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Steric Forces in Substituted Aromatics: Conformation of the Hexahalobenzenes As Determined by ab Initio Calculations

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Abstract: The fully halogenated benzenes C_6F_6, C_6Cl_6, C_6Br_6, and C_6I_6 have been studied in a series of all-electron ab initio Hartree–Fock calculations using basis sets of double-ζ quality or better. Geometry optimizations have been performed with the aim of resolving controversies among experimental results with regard to the planarity of the heavier molecules in the series. The compounds are all found to be planar, and the present results therefore reject the notion of geometrical distortions due to steric overcrowding in these compounds.

I. Introduction

The question of nonplanarity in overcrowded aromatic systems has long been a matter of debate. In particular, the situation in fully halogenated benzenes has been discussed by Coulson and Stocker[1] and for halogenated aromates in general by Gafner and Herbstein.[2]

In halogen-substituted aromates, the distances between substituent atoms in ortho positions will often be shorter than the sum of the van der Waals radii[3] if standard geometries are assumed.[4] In particular, this applies to Cl-, Br-, and I-substituted aromates, which show increased ortho X–X distances with a minimum of other geometry distortions. An analogous case is offered by the heavier tetrahaloethylenes, which are planar with distorted bond angles.[8] On the other hand, no deviation is expected or detected for the fluorine compounds.[9–11] In fully or nearly fully substituted halogenated benzenes, however, it is no longer possible to diminish the steric repulsion by splaying the atoms apart in the molecular plane. Out-of-plane distortions should therefore also be considered, being the only realistic way for the molecules to relieve some of their repulsive strain.

In their survey article,[1] Coulson and Stocker discussed the question of planarity for the hexahalobenzenes on the basis of the amount of experimental data available at that time. They pointed out several discrepancies that seemed to exist among the different experimental results. Much effort has been spent on this problem since then, using a variety of techniques, but the conclusions that have been reached are contradictory or indecisive.

Table I. Gaussian Basis Sets Used in the Calculations

compd	basis for C prim	basis for C contr	basis for X prim	basis for X contr	total no. of prim	total no. of contr
C_6H_6						
I	7s3p^a	4s2p	3s^b	2s	114	72
II	9s5p1d^c	4s3p1d	4s1p^d	2s1p	222	144
C_6F_6						
III	7s3p^a	4s2p	7s3p^a	4s2p	192	120
IV	9s5p1d^c	4s3p1d	9s5p1d^c	4s3p1d	360	228
C_6Cl_6	7s3p^a	4s2p	10s7p1d^d	6s5p1d	318	222
C_6Br_6	7s3p^a	4s2p	14s11p5d^f	8s7p2d	558	306
C_6I_6	7s3p^a	4s2p	15s11p7d^g	10s8p5d	636	444

[a] Reference 12. [b] Reference 13. [c] Reference 14, polarization functions from ref 15. [d] Reference 13, p exponent of 0.8. [e] Reference 12, d exponent of 0.68. [f] Reference 16. [g] T. H. Dunning, Jr., unpublished results.

With this background we decided to study the question of planarity in these compounds from a theoretical viewpoint. Ab initio calculations of rather good quality may today be performed for all the compounds in the series. The details of our computational procedure are given in section II of this paper, whereas the presentation of the results appears in section III. In section IV, finally, we discuss the results obtained in the light of the approximations used and compare them with experimental investigations.

II. Computational Details

The calculations were performed at the Hartree-Fock level of approximation, using Gaussian basis sets of essentially double-ζ quality. Details about the basis sets are presented in Table I. For chlorine, the basis was augmented by a diffuse p shell with exponents of 0.06 and by a polarization d shell with exponents of 0.68.[15]

The d basis used for iodine in the present calculations was not suited for a double-ζ contraction. Four functions in the primitive set represent the 3d shell of the atom and two are 4d, whereas one is intermediate. A contraction to five sets of d-type functions was therefore applied, giving some additional flexibility to the basis set. Similarly, the primitive p basis used for Br suggested a contraction to seven functions rather than six.

In addition to these calculations, benzene and hexafluorobenzene were also studied with larger basis sets in order to assess the degree of convergence for the properties investigated.

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(2) G. Gafner and F. H. Herbstein, *Acta Crystallogr.*, **13**, 706 (1960).

(3) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell, University Press: Ithaca, NY, 1969, p 206.

(4) The distances between halogen atoms in ortho positions would be 2.8, 3.1, 3.3, and 3.5 Å for F, Cl, Br and I, whereas the sums of the van der Waals radii are 2.7, 3.6, 3.9, and 4.3 Å, respectively.

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(10) J. E. Boggs, F. Pang, and P. Pulay, *J. Comput. Chem.*, **3**, 344 (1982).

(11) H. Schei, private communication; V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, **38**, 2693 (1963); J. Gerritsen and C. Maclean, *Spectrochim. Acta*, **27A**, 1495 (1971); C. T. Yim and D. F. R. Gilson, *Can J. Chem.*, **47**, 1057 (1969).

(12) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 209 (1970).

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(14) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).

(15) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 199 (1970). (In all cases where d orbitals were used, the sixth, totally symmetric component of a Cartesian d-type basis set was also included.)

(16) T. H. Dunning, Jr., *J. Chem. Phys.*, **66**, 1382 (1977).

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Table II. Calculated Bond Distances (Å) for the Hexahalogenated Benzenes, in Comparison with Experimental Data and with Results Obtained in Other Calculations

compd	type of investigation	R_{CC}	R_{CX}
C_6H_6	double-ζ (I)	1.383	1.070
	large basis (II)	1.386	1.076
	4-21G basis[a]	1.384	1.072
	electron diffr[b]	1.398	1.094
	Raman[c]	1.397	1.084
C_6F_6	double-ζ (III)	1.375	1.349
	large basis (IV)	1.378	1.310
	4-21G basis[d]	1.372	1.349
	MNDO[e]	1.434	1.317
	electron diffr[f]	1.394	1.327
C_6Cl_6	double-ζ	1.383	1.734
	STO-3G[g]	1.40	1.77
	electron diffr[h]	1.404	1.717
	X-ray[i]	1.393	1.715
C_6Br_6	double-ζ	1.385	1.920
	electron diffr[h]	1.406	1.886

[a] Reference 19. [b] Reference 20. [c] Reference 21. [d] Reference 10. [e] Reference 22. [f] Reference 23. [g] Reference 24. [h] Reference 6. [i] Reference 25.

The calculations were carried out on a ND 100/500 minicomputer system, using the program system DISCO.[17] DISCO fully accounts for the molecular symmetry in all respects and is therefore ideally suited for the present problem. Another feature that facilitates the study of large systems is the fact that no storage space for two-electron integrals is needed. The potentials of that approach are illustrated by the calculations on the 354-electron system C_6I_6 involving 444 basis functions, which were carried out on a minicomputer.

For all the compounds studied except C_6I_6, the energies were calculated for 10–15 planar geometries of D_{6h} symmetry. The equilibrium geometries were determined by fitting polynomials to the computed energies and determining the minima. Out-of-plane "puckering" distortions were then applied, maintaining the bond distances obtained for the planar conformer. D_{3d} symmetry was kept in these calculations, as this type of deviation from planarity is the only one seriously suggested by experimental investigators. The calculations were performed at different puckering angles (2 and 5°) in order to assess the degree of harmonicity for the puckering vibration.

The geometry optimization on C_6Br_6 gave a C–Br distance 0.03 Å longer than experiment (best gas-phase study[6]). Although an agreement of that order is still rather satisfactory considering the size of the system, one may expect errors of a similar magnitude also in C_6I_6. For such a heavily overcrowded system the nonbonded repulsion, and therefore the entire issue of planarity or not, may be crucially dependent on the C–I distance at which the out-of-plane bending is performed. Rather than optimizing the C–I distance, it was therefore considered more satisfactory to perform the study of planarity at the experimentally determined C–I distance.[18] The C–C distance, on the other hand, shows a quite minor variation through the series; the optimized values being 1.375, 1.383, and 1.385 Å for C_6F_6, C_6Cl_6, and C_6Br_6, respectively. The study of the out-of-plane distortion for C_6I_6 was therefore performed at fixed C–C and C–I distances of 1.385 and 2.080 Å, respectively.

III. Molecular Conformation and Structure

The calculated bond distances are shown in Table II together with the experimental values. For benzene, where accurate electron diffraction[20] and Raman[21] data are available, the agreement is seen to be quite satisfactory. As usual for compounds with only first- and second-row elements, the near Hartree–Fock values are 0.01–0.02 Å shorter than experiment. Our results at the double-ζ level are seen to be rather close to those obtained with the larger basis, with bond distances 0.014 Å shorter than the values obtained from the rotational fine struture of the Raman spectrum. These results are also in good agreement with previous accurate ab initio calculations on benzene.[19]

Table III. Atomic Populations Obtained for the Hexahalogenated Benzenes in the Double-ζ Calculations

compd	$Q_C(\sigma)$	$Q_C(\pi)$	Q_C(net)
C_6H_6	5.23	1.00	−0.23
C_6F_6	4.59	1.07	+0.34
C_6Cl_6	5.00	1.05	−0.05
C_6Br_6	5.26	1.04	−0.30
C_6I_6	5.35	1.04	−0.39

The agreement of our large basis results for C_6F_6 with the gas-phase ED structure[23] is satisfactory. The X-ray structure determination,[19] on the other hand, shows a spread in C–C distances from 1.33 to 1.39 Å and C–F bond lengths in the range 1.29–1.34 Å.[26] As a plausible explanation for that result we suggest an inaccurate determination of the cell dimensions; in fact the values obtained in three independent studies[26–28] are at variance by more than 5%. These inaccuracies certainly affect the bond distances derived from the data but are immaterial to the conclusion about planarity. No such disagreement between independently determined cell parameters can be seen for C_6I_6.[18] However, these studies suffer from problems of inaccurately located carbon atoms due to the presence of much heavier elements. Accordingly, we primarily compare our calculated bond lengths with gas-phase electron diffraction data whenever available. On doing so, we may first note that the C–X distances computed with a double-ζ basis set are somewhat longer than the experimental ones. Further comparisons with the large-basis calculations for C_6F_6 suggest that this agreement may be interpreted as a basis set deficiency. In a recent basis set investigation[25] we have shown that the attachment of an electron-withdrawing substituent in an aromatic system leads to a rather contracted electron distribution on carbon, which is difficult to describe satisfactorily with a standard basis set of moderate size. The atomic populations shown in Table III indicate that the effect should be most important for hexafluorobenzene and decrease down the series, in agreement with the generally accepted trend of electronegativity within group 7b elements.

In this context it is also of interest to consider the variation of C–C bond lengths through the series of molecules under consideration. As shown in Table II, the distance increases as we descend through the periodic table. There is thus an apparent correlation between the C–C bond distance and the population on carbon. Incidentally, we note that the parent compound benzene itself fits nicely into that series, the optimized C–C distance and the calculated atomic populations both being rather close to the values obtained for hexachlorobenzene. The notion of bromine and iodine as strongly electron-withdrawing atoms must clearly be modified in this context, even though the large positive charges obtained on these atoms should not be taken too literally. It appears reasonable to assume, however, that a proportionately larger amount of charge resides on the benzene ring in C_6I_6 and C_6Br_6 than in the lighter compounds of the series. With that charge primarily entering antibonding σ orbitals, the trend in the C–C bond distances is easily rationalized.

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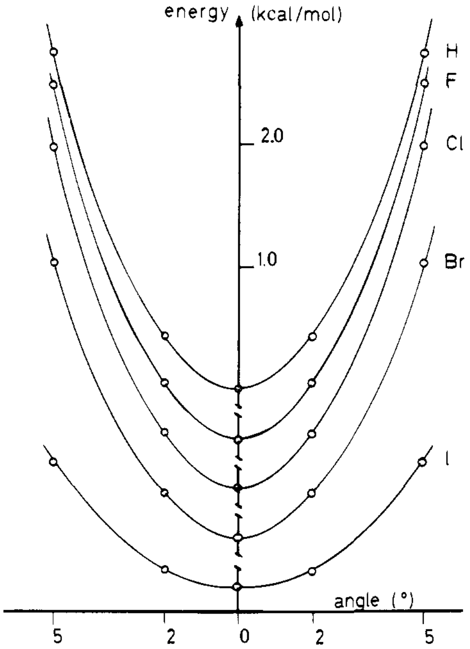

Figure 1. Total energies of the hexahalobenzenes as a function of the puckering angle.

On comparing the double-ζ results for R_{CC} with those obtained in larger calculations on C_6H_6 and C_6F_6, we note that the result is quite stable and that the change of basis set for C_6F_6 only affects the C–F bond distance. We can therefore rather safely predict the C–C distance in C_6I_6 to be even somewhat longer than in C_6Br_6. Such a trend in C–C bond lengths is also predicted by electron diffraction data for all the molecules in the series except C_6I_6.[6,20,23] Again an analogy is offered by gas electron diffraction data on the entire series of tetrahaloethylenes.[8]

For all the compounds investigated, the lowest energy was obtained with a planar conformation, indicating a global minimum on the potential-energy hypersurface of D_{6h} symmetry. The puckering force constants calculated with the double-ζ basis sets were 219, 230, 224, 179, and 82 cal mol^{-1} deg^{-2} for X = H, F, Cl, Br, and I, respectively, and the potentials are quite harmonic as shown in Figure 1. The calculated energies may indicate a slight anharmonicity for C_6I_6, but the effects are of the order of 0.1 kcal/mol only, and it appears inappropriate to pay them further attention in light of the large total energy of the system (2.6×10^7 kcal/mol).

IV. Discussion and Comparison with Experiment

The calculations unequivocally show all compounds studied here to be planar. It therefore appears appropriate to consider the approximations and possible sources of error in our own investigation before discussing the various experimental studies—a number of which claim the same molecules to be nonplanar.

The basis of all our calculations is the nonrelativistic Schrödinger equation, and any effect beyond that level of approximation is therefore entirely neglected. This might possibly have some influence on the results obtained for C_6I_6, the heaviest compound in our series, but should be quite unimportant for the other molecules. Next, the many-electron problem is reduced to the one-electron Hartree–Fock equations, thereby neglecting electron correlation. This error is probably more serious than the neglect of relativistic effects, and it has indeed been suggested that electron correlation may affect the relative stability of different conformers for halogen-substituted hydrocarbons. Finally, the Hartree–Fock equations are solved in a finite LCAO basis, introducing also a basis set error. The physical nature of these three errors are quite different. Starting with the basis set truncation, it is evident that results obtained by using a double-ζ basis cannot be expected to represent Hartree–Fock limit values.

The reliability of the present calculations regarding the question of planarity for the molecules depends crucially on their ability to correctly describe the interaction between halogen atoms in ortho position. As far as basis set effects on that interaction are concerned, the studies carried out with larger basis sets on C_6F_6 are rather encouraging, inasmuch as the puckering vibrational frequency ν_5 in fact increases somewhat with larger basis set. The trend thus corroborates our conclusions regarding the planarity of the molecules, and the same qualitative results might be anticipated from calculations at the Hartree–Fock limit on the heavier compounds. However, the applicability of the Hartree–Fock approximation as such to the present problem remains an open question. The most important physical effect not accounted for in a calculation on the Hartree–Fock level is dispersion interaction between adjacent halogen atoms. This would give rise to attractive forces, particularly between bulky and easily polarizable substituents. Thus, inclusion of correlation effects in our present calculations would rather strengthen our conclusions with regard to planarity of the molecules.

The nonrelativistic approach used here is also a source of error that might be of some significance for predicting the conformation of C_6I_6. The relativistic effects worth noting in this context arise from contraction of the heavy-atom core, which may penetrate to the valence region and change the effective size of the atom.[32] Such effects have indeed been shown to influence the geometries calculated for heavy-atom molecules.[33] The atomic orbitals are affected differently in that s and $p_{1/2}$ orbitals contract, whereas $p_{3/2}$ and d functions expand (though to a lesser extent).

The chemistry of iodine is largely governed by the 5p shell, and in particular the lone pairs of p type are responsible for the nonbonded interaction among the iodine atoms in C_6I_6. One may therefore expect relativistic effects to cause a slight reduction of the steric repulsion in that system, as compared to the nonrelativistic approach used here. If these errors were large and if the molecules were truly planar, the calculations might have incorrectly predicted nonplanar geometries or at least too low out-of-plane vibrational frequencies for planar molecules. On the other hand, since the calculations actually suggest a planar structure even when these effects are neglected, that particular conclusion can hardly be questioned for the above reasons. Inclusion of relativistic effects would therefore diminish the tendency toward puckering and, as was the case with dispersion forces, reinforce our conclusion with regard to planarity.

Summing up, the conclusions arrived at in the present calculations cannot easily be refuted on the basis of the approximations involved. We therefore turn to the experimental investigations and the conclusions drawn in those about nonplanar molecules.

The most direct and reliable experimental methods for determining molecular geometry are probably those of X-ray or neutron diffraction. According to several independent investigations, all the molecules studied here are planar in the solid to within 0.04 Å,[7,18,25-27,34,35] the largest distortion being reported for C_6I_6.[18]

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(36) It should be noted here that all comments regarding the presence or absence of distortions in an experimental study are made with reference to the 3σ test of statistical significance. Thus, deviations from planarity within three estimated standard deviations are not considered significant, whereas distortions larger than 3σ are interpreted in terms of a nonplanar molecule at a 99.7% level of significance.

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Results from X-ray diffuse scattering[41] and NQR,[42] indicating a highly nonplanar C_6Cl_6 molecule in the solid, must clearly be disregarded in favor of the more reliable X-ray diffraction results. The deviations in the four compounds are 0.4, 0.7, 0.2, and 1.1°, respectively, for F, Cl, Br, and I. (The deviations from planarity are in all cases chiefly along the v_5 mode of B_{2g} symmetry, lowering the molecular symmetry to approximately D_{3d} in the solid.) However, a direct comparison of our results with crystal structure data is complicated by the fact that for many molecules the conformation in the vapor state is not the same as in condensed phases. As an example, the biphenyl molecule is twisted by 30–40° in the gas phase and by 20° in the liquid,[43,44] whereas crystal forces appear to impose a conformation in the solid with a twist of only 9–10° and with a barrier of 40 cm^{-1}.[45] Similar situations are found in, e.g., *trans*-azobenzene.[47] According to the ab initio calculations for biphenyl[43] such a structural change will require about 1 kcal/mol, an energy quantity that is apparently provided by the crystal packing forces. For comparison, the deviation from planarity in solid C_6I_6 by the observed amount would correspond to an energy loss of less than 0.1 kcal/mol. As this is well within the range of crystal packing forces, no definitive conclusion can be drawn on the basis of the X-ray data alone as to the nonplanarity of hexaiodobenzene in other physical states. The slightly puckered structure of solid pentachlorobenzene[48] may also be rationalized as a result of packing effects. The situation in all these compounds is quite different from that found in a number of chlorine-substituted aromates, which are severely distorted from a planar geometry.[49] Those molecules are much more overcrowded than the substituted benzenes, however, the distances between the closest substituents being only 2.3 Å if standard geometry were maintained.

Table IV. Calculated and Experimental Vibration Frequencies (cm^{-1}) for the Hexahalobenzenes (Experimental Values in Parentheses Refer to Alternative Assignments)

compd		ν_1 (CC stretch)	ν_2 (CX stretch)	ν_5 (puckering)
C_6H_6	double-ζ (I)	3411	1089	1220
	large basis (II)	3414	1076	1057
	exptl[a]	3073	993	990
C_6F_6	double-ζ (III)	1648	596	186
	large basis (IV)	1665	609	207
	exptl[b]	1490	559	248 (200)
C_6Cl_6	double-ζ	1330	381	117
	exptl[c]	1226	372	103 (172)
C_6Br_6	double-ζ	1250	239	63
	exptl[e]	1159	232	68 (125)
C_6I_6	double-ζ			31
	exptl[e]	1057	161	59 (71)

[a] Reference 21. [b] Reference 37. [c] Reference 38. [d] Reference 39. [e] Reference 30.

Results from spectroscopic investigations are rather contradictory, and it appears difficult to assess the planarity of the hexahalobenzenes on the basis of these investigations. Interestingly, the solid-state spectra recorded under similar conditions are surprisingly similar for the four compounds.[30,50] Knowing that spectroscopic investigations are normally a powerful tool for determining molecular symmetry, one would therefore tend to assume that the conformation does not change substantially when going from the fluoro compound to the heavier species. It is further important to note that for C_6Cl_6, where vapor, crystal, solution, and melt data are available, the spectra appear surprisingly similar on comparison. The major difference is that the symmetry-forbidden lines seen in the crystal studies are absent in the gas-phase spectra. Unfortunately, no such comparative studies have been carried out for the heavier species. In the solid state, the occurrence of symmetry-forbidden lines is often field induced, and in that case they only to a minor extent reflect distortions of the nuclear positions from an idealized symmetry.

The spectroscopic data thus give no evidence to indicate that the deviations from planarity in any of the compounds studied here should be larger in the vapor or liquid state than in the solid. Furthermore, our calculated vibrational frequencies shown in Table IV are in satisfactory agreement with experiment. Especially the puckering mode v_5 would experience a quite different potential if the molecule were not planar, and the agreement with experimental frequencies therefore supports our conclusions about planarity.

Finally, gas electron diffraction provides a method for direct determination of gas-phase structure, and such experiments would seem to offer data suited for a direct comparison with our calculations. GED structures have been published for C_6F_6,[23] C_6Cl_6,[6] and C_6Br_6,[6] according to which the first two are planar and the bromine compound puckered ($\beta = 7°$). However, although the nonplanar model was chosen as the best alternative for C_6Br_6, satisfactory agreement was not obtained for independently determined C–Br and Br–Br distances.

Our conclusions may then be summarized as follows:

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(1) Ab initio Hartree–Fock calculations at the double-ζ level show all hexahalogenated benzenes to be planar. It is highly unlikely that this result is an artifact of the approximations used.

(2) Deviations from planarity observed in the solid state are well within the range of crystal packing forces and are not caused by steric overcrowding.

(3) Spectroscopic investigations indicate that the deviation from planarity in vapor should be no larger than in the solid state.

(4) Electron diffraction investigations claim C_6Br_6 to be significantly nonplanar in the gas phase, contrary to our conclusions above. We suggest a redetermination of this structure with present-day tools. A GED investigation on C_6I_6, hitherto not attempted, is also within reach and would provide data of vital interest for the subject studied here.

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Registry No. C_6H_6, 71-43-2; C_6F_6, 392-56-3; C_6Cl_6, 118-74-1; C_6Br_6, 87-82-1; C_6I_6, 608-74-2.

Photoelectron Spectroscopy of the Allenyl Ion $CH_2{=}C{=}CH^-$

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Abstract: We have studied the photodetachment spectra of $CH_2{=}C{=}CH^-$, $CD_2{=}C{=}CH^-$, and $CH_2{=}C{=}CD^-$. By comparing the photoelectron spectra of these selectively labeled species, we conclude that the ion has an allenyl (rather than propargyl) structure. The electron affinities (EA) of a set of propargyl radicals are as follows: $EA(CH_2C\equiv CH) = 0.893 \pm 0.025$ eV, $EA(CD_2C\equiv CH) = 0.907 \pm 0.023$ eV, and $EA(CH_2C\equiv CD) = 0.88 \pm 0.15$ eV. A single active vibration is observed in the photoelectron spectra of $CH_2{=}C{=}CH^-$ and $CD_2{=}C{=}CH^-$. This mode has a frequency of 510 cm^{-1} and is assigned as an out-of-plane bend of the acetylenic hydrogen of the propargyl radical (either $CH_2C\equiv CH$ or $CD_2C\equiv CH$). The gas-phase acidity of allene and methylacetylene are reported as $\Delta H^\circ_{\rm acid}(H{-}CH_2CCH) = 382.3 \pm 1.2$ kcal/mol and $\Delta H^\circ_{\rm acid}(H{-}CH{=}C{=}CH_2) = 380.7 \pm 1.2$ kcal/mol. The $\Delta H_f{}^\circ{}_{298}(CH_2{=}C{=}CH^-)$ is 59.4 ± 1.2 kcal/mol.

Introduction

The propargyl radical ($CH_2C\equiv CH$) is of great interest to many chemists because it is one of the simplest conjugated organic radicals. For this reason, there has been much effort to determine its "resonance energy" and heat of formation.[1-4] The radical C_3H_3 was first observed, and its ionization potential measured, by Farmer and Lossing[5] in 1955 from the thermal decomposition of propargyl iodide ($HC\equiv CCH_2I$). In addition, the electronic absorption spectrum of C_3H_3 has been observed[6] in gas-phase flash photolysis, as well as in matrix isolation[7] experiments. From the electronic spectra, several vibrational modes were extracted, although not definitely assigned.

Relatively little is known about the corresponding anion, $C_3H_3^-$. The gas-phase acidity of methylacetylene ($CH_3C\equiv CH$) has been measured[8,9] as 379.6 ± 2 kcal/mol. However, due to the coincidentally close acidities of the methyl hydrogens and the acetylenic hydrogen,[10] it was difficult to be sure which of the $C_3H_3^-$ isomers was produced in the experiment. In fact, attack by a base on $CD_3C\equiv CH$ has been shown[11,12] in the gas phase to produce both CD_2CCH^- and $CD_3C\equiv C^-$. Fluoride ion displacement on $(CH_3)_3SiC\equiv CCH_3$ and $HC\equiv CCH_2Si(CH_3)_3$ in a flowing afterglow[13] has separately produced the $CH_3C\equiv C^-$ and CH_2CCH^- ions. The chemistry of these isomeric ions has been shown to differ.[14]

We have used the method of negative ion photoelectron spectroscopy[15] to study the photodetachment of a mass-selected (*m/z* 39) negative ion beam produced by using methylacetylene or allene as ion precursors. In this experiment, a fixed-frequency argon ion laser is crossed with the ion beam, and the kinetic energy of the resulting detached electrons is measured. In order to determine which of the two possible isomers of the *m/z* 39 ion (i.e., $CH_3C\equiv C^-$ or CH_2CCH^-) is being observed in detachment, we have also used $CH_3C\equiv CD$ and $CD_3C\equiv CH$ as ion precursors. If hydrogen/deuterium (H/D) scrambling does not occur, we can separte the two isomers [e.g., $CH_3C\equiv CD \rightarrow CH_3C\equiv C^-$ (*m/z* 39) and CH_2CCD^- (*m/z* 40)] to decide which species is detaching. We conclude that the observed photodetachment spectrum results exclusively from CH_2CCH^-. In addition, by observing the effect

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