mechanisms (e.g., a cyclic intermediate), the absolute values of the barrier heights may vary considerably.

Table I gives the results for [1,3], [1,4], [1,5], and [1,6] suprafacial shifts. We discuss the results for thermal and photochemical reactions separately with an emphasis on even-electron systems.

A. Thermal Reactions. The stereospecificity of the [1,3] and [1,5] neutral and the [1,4] cation reactions determined from the table are in agreement with much observed chemistry and with the Woodward–Hoffmann predictions. The barrier heights along the S_0 path do not vary significantly with increasing j.

In order to study the effects of π-electron configuration interaction, Table I presents activation energies computed both with and without the Hubbard term. In most cases, the effect is to lower somewhat all barriers encountered. However, in even-electron systems, one can see a more pronounced lowering of the activation energy of the forbidden path for [1,3] and [1,5] neutral shifts while the energy along the allowed path is virtually unaffected. It is tempting to conclude from this that the electron correlation stabilizes the antiaromatic transition state compared to the Hückel treatment. However, consideration of the [1,4] and [1,6] cation rearrangements fails to confirm the preferential lowering of the antiaromatic transition state. In these cation reactions, however, there are more sites than electrons, which reduces the effects of electron repulsion by the increased electron delocalization. A similar behavior was noted previously in electrocyclic reactions[9] as well as in recent full CI calculations on cyclobutadiene which indicate a positive electron delocalization energy.[10]

The odd-electron systems agree quite closely with the MO picture both quantitatively and qualitatively.

B. Photochemical Reactions. Table I also shows the results for the first excited MO surface and the two low-lying HH excited surfaces (degenerate in MO). Again there is qualitative agreement between the methods, but in this case some new features emerge from the Hückel–Hubbard model. The most striking feature is difference in the barrier heights of the singlet

and triplet paths in the [1,3] neutral sigmatropic shift which was noted earlier. For even-electron systems, the MO barriers lie between those in the lowest excited HH states but have values closest to the T_1 paths. For neutral radicals, the barriers are considerably higher with CI, but there is no stereospecificity in either treatment.

IV. Conclusion

As we found in the treatment of electrocyclic reactions, our results for [1,j] sigmatropic shifts are in general agreement with the stereochemical predictions of the Woodward–Hoffmann approach (particularly for S_0 and T_1). The introduction of electron repulsion, however, splits the S_1,T_1 exchange degeneracy, yielding lower barriers along S_1 paths. This prediction suggests that the photochemistry of these two states may differ as is indeed observed in the laboratory. In the [1,3] shift, the barrier is reduced so much that the S_1 stereochemistry is open to question and may require more detailed study.

We have not discussed the odd-electron systems in detail because they are of lesser experimental interest. We note that these systems are in many respects similar to even-electron systems with regard to the effects of the introduction of the Hubbard electron repulsion term.

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Ab Initio Study of the Benzene Radical Anion

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Abstract: Ab initio molecular orbital calculations with the STO-3G and 4-31G basis sets have been carried out for the radical anions of benzene (Bz⁻) and fluorobenzene (FBz⁻). In accordance with the Jahn–Teller theorem, Bz⁻ is predicted to distort from regular hexagonal (D_{6h}) symmetry. The best structures of Bz⁻ have D_{2h} symmetry. Two quite different D_{2h} structures are found, one with four longer and two shorter C–C bonds and the other with two longer and four shorter C–C bonds. Configuration interaction calculations suggest that these two structures have very similar energies. Interconversion of equivalent D_{2h} structures requires little activation energy, a result consistent with the experimental ESR spectrum. The ring skeletons of FBz⁻ and Bz⁻ are similar suggesting that the Bz⁻ structures might usefully serve as models in studies of radical anions of substituted benzenes.

The benzene radical anion (Bz⁻) is of interest in experimental organic chemistry as the species formed in the first stage of the Birch (metal/ammonia) reduction of benzene.[2] It is also of interest theoretically since it represents a Jahn–Teller situation[3] and in this capacity it has received considerable attention in the literature.[4-14] In this paper, and as part of a wider theoretical study of the Birch reduction, we present

the first application of ab initio molecular orbital theory to the problem. Our aim is to establish a model for Bz⁻ suitable for subsequent studies of the effect of substituents. To this end, we have carried out ab initio calculations on several possible structures of Bz⁻. In addition, for reasons given below, we have also performed similar calculations on the radical anion of fluorobenzene.
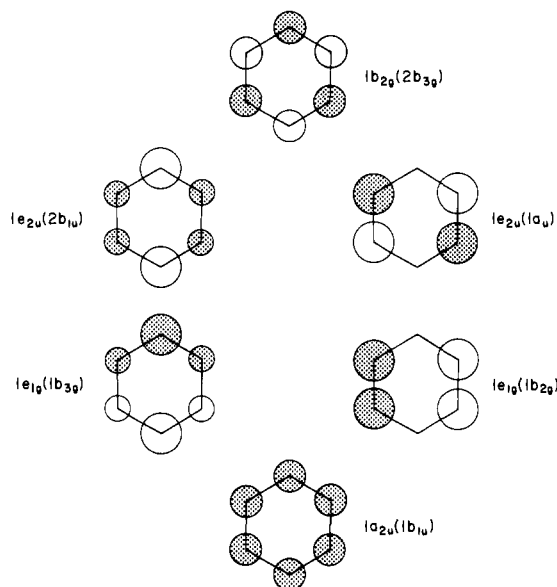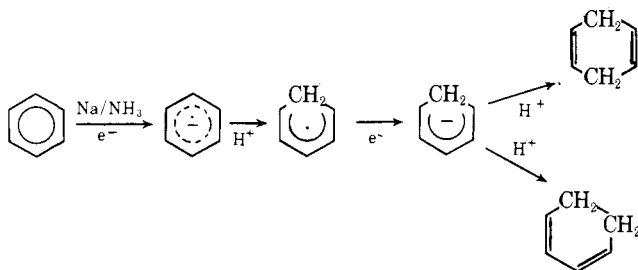
Figure 1. Symmetry classifications of π-type molecular orbitals of benzene. Symmetries refer to point groups D_{6h} (D_{2h}).

Figure 2. Optimized RHF/STO-3G structures for Bz⁻. Bond lengths in Å, bond angles in deg, C–H lengths assumed equal to 1.082 Å in D_{2h} structures.

Hückel Molecular Orbital Considerations

It is convenient to examine initially the π (Hückel) molecular orbitals of benzene and these are shown schematically in Figure 1. In neutral benzene, there are six π electrons and the electronic configuration is $(1a_{2u})^2 (1e_{1g})^4$, $^1A_{1g}$. In the benzene negative ion, an extra electron is present and can be accommodated in either of the degenerate e_{2u} orbitals. The Jahn–Teller theorem tells us that, in such a situation, the molecule distorts from D_{6h} symmetry and the degeneracy is removed. The allowed distortions belong to the E_{2g} representation of D_{6h}.

Previously reported Hückel calculations[4,8,9] suggest a distortion to structures of D_{2h} symmetry. In the D_{2h} point group, the degenerate pair of e_{2u} (D_{6h}) orbitals is split into nondegenerate b_{1u} and a_u orbitals. If the unpaired electron occupies the a_u orbital, the electronic configuration is $(1b_{1u})^2$-$(1b_{2g})^2(1b_{3g})^2(1a_u)^1$, ^2A_u. A qualitative prediction of the geometric structure comes from the nodal pattern of the a_u orbital. The two carbon–carbon bonds which are intersected by a nodal plane should be weakened (lengthened) relative to benzene while the other bonds will be relatively unaffected. If the unpaired electron occupies the $2b_{1u}$ orbital, then the electronic configuration is $(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^1$, $^2B_{1u}$. Here, two of the carbon–carbon bonds are expected to be strengthened (shortened) and the other four weakened. Both distorted structures represent E_{2g} distortions from the D_{6h} structure as required. They are special cases of the more general permitted E_{2g} displacements that have C_{2h} symmetry and correspond to stationary points in the E_{2g} surface.

Ab Initio Calculations

In order to quantify these predictions, we have carried out ab initio calculations within the framework of single deter-
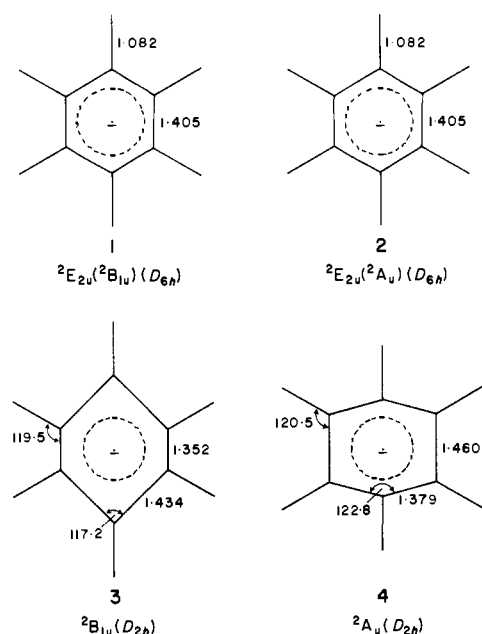
minant SCF–MO theory for closed[15] and open[16] shells using a modified version of the Gaussian 70 system of programs.[17] In a previous publication,[18] we have shown that unrestricted Hartree–Fock (UHF) theory[19] can lead to erroneous results for Jahn–Teller distorted radicals. Spin-restricted (RHF) open-shell theory[16] leads to superior results and is therefore used for all open shell systems treated in the present work.

In addition, we employ a limited configuration interaction (CI) approach which is designed to correctly describe, at least in a qualitative sense, the doubly degenerate electronic ground state of D_{6h} Bz⁻ and its splitting into the ^2A_u and $^2B_{1u}$ components. The configuration list includes the ^2A_u and $^2B_{1u}$ main configurations plus all single excitations from these two reference configurations. The molecular orbitals used in the CI calculations were optimum for neutral benzene at the appropriate anion optimized geometries. Excitations from the six lowest orbitals were not included. We note that this CI calculation is not designed to pick up a significant part of the correlation energy. For such a purpose, the inclusion of at least all doubly excited configurations would be required as well as a more flexible basis set than the ones used in this work.

Geometry optimizations were performed on D_{6h} and D_{2h} structures with the minimal STO-3G basis set using standard exponents.[20] Single calculations with the split-valence 4-31G basis set[21] were carried out on the STO-3G optimized structures. The CI calculations were also performed at STO-3G (RHF) optimized geometries. In our previous related study of the cyclopropenyl radical,[18] we found that optimized geometric parameters at the RHF and CI levels were quite similar and this lends support to the use of the RHF geometries for the CI calculations in this paper. Optimized geometries are summarized in Figure 2 and calculated total energies in Table I. The Mulliken π electron populations for the D_{2h} structures are shown in Figure 3.

There are several shortcomings in this general method as applied to Bz⁻.

(i) First, single determinant calculations on anions are often found to yield energies higher than for the neutral molecule, whereas in fact the anion, if it is stable in the gas phase, must have lower energy.[22] In this connection, we note that most experimental evidence indicates that Bz⁻ is a metastable species. At low pressures in the gas phase, Bz⁻ appears to be

Table I. Calculated Total Energies (E, hartrees) and Relative Energies (ΔE, kcal mol^{-1}) for Structures of Bz$^-$

	1	2	3	4
symmetry	D_{6h}	D_{6h}	D_{2h}	D_{2h}
state	$^2E_{2u}(^2B_{1u})$	$^2E_{2u}(^2A_u)$	$^2B_{1u}$	^2A_u
E(RHF/STO-3G)	-227.64896	-227.64755	-227.65936	-227.65679
ΔE(RHF/STO-3G)	6.5	7.4	0	1.6
E(RHF/4-31G)	-230.25015	-230.24950	-230.25612	-230.25513
ΔE(RHF/4-31G)	3.7	4.2	0	0.6
E(CI/STO-3G)	-227.69480	-227.69480	-227.70338	-227.70326
ΔE(CI/STO-3G)	5.4	5.4	0	0.1

a short-lived resonance state lying about 1.1 eV above neutral benzene and decays by ejecting the extra electron into the continuum.[23,24] On the other hand, high-pressure experiments[25] suggest a positive adiabatic electron affinity for benzene and a minimum in the Bz$^-$ potential energy surface somewhat lower than, and at a different geometry from, that of neutral benzene. We do not attempt to resolve this dispute here. Because of our use of small basis sets and neglect of virtually all correlation effects, an energetic comparison of Bz$^-$ and neutral benzene would not be meaningful and we therefore do not quote a theoretical value for the adiabatic electron affinity for benzene.
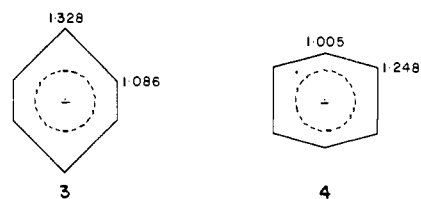
(ii) Krauss and co-workers,[26] following detailed calculations on N$_2^-$ and CO$_2^-$, have recommended that for SCF calculations on resonant states, the basis sets should be restricted to valence in character. They have noted that basis set optimization is likely to lead to very diffuse orbitals and a description of the anion corresponding to that of a neutral molecule and a separated electron. Most of their calculations appear to have been carried out with double ζ basis sets. We have consequently used the STO-3G and 4-31G basis sets in the present work. Although these basis sets satisfy the restriction of limited size, it is uncertain whether our use of standard[20,21] scale factors is appropriate. However, unconstrained exponent optimization is likely to lead to the undesirable very diffuse orbitals[27] and has been found in some cases to lead consequently to poor structural predictions.[28] We have not attempted an alternative constrained optimization similar to that carried out by Krauss.[26] We feel that for systems such as Bz$^-$ where the negative charge is delocalized over several carbon centers, the standard exponents derived from neutral systems might not be unreasonable.

(iii) Finally, our calculations are carried out within the framework of the Born-Oppenheimer approximation,[29] i.e., the electronic and nuclear motions are assumed to be independent. In fact, in Jahn-Teller situations such as Bz$^-$, the two types of motion are usually strongly coupled and the Born-Oppenheimer approximation breaks down. To describe this dynamic Jahn-Teller effect, a vibronic analysis is required and this has been done at an approximate level by other workers.[10,13,14] We shall concern ourselves here only with the static Jahn-Teller effect.

Despite the problems posed above, there have been a large number of calculations on anions reported in the literature and these have produced some interesting results.[22] Unfortunately, there is relatively little experimental structural data available to assess the reliability of these calculations. However, some encouragement comes from recent STO-3G and 4-31G calculations which have reproduced geometries of anions[28] and heats of reactions involving anions[30] with an accuracy comparable to that of similar calculations on cations.[31]

Discussion

The theoretical D_{6h} structures (1 and 2) both show C–H bond lengths (1.082 Å) similar to that calculated[29] for benzene (1.083 Å) but the C–C bonds are somewhat lengthened (1.405 Å vs. 1.387 Å). The latter result is expected because the extra

Figure 3. Mulliken π electron populations for structures of Bz$^-$.

electron in Bz$^-$ goes into a molecular orbital which is net antibonding. At the RHF level, the $^2B_{1u}$ component of the $^2E_{2u}$ state is slightly lower in energy than the ^2A_u component by 0.9 kcal mol^{-1} (STO-3G) or 0.4 kcal mol^{-1} (4-31G). We note that UHF/STO-3G calculations[33] give a much poorer result, predicting the ^2A_u component to lie 3.8 kcal mol^{-1} below $^2B_{1u}$. The correct (doubly degenerate) behaviour is produced by the CI calculations which yield identical energies for the $^2B_{1u}$ and ^2A_u components.

If the symmetry constraint is relaxed to D_{2h}, both the $^2B_{1u}$ and ^2A_u components distort in terms of both bond lengths and bond angles. In the $^2B_{1u}$ case (3), four of the C–C bonds are lengthened and two are shortened with respect to the D_{6h} structure (1) or with respect to benzene. This is consistent with the occupation of the $2b_{1u}$ molecular orbital (cf. Figure 1). The distortion of the ^2A_u component leads to a structure (4) in which four of the C–C bonds are shortened and two are lengthened as expected from the nodal pattern of the a_u orbital. Alternatively, if we compare 4 with benzene, we see that four of the C–C bonds remain very close to the benzene length (1.387 Å) while the other two, which are intersected by a nodal plane, are lengthened toward a carbon-carbon single bond value. The distortions we obtain (+0.029 and -0.053 Å for 3, and -0.026 and +0.055 Å for 4 compared with the D_{6h} structures 1 and 2) are similar to those of previous approximate theoretical treatments.[4,8,9]

Distortion of the D_{6h} structure to the optimized D_{2h} structures leads to an energy lowering of 4–6 kcal mol^{-1}. Our RHF calculations predict that 3 lies 1.6 kcal mol^{-1} (RHF/STO-3G) or 0.6 kcal mol^{-1} (RHF/4-31G) below 4. Our best (CI/STO-3G) calculations suggest that 3 and 4 have almost identical energies.

Since our previous study[18] of the related cyclopropenyl radical (C$_3$H$_3$) revealed that not only is there a Jahn-Teller distortion from D_{3h} symmetry but that the resultant C_{2v} structures relax by out-of-plane hydrogen motion to structures of C_s and C_2 symmetries, we decided to explore similar possibilities for Bz$^-$. The six out-of-plane symmetry distortions of the hydrogen atoms in the D_{2h} structure of Bz$^-$ were examined. The carbon skeleton was held planar in these calculations while the hydrogen atoms in these distorted structures had D_2, C_{2v} (two times), and C_{2h} (three times) symmetry. All of these distortions resulted in an increase in calculated (STO-3G) energy. In addition, distortions of the carbon skeleton toward chair (C_{2h}) and boat (C_{2v}) structures were also found to be energetically unfavorable.

The ESR spectrum of Bz$^-$ corresponds to the splitting

Table II. Calculated Total Energies (E, hartrees) and Relative Energies (ΔE, kcal mol^{-1}) for Structures of FBz$^-$

	5	6	7	8
symmetry[a]	D_{6h}	D_{6h}	D_{2h}	D_{2h}
state[b]	$^2B_1$	$^2A_2$	$^2B_1$	$^2A_2$
E(RHF/STO-3G)	−325.10935	−325.11817	−325.12045	−325.12632
ΔE(RHF/STO-3G)	10.6	5.1	3.7	0

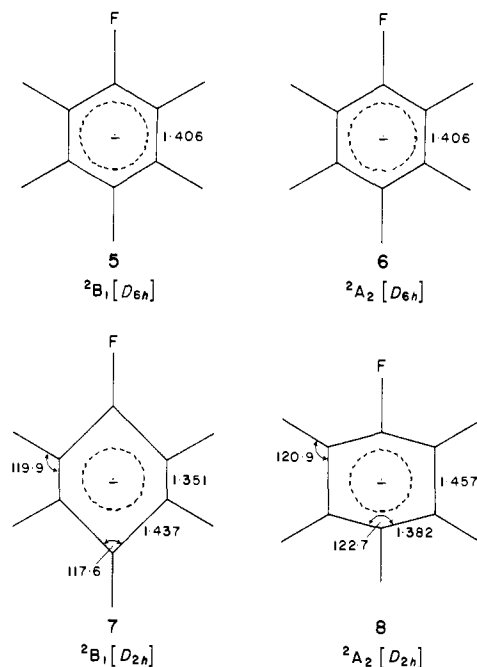[a] Ring symmetry. [b] Classified according to C_{2v} point group.

Figure 4. Optimized RHF/STO-3G structures for FBz$^-$. C–H lengths assumed as 1.082 Å, C–F = 1.33 Å; states classified according to C_{2v} symmetry; ring symmetries given in square brackets.

pattern expected from six equivalent protons.[34] Although the signals are somewhat broad, this suggests that on the time scale of the ESR experiment ($\sim 10^{-7}$ s) Bz$^-$ has D_{6h} symmetry. This is most easily interpreted in terms of a rapid interconversion of the equivalent D_{2h} structures of minimum electronic energy.

We have been able to find a path connecting **3** and **4** via structures of C_{2h} symmetry along which the (STO-3G) energy varies monotonically, i.e., there is no barrier along this path. Given the low energy difference (0.1 kcal mol^{-1}, CI/STO-3G) between **3** and **4**, this means that equivalent structures of **3** or **4** can indeed interconvert rapidly.

One of our main aims in obtaining optimum structures for Bz$^-$ was to use these as models in forthcoming studies of substituted benzene radical anions. However, as mentioned previously, because Bz$^-$ under D_{6h} symmetry has an electronically degenerate ground state, shortcomings in the Born–Oppenheimer approximation may invalidate our static treatment for Bz$^-$ itself as a model for the experimental situation. Fortunately, substituents remove this degeneracy and we would expect that for substituted benzene radical anions, a static model should suffice.

In order to check the suitability of using the Bz$^-$ structures as models for the radical anions of substituted benzene, we have carried out additional calculations on the fluorobenzene anion (FBz$^-$). Geometry optimizations were performed on structures of FBz$^-$ in which the rings were constrained to have D_{6h} and D_{2h} symmetries. The C–H lengths were held at 1.082 Å and the C–F bond was assigned the standard[35] length of 1.33 Å. Optimum structures are shown as **5–8** in Figure 4 and calculated energies are given in Table II.

Comparison of the results in Figures 2 and 4 shows that the optimum C–C bond lengths for Bz$^-$ and FBz$^-$ are similar, i.e., the fluorine substituent does not appear to cause significant changes in the geometry of the ring framework. The Bz$^-$ structures **3** and **4** might therefore usefully serve as models in studies of the radical anions of substituted benzenes. An alternative model for substituted benzene radical anions involves the use of the optimized D_{6h} structure for Bz$^-$ for the ring, i.e., all C–C = 1.405 Å. Such a model applied to FBz$^-$ leads to an energy difference of 5.5 kcal mol^{-1} (RHF/STO-3G) compared with the better estimate (Table II) of 3.7 kcal mol^{-1}.

The ground state of FBz$^-$ is $^2A_2$ (**8**). This corresponds to single occupation of an a_2 type orbital, analogous to the a_u orbital of Bz$^-$ (Figure 1). The key feature of this orbital is the nodal plane perpendicular to the ring and passing through the C_1–F bond leading to a zero contribution to the electron density at C_1. The $^2B_1$ state (**7**) arises through single occupancy of a b_1 orbital and in this case there is nonzero electron density at C_1. Because the fluorine substituent is a π electron donor, the $^2A_2$ state is favored. Results for other substituents will be reported in a forthcoming paper.

Conclusions

Ab initio molecular orbital theory predicts that in accordance with the Jahn–Teller theorem, the benzene radical anion is distorted from regular hexagonal (D_{6h}) symmetry. The best calculated structures have D_{2h} symmetry. Two quite different D_{2h} structures are found but these have very similar energies. Interconversion of the D_{2h} structures requires little energy, a result consistent with the experimental ESR spectrum. The ring skeleton of the fluorobenzene radical anion is found to be similar to that of Bz$^-$ suggesting that the Bz$^-$ structures might usefully serve as models in forthcoming studies of the radical anions of substituted benzenes.

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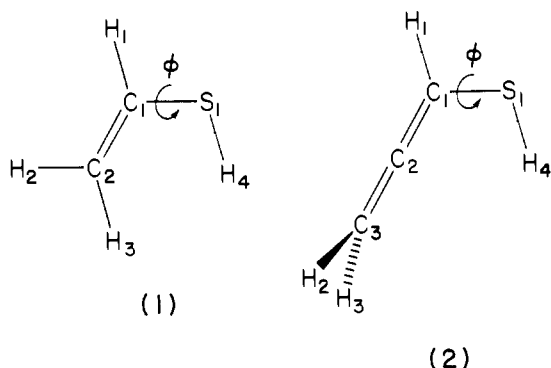(35) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

Ab Initio Study of the Conformations of Vinyl Mercaptan, Methyl Vinyl Sulfide, and Methyl Allenyl Sulfide
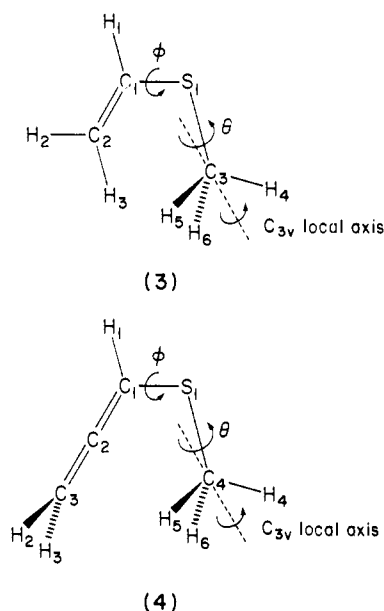
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Abstract: Ab initio (STO-3G and 44-31G) molecular orbital theory has been employed to investigate the rotational potential surfaces of methyl mercaptan, methyl vinyl sulfide, and methyl allenyl sulfide. Both STO-3G and 44-31G predict, for internal rotation along the C_{sp^2}–S bond, two stable conformations and the syn is the more stable one. However, for each molecule, a gauche form is found as the second stable conformation by 44-31G, as opposed to the anti by STO-3G. The corresponding rotational barriers predicted by STO-3G are apparently too high, while those by 44-31G are reasonable. The rotational barrier for a methyl group has also been studied for the syn and anti conformations of methyl vinyl sulfide and methyl allenyl sulfide. The methyl rotational barrier (STO-3G) for the syn is much larger in methyl vinyl sulfide (3.1 kcal mol^{-1}) than in methyl allenyl sulfide (1.9 kcal mol^{-1}) presumably due to steric interactions. Structural variations and conformational energies are rationalized in terms of orbital and steric interactions.

From the structural point of view, vinyl mercaptan (**1**), allenyl mercaptan (**2**), methyl vinyl sulfide (**3**), and methyl

(1)

(2)

(3)

(4)

allenyl sulfide (**4**) can be considered as the second-row analogue of vinyl alcohol, allenyl alcohol, methyl vinyl ether, and methyl allenyl ether, respectively. Just as their oxygen counterparts,[1,2a] the potential function about the C_{sp^2}–S bond has been the subject of some controversy.[2-6] Only a syn form of methyl vinyl sulfide (syn is defined as the structure having C_{sp^2}=C_{sp^2}—S—R coplanar and having S—R and C_{sp^2}=C_{sp^2} bonds on the same side of the C_{sp^2}—S bond) was reported to exist by microwave and photoelectron data.[3] A study of temperature-dependent IR spectra showed, on the other hand, that methyl vinyl sulfide existed in two conformations.[5] Electron diffraction studies reported by two independent research