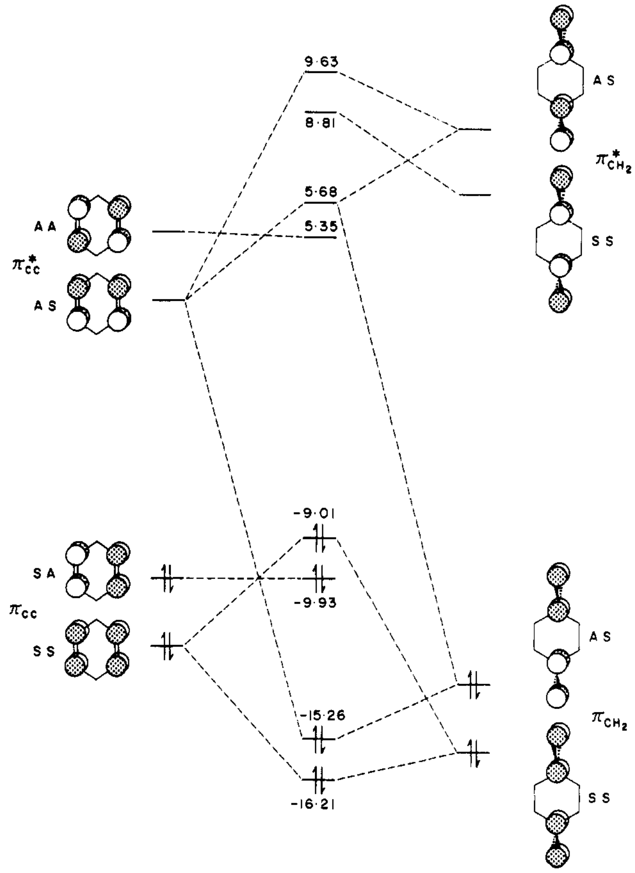

Figure 3. Schematic orbital interaction diagram generating the π orbitals of 1,4-cyclohexadiene. Also shown are the calculated (4-31G) orbital energies (eV).

1,4-CHD was also examined in boat (**6**) and chair (**7**) structures in order to decide between conflicting electron diffraction predictions of a planar[47] or nonplanar boat[42] form. For these, the CH_2 groups were deflected out of the plane so that the C(6)C(1)C(5)C(4) and C(3)C(2)C(4)C(5) dihedral angles were kept at 10°, and atoms H(1), H(2), H(4), and H(5) were deflected so as to maintain planarity at the corresponding carbon atoms. Apart from the C—H lengths, all other parameters were optimized within C_{2v} (boat) and C_{2h} (chair) constraints.

The boat[50] and chair[51] structures are found to lie 2.1 and 27.5 kJ mol^{-1}, respectively, above the planar (D_{2h}) form, suggesting that the equilibrium structure is planar but that distortions to nonplanar boat structures are not energetically costly. This result agrees with most of the previous theoretical and experimental predictions[29,47,52-55] although we should note as a cautionary remark

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Table I. Calculated Total Energies (STO-3G, hartrees) for Conformations of Substituted 1,4-Cyclohexadienes

substituent	1-position	3-position
H	−229.04308[a]	−229.04308[a]
CH_3	−267.62782 [HCC=C (cis)][b]	−267.62229 [HCCH (trans)]
CN	−319.59715	−319.58601
NO_2	−429.73831	−429.73725 [ONCH (cis)][c]
F	−326.50264	−326.49019
OH	−302.88176 [HOC=C (cis)][d]	−302.86896 [HOCH (trans)]
NH_2	−283.35541	−283.35052 [:NCH (60°)][e]

[a] 4-31G energy is −231.49727. [b] Energy for HCC=C (trans) is −267.62509. [c] Energy for ONCH (90°) is −429.73611. [d] Energy for HOC=C (trans) is −302.87967. [e] Energies for other :NCH dihedral angles are as follows: cis, −283.34512; 120°, −283.34512; trans, −283.34800.

based on previous studies[56] that the STO-3G basis set does not describe well the slight nonplanarity of the cyclobutane ring.

(ii) 1,3-Cyclohexadiene. The optimized structure for 1,3-CHD is compared with one of the electron diffraction structures[42] in Figure 2. For this molecule, the calculated C(2)—C(3), C=C, and C—H bond lengths are very similar to corresponding (theoretical[57] and experimental[58]) values for *trans*-1,3-butadiene. The C=C—C=C dihedral angle of 13.9° is somewhat smaller than that found experimentally (17–18°).[39-42]

B. Orbital Interactions in 1,4-Cyclohexadiene. The π-MO's of 1,4-CHD can be constructed from two ethylene and two methylene fragments by using perturbation molecular orbital (PMO) theory. This was considered previously in relation to through-bond and through-space interactions.[31] The interaction diagram of Figure 3 shows the effect of through-bond and through-space coupling. The four π orbitals on the left of the diagram represent orbitals obtained by through-space interaction of two ethylene groups. The orbitals are labeled according to their behavior upon reflection in the *xz* and *yz* symmetry planes, respectively (see Figure 1 for orientation of axes). The doubly occupied π_{CC}(SA) orbital, for example, is symmetric with respect to reflection in the *xz* plane, but antisymmetric with respect to the *yz*-plane, and lies above the symmetric π_{CC}(SS) orbital.

Particular interest has arisen for 1,4-CHD because of the effect of the mixing in of the methylene pseudo-π-orbitals (right-hand side of Figure 3) with the ethylene orbitals, i.e., the effect of through-bond interactions. The resultant orbitals are shown in the center of Figure 3. Since, by symmetry, π_{CC}(SS) and not π_{CC}(SA) can interact with π_{CH_2}, the two HOMO's have reversed their order, with the symmetric orbital π_{CC}(SS) lying above the antisymmetric orbital π_{CC}(SA). This is an unusual feature among nonconjugated dienes.[31,59]

Calculated (4-31G) orbital energies are included in Figure 3, and the differences are similar to those of previous calculations.[30,60] The energy difference between the two highest doubly occupied molecular orbitals (0.92 eV) is in good agreement with photoelectron spectroscopic data (1.0[61] and 1.06 eV[62]). The energy difference between the two lowest unoccupied MO's (0.11 eV), however, is in poor agreement with vertical electron affinity measurements (ΔE = 0.33 eV).[59,63]

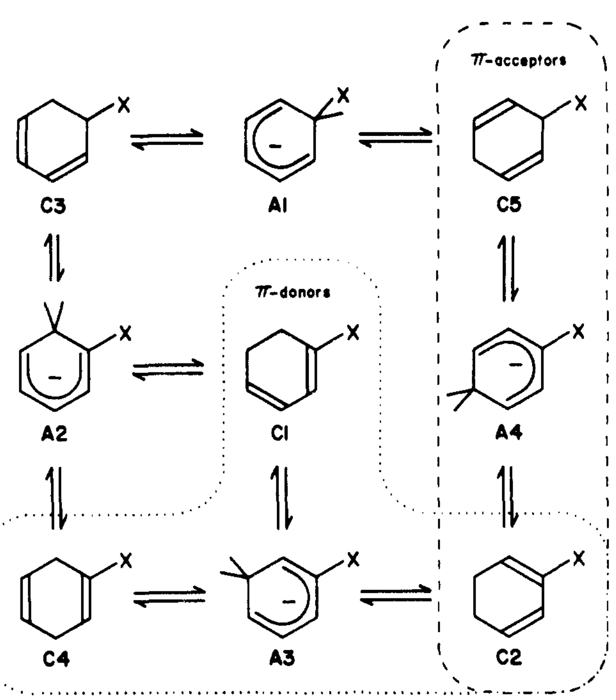

Figure 4. Isomerization scheme for interconversion of substituted cyclohexadiene isomers via intermediate substituted cyclohexadienyl anion isomers. The region bounded by dotted lines (···) is that most readily accessible to π-donor substituents and that bounded by dashed lines (---) to π-acceptor substituents.

C. Relative Energies. Total energies for the substituted 1,4-CHD's and 1,3-CHD's are given in Tables I and II. Relative energies of the best conformers of all five 1,4-CHD and 1,3-CHD isomers, relative to the most stable (1,3-CHD) isomer, are given in Table III. These relative energies can be used to predict the thermodynamically preferred protonation products.

The energy difference between the unsubstituted isomers is 1.4 kJ mol^{-1} (STO-3G) in favor of the conjugated diene. At the 4-31G level, however, the difference is 2.4 kJ mol^{-1} in favor of 1,4-CHD. This discrepancy may possibly be due to the use of a geometry unoptimized at the 4-31G level. The reaction 1,4-CHD → 1,3-CHD is isodesmic, and results at the STO-3G level are usually reliable for such reactions. Our main conclusion, however, which agrees with experimental results,[25] is that 1,4-CHD and 1,3-CHD have very similar energies.

The most stable isomer for all the substituted cyclohexadienes is the 1-substituted 1,3-CHD. Except for NO_2, substitution at the saturated carbons results in comparatively higher energies. For both π-electron acceptor and π-electron donor substituents, the preference for the 1,3-CHD over the 1,4-CHD is increased compared with that in the parent system due to the possibility of extended conjugation.

D. Isomerization Reactions. The relative energies presented in Table III should predict the preferred substituted CHD isomers formed under equilibrium experimental conditions. It is seen that the 1-substituted 1,3-CHD is favored for all substituents. This is in agreement with experimental Birch reductions (under reversible conditions) for π-donor substituents such as OCH_3, leading to **1**. For π-acceptor substituents, however, early experiments[9] indicated a preference for the 2-substituted 1,3-CHD isomer, **2**, and this disagrees with the calculations. Very recent studies[18] with $(CH_3CN)_3Cr(CO)_3$ as catalyst suggest, however, that for such substituents (e.g., $COOCH_3$), the 1-substituted 1,3-CHD is in fact the thermodynamically preferred isomer; the previous results[9] may therefore reflect incomplete equilibration. The equilibration process involves the abstraction of a proton from the

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Table II. Calculated Total Energies (STO-3G, hartrees) for Conformations of Substituted 1,3-Cyclohexadienes

substituent	1-position	2-position	5a-position (axial)	5e-position (equatorial)
H	−229.04362[a]	−229.04362[a]	−229.04362[a]	−229.04362[a]
CH_3	−267.62914 [HCC=C (cis)][b]	−267.62824 [HCC=C (cis)][c]	−267.62276 [HCCH (trans)]	−267.62280 [HCCH (trans)]
CN	−319.59872	−319.59738	−319.58692	−319.58689
NO_2	−429.73960	−429.73788	−429.73839 [ONCH (90°)][d]	−429.73824 [ONCH (cis)][e]
F	−326.50458	−326.50225	−326.49269	−326.49247
OH	−302.88461 [HOC=C (cis)][f]	−302.88132 [HOC=C (cis)][g]	−302.87069 [HOCH (trans)][h]	−302.86959 [HOCH (trans)]
NH_2	−283.35915	−283.35529	−283.35224 [:NCH (60°)][i]	−283.35133 [:NCH (300°)][j]

[a] 4-31G energy is −231.49636. [b] Energy for HCC=C (trans) is −267.62630. [c] Energy for HCC=C (trans) is −267.62570. [d] Energy for ONCH (cis) is −429.73796. [e] Energy for ONCH (90°) is −429.73712. [f] Energy for HOC=C (trans) is −302.88235. [g] Energy for HOC=C (trans) is −302.87969. [h] Energy for HOCH = 60° is −302.86832 and for −60° is −302.86938. [i] Energies for other :NCH dihedral angles are as follows: −283.34610 (cis), −283.34724 (120°), −283.34973 (trans), −283.34497 (240°), and −283.35140 (300°). [j] Energies for other :NCH dihedral angles are as follows: −283.34547 (cis), −283.35129 (60°), −283.34644 (120°), −283.35026 (trans), and −283.34644 (240°).

Table III. Relative Energies (STO-3G), kJ mol^{-1}) for Lowest Energy Conformations of Substituted 1,3-Cyclohexadienes and 1,4-Cyclohexadienes

	1,3-CHD			1,4-CHD	
substituent	1-position	2-position	5-position	1-position	3-position
H	0	0	0	1.4[a]	1.4[a]
CH_3	0	2.4	16.6	3.5	18.0
CN	0	3.5	31.0	4.1	33.4
NO_2	0	4.5	3.2	3.4	6.2
F	0	6.1	31.2	5.1	37.8
OH	0	8.6	36.5	7.5	41.1
NH_2	0	10.1	18.2	9.8	22.7

[a] 4-31G value is −2.4 kJ mol^{-1}.

Table IV. Stabilization Energies of Substituted Cyclohexadienes (or Hydrogen Molecule Affinities of Substituted Benzenes Relative to Benzene) (kJ mol^{-1})[a]

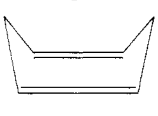
	1,3-CHD			1,4-CHD	
substituent	1-position	2-position	5-position	1-position	3-position
H	0	0	0	0	0
CH_3	4.6	2.3	−12.0	2.5	−12.0
CN	4.9	1.4	−26.1	2.1	−27.1
NO_2	7.4	2.9	4.2	5.4	2.6
F	4.3	−1.8	−27.0	0.6	−32.1
OH	6.4	−2.2	−30.1	0.3	−33.3
NH_2	2.7[b]	−7.5[b]	−26.9[c]	−5.8[b]	−30.0[c]

[a] As defined in reactions 2 and 3. [b] Planar NH_2. [c] Pyramidal NH_2.

initially formed 1,4-CHD, and reprotonation of a CHD^- intermediate. Proton abstraction from those sites that lead to a relatively unstable $SCHD^-$ is likely to be very slow and may effectively block some of the isomerization pathways.

Figure 4 shows the scheme by which the cyclohexadiene isomers can interconvert. The five cyclohexadienes are at the four corners and center of the diagram, and the four intermediate anions are at the edge centers. Each double arrow represents a path involving the addition or abstraction of one proton.

π-Donor-substituted cyclohexadienes enter the diagram at the bottom left corner (structure C4) after kinetic protonation of a cyclohexadienyl anion (A2 or A3). Isomerization to the most stable CHD isomer (center, C1) takes place readily via the relatively stable anion A3.[9,64] Isomerization outside the region enclosed by the dotted line, however, is prevented or retarded by the necessity of forming the relatively unstable structures A2 and A4. Looked upon in another way, the most acidic proton of C4 (X = π donor) is H(6), which is most readily lost to give A3, while H(3) which would give rise to A2 is much less acidic.



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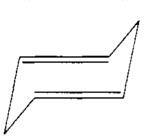

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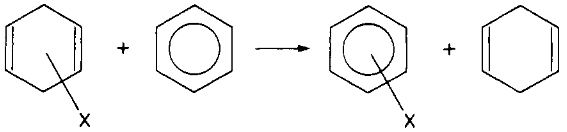
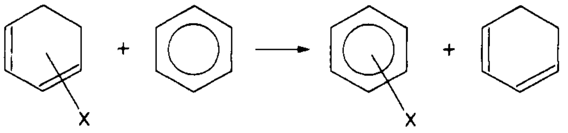
CHD's substituted by π-acceptors enter the diagram at the top right (C5) after kinetic protonation of A1 or A4, but isomerization is confined to the region enclosed by the broken line due to the relatively low stability of A1 or A3, compared to A4.[9,64] Hence the formation of the thermodynamically most stable isomer, C1, is hindered for π-acceptor substituents. This provides a possible explanation for the experimental results and is partly supported by work on the isomerization of unsubstituted 1,4-CHD to 1,3-CHD,[14] in which the "equilibrium" ratios varied according to the experimental conditions as well as on the starting materials. Further support comes from the $(CH_3CN)_3Cr(CO)_3$-catalyzed equilibrium studies[18] which, for the $COOCH_3$ substituent, yielded the 2,3-dihydro derivative as the major product.

In the gas phase, considerations involving anionic intermediates do not apply and the prospect of observing true equilibrium is improved. Indeed, experimental gas-phase isomerizations of CH_3-1,3-CHD's[19] give relative isomer stabilities in agreement with the calculations. The observed equilibrium concentrations are in the order 1-CH_3-1,3-CHD > 2-CH_3-1,3-CHD > 5-CH_3-1,3-CHD. The mechanism proposed[19] for these isomerizations involves successive 1,5-hydrogen shifts and accounts for the absence of any CH_3-1,4-CHD.

E. Stabilization Energies. Stabilization energies (SE's) for cyclohexadienes are conveniently defined, with corresponding substituted benzenes as reference, as energy changes in reactions 2 (for 1,4-CHD's) and 3 (for 1,3-CHD's). Values calculated by



(2)



(3)

using previously published energies for the substituted benzenes[65] are listed in Table IV. Positive values imply a relative stabilization of the cyclohexadiene. The SE's can also be interpreted as relative hydrogen molecule affinities (monohydrogenation energies) of substituted benzenes.

The results shown in Table IV indicate that substituents are generally destabilizing (compared with their effect in benzene)

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(64) Our previous study[5] on $SCHD^-$ isomers showed that π-donor substituents prefer structures A3 and A1 while π acceptors prefer A2 and A4. For example, calculated relative energies (in kJ mol^{-1}) for A1, A2, A3, and A4 are respectively 0, 56, 33, and 75 for OCH_3 and 72, 23, 114, and 0 for NO_2.

(65) Hinde, A. L.; Radom, L.; Rasmussen, M. *Aust. J. Chem.* **1979**, *32*, 11.

J. Am. Chem. Soc. **1981**, *103*, 289-295

at the saturated positions and stabilizing at the unsaturated 1-positions of the cyclohexadienes. NO_2 is stabilizing at all positions while NH_2 is destabilizing at all except the 1-position of 1,3-CHD.

F. Comparison of Kinetically and Thermodynamically Favored Sites of Protonation of Cyclohexadienyl Anions. In previous papers,[4,65] we have compared kinetically preferred protonation sites (as reflected in minima, V_{min}, in molecular electrostatic potential[66] [MEP] maps) with thermodynamically favored sites (as indicated by relative product energies or protonation energies, ΔH_{prot}). Our present calculations show that in contrast to the protonation of benzene radical anions,[3,4] the MEP preferred protonation sites of $SCHD^-$ do not correspond to the thermodynamically favored sites. The MEP minima in the vicinity of $SCHD^-$ are deepest near C(3) whereas the lowest energy cyclohexadiene isomer corresponds to protonation at C(1) or C(5).

Despite this situation, the correlation coefficient between V_{min} values for the $SCHD^-$'s and ΔH_{prot} for the reaction $SCHD^- + H^+ \rightarrow SCHD$ is 0.868, indicating a linear relationship (at the 95% confidence level).[67] This reflects an overall trend in the electrostatic contribution to the total protonation energy for the $SCHD^-$ system. The regression line is $\Delta H_{prot} = 1.264 V_{min} - 1206.3$ (kJ mol^{-1}) and is close to that found[4] for protonation of SBz^-. The correlation coefficient is not as good as that for SBz^-, and this may reflect the greater variability in electronic environment in $SCHD^-$ compared with SBz^-.

Conclusions

(1) In agreement with experimental results, 1,4-CHD is found to prefer a planar D_{2h} structure although distortions to nonplanar boat-type structures are not energetically costly. 1,3-CHD has a nonplanar C_2 structure.

(2) The energies of 1,4-CHD and 1,3-CHD are found to be quite similar.

(3) The 1-substituted 1,3-CHD isomer is uniformly preferred over all the other cyclohexadiene isomers for all the substituents examined. This is in agreement with experimental results in solution (under "equilibrium" conditions) for π-donor substituents, but for π-acceptor substituents the experimental situation is less clear-cut because of difficulties in achieving true equilibrium.

(4) A linear correlation exists between the MEP minimum values of $SCHD^-$ and the corresponding protonation energies. The correlation is not as good as was obtained for SBz^-'s, a fact which can be attributed to the greater variability of the electronic environments in $SCHD^-$ compared with SBz^-. The regression lines obtained for SBz^- and $SCHD^-$ are similar and represent for these systems an overall trend, upon which additional electronic effects may be superimposed (as in $SCHD^-$).

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[66] Reviews: (a) Scrocco, E.; Tomasi, J. *Top. Curr. Chem.* **1973**, *42*, 95; (b) Scrocco, E.; Tomasi, J. *Adv. Quantum Chem.* **1978**, *11*, 115.

[67] A full tabulation of the V_{min} and ΔH_{prot} values is presented in: Hinde, A. L. Ph.D. Thesis, Australian National University, 1979.

Molecular Structure of Selected *S*-Methylthiophenium Tetrafluoroborates and Dibenzothiophene 5-Oxide

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Abstract: Molecular structures of 5-methyldibenzothiophenium tetrafluoroborate (I), 1-methylnaphtho[2,3-*b*]thiophenium tetrafluoroborate (II), and dibenzothiophene 5-oxide (III) were determined by X-ray diffraction. The effect of increase of coordination at the sulfur atom (with respect to sulfur atom in thiophene-like molecules) was evaluated by examining the planarity of the structure, stereochemistry at the sulfur atom, CS bond distances, and the CC bonds alternation in the carbon atom framework. The experimental results parallel the results of MNDO semiempirical calculations of model species, i.e., thiophene (IV), the *S*-methylthiophenium ion (V), and thiophene *S*-oxide (VI). The changes of aromaticity of the thiophene-like molecules resulting from the substitution at the sulfur atom are discussed in terms of the perturbation theory by using HMO models.

The sulfur atom in thiophene-like molecules is characterized by exceedingly low reactivity compared to that of the sulfur atom in organic sulfides. For example, perbenzoic acid oxidized dibenzothiophene to the sulfoxide 100-fold more slowly than it oxidizes diphenyl sulfide.[1] The lack of reactivity of thiophenoid sulfur toward methyl iodide is even used to differentiate thiophenes from sulfides in coal analysis.[2] *S*-Alkylthiophenium salts can be prepared only by using the most vigorous alkylating agents, e.g., trialkyloxonium tetrafluoroborates[3] or methyl iodide–silver tetrafluoroborate (or silver perchlorate).[4]

The products of reaction at an "aromatic" sulfur are less stable and much more reactive than those derived from sulfides. Thus, thiophene *S*-oxide undergoes spontaneous Diels–Alder dimerization.[5] The reductive electrochemical deoxygenation of dibenzothiophene 5-oxide is about 0.6 V more positive than that of diphenyl sulfoxide under the same conditions.[6] *S*-Alkylthiophenium ions exist only with nonnucleophilic counterions such as tetrafluoroborate or perchlorate anion[4] in contrast to such ions as triphenylsulfonium ions which are stable even in the presence of bromides as contraion.[7] Nonaromatic or antiaromatic character of thiophene *S*-oxides and *S*-alkylthiophenium ions has been postulated by Mock[8] and Acheson,[4] respectively, on the basis of interpretation of the NMR spectra which indicated the third ligand (O, alkyl) to be located off the molecular plane. Both the decrease of the aromatic stabilization and antiaromatic destabilization would explain the difference in properties of the thiophene-like molecules and their S derivatives.

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