J. Am. Chem. Soc. 1983, 105, 1713-1716

Theoretical Study of the Allyl Radical: Structure and Vibrational Analysis[†]

T. Takada[‡] and M. Dupuis*[§]

Contribution from the National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. *Received May 6, 1982*

Abstract: The electronic structure of the allyl radical CH_2CHCH_2 and its vibrational spectrum have been calculated from ab initio multiconfiguration Hartree–Fock (MCHF) wave functions. While the Hartree–Fock (HF) model incorrectly predicts a nonsymmetric structure, the MCHF calculations indicate that the allyl radical has C_{2v} symmetry in accord with ESR evidence. Harmonic vibrational frequencies of all the normal modes are reported for the allyl radical and various deuterium-substituted analogues. Most noteworthy are the out-of-plane bending mode frequencies calculated at 760–790 cm^{-1} which are predicted to give rise to a very intense and characteristic band of the allyl radical.

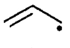
I. Introduction

Allyl-type radicals having delocalized unpaired electrons in a conjugated π system have been the subject of several studies. Of special interest is the fact that the theoretical work of McConnell and Chesnut[1] predicted a negative spin density in the p orbital of the central carbon of an allyl system. The allyl radical is the simplest odd alternate hydrocarbon which exhibits the feature of negative spin density. The ESR study of Fessenden and Schuler[2] showed that the allyl radical has C_{2v} symmetry and confirmed the negative spin density on the central carbon atom ($\rho = -0.16$) and a positive spin density on the end carbon atoms ($\rho = +0.58$).

The allyl radical is also known to result from ring fission of the cyclopropyl radical. Grieg and Thynne[3] estimated the activation energy for the ring fission to be about 20 kcal/mol. In fact a spectroscopic observation of the cyclopropyl radical in an Argon matrix was ambiguous probably because of the presence of the allyl radical.[4]

Previously Dupuis and Pacansky[4] reported a study of the cyclopropoyl radical and its vibrational analysis. In this paper we present an ab initio study of the allyl radical and its vibrational analysis. The two studies are complementary and should be a valuable aid for the identification of the IR spectra of the allyl radical and of the cyclopropyl radical.

The electronic structure of the allyl radical has been the subject of numerous theoretical treatments. Early studies focused on the calculation of the unpaired spin density.[1] Recent studies[5-7] discussed the doublet instability of the allyl radical, a manifestation of the broken symmetry dilemma.[8] Kikuchi showed that the instability problem is resolved by using a multiconfiguration Hartree–Fock (MCHF) wave function which include the $\pi \rightarrow \pi^*$ singly excited configurations. Within the semiempirical MINDO/3 framework, Kikuchi calculated a C_{2v} structure as the lowest energy structure of the allyl radical. Alternatively, Voter and Goddard[9] introduced the generalized resonating valence bond (GRVB) model to describe the resonance interaction of the two bonding structures of the allyl radical (A and B) which are responsible for the doublet instability.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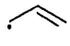
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The organization of this paper is as follows: in section II we describe the theoretical method used; in section III we discuss the structure of the allyl radical; and in section IV we report its vibrational analysis.

Table I. Calculated Bond Length (Å) and Bond Angles (deg) of Propene and Allyl[a]

	$CH_3-CH{=}CH_2$	$CH_2-CH\cdot-CH_2$
$R(C_1H_1)$	1.076	1.075
$R(C_1C_2)$	1.337	1.388
$R(C_2C_3)$	1.512	1.388
$R(C_2H_2)$	1.075	1.073
$R(C_2H_3)$	1.073	1.072
$R(C_3H_4)$	1.083	1.073
$R(C_3H_5)$	1.086	1.072
$\angle(C_2C_1C_3)$	124.3	124.4
$\angle(C_1C_2H_2)$	121.8	121.2
$\angle(C_1C_2H_3)$	121.7	121.4

[a] GVB wave function of propene, MCHF wave function for allyl (see text).

II. Computational Method

In this study we used a multiconfiguration Hartree–Fock wave function (MCHF) to describe the allyl radical. The configurations included in the wave function were obtained by distributing the three π electrons of the allyl radical among the three low-lying π orbitals (bonding π, nonbonding π, and antibonding π orbitals) in all possible ways resulting in eight configurations in C_1 symmetry. This wave function is closely related to Voter and Goddard's[9] GRVB wave function and contains the recoupling singly excited configuration shown by Kikuchi[7] to be necessary for a qualitatively correct description of the allyl radical.

In the next sections we compare the allyl radical with the propene molecule. A propene wave function of comparable accuracy to the allyl MCHF wave function is one in which the π bond is represented with a GVB pair. This is a two configuration wave function which includes the π^2 and π^{*2} configurations.

The one-particle basis set used for the molecular orbital expansions is the split valence 3-21G basis set of Binkely et al.[10] This basis set, efficient computationally, provides reliable equilibrium geometries and vibrational frequencies. The force method of Pulay[11] was applied to calculate the force constant matrix (the first derivatives of the MCHF energy with respect to nuclear coordinates is calculated analytically, and the second derivatives are evaluated by finite difference). The computer code used in this work in the HONDO[12] program which includes a New-

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[†] This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC03-76SF00098 and by the National Science Foundation under Grant CHE-7721305.

[‡] Present address: Department of Chemistry, The University of Chicago, Chicago, IL 60637.

[§] Present address: Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

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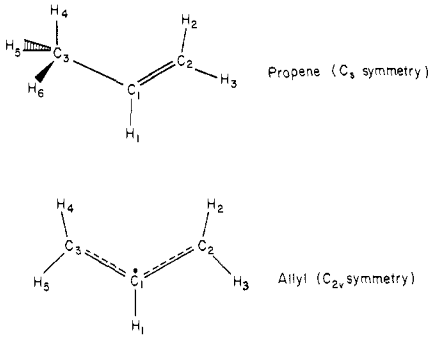

Figure 1. Propene molecule and allyl radical.

Table II. Calculated Bond Lengths (Å) of Ethane[a] and Ethylene[b]

C_2H_6	R(C–C) = 1.542	R(C–H) = 1.084
C_2H_4	R(C=C) = 1.336	R(C–H) = 1.074

[a] HF wave function for C_2H_6. [b] GVB wave function for C_2H_4.

ton–Raphson orbital optimization algorithm[13] for the MCHF wave function calculation.

III. Structure of the Allyl Radical

A consistent picture of the structure of the alkyl radicals[14] was obtained from experimental and theoretical studies of the radicals. One important feature commonly observed is the shortening of the bonds in position α to the radical center, and a lengthening of the bonds in position β to the radical center. For example, the radical center of the ethyl radical is ethylene-like with short CH bonds and CC bond, while the CH bond eclipsed with the half-filled orbital of the radical center is longer than the other CH bonds. In the cyclopropyl radical[4] the α-CH bond is again predicted to be short, and the CC bond opposite to the radical center is predicted to be long. The shortening and lengthening of bonds in the radicals result in characteristic bands of the IR spectrum. Another feature characteristic of the ethyl radical is a low-frequency (~540 cm^{-1}) pyramidal bending motion of the radical center. This pyramidal distortion of the radical center in the ethyl radical has a lower frequency than the out-of-plane bend of the ethylene molecule (~960 cm^{-1}). In light of the differences between the ethyl radical and ethane and ethylene, in what follows we compare the structure and vibrational spectrum of the allyl radical with those of propene.

The structure of propene and of the allyl radical are shown in Figure 1, and the bond lengths and bond angles are given in Table I. The change in CC bond lengths from propene to allyl is readily noted. In propene the C_1C_2 bond is a double bond (1.337 Å), and the C_1C_3 bond is a single bond (1.512 Å). The allyl radical has two equivalent C_1C_2 and C_1C_3 bonds intermediate between a single bond and a double bond. The change in bond lengths is the result of the three π electron delocalization over the three carbon atoms because of the resonance interaction of the two bonding structures A and B. In propene the CH bonds fall in two categories: C_1H_1, C_2H_2, and C_2H_3 are ethylenic CH bonds (~1.075 Å); the three CH bonds of the methyl group in propene are longer (~1.084 Å) than the ethylenic CH bonds. For comparison the bond lengths in ethylene and ethane obtained with the same 3-21G basis set are given in Table II.

Thus, upon elimination of a hydrogen atom from the methyl group of propene, the two remaining CH bonds acquire a strong ethylenic character, the CC bond in α position to the former methyl group becomes shorter, and the CC bond in β position (the double bond in propene) becomes longer. The planar configuration of the allyl radical is the most energetically favorable for delocalization of the electrons. Similar changes in structure had previously been noted for the ethyl radical[14] and the n-propyl radical.[14] In the allyl radical all the CH bonds have approximately the same length (1.073 Å), with the CH bond on the central carbon C_1 slightly longer (1.075 Å).

In the cyclopropyl radical[4] the CH bond α to the radical center is slightly shorter (1.067 Å) than the other CH bonds (1.073 Å) which are ethylenic (the values were obtained with the 4-31G basis set,[15] also a split valence basis set very similar to be 3-21G basis set used in this study). Thus upon fission of the β-CC bond of the cyclopropyl radical, the formerly CH bond of the cyclic radical goes from 1.067 to about 1.075 Å while the unpaired electron of the radical center delocalizes over the C–C–C chain.

IV. Vibrational Analysis of the Allyl Radical

Theoretically determined harmonic frequencies are a valuable aid for assigning vibrational spectra.[11] Although the calculated values are higher (~10–15%) than the observed frequencies, they appear in the correct order. Exceptions to this usually occur when the vibrational frequencies are closely spaced. When this situation arises, it is difficult to make a meaningful comparison between the theoretical and experimental results because the theoretical values are harmonic frequencies while the experimental values are usually the observed frequencies and thus include anharmonicity.

The calculated harmonic frequencies (in cm^{-1}) of the allyl radical and of some deuterium-substituted analogues are given in Table III. The harmonic frequencies of the propene molecule are given in Table IV, along with the experimental frequencies observed by Silvi et al.[16] As pointed out earlier, the ordering of the calculated harmonic frequencies agrees with the ordering of the observed frequencies for propene. There is a close correspondence between the calculated spectra of propene and allyl. In what follows, we analyze the differences.

The computed structure of the allyl radical shows all five CH bonds to be ethylenic. the stretching frequencies are predicted to be in the region of ethylenic CH stretches (greater than 3300 cm^{-1} for harmonic frequencies). The stretches assigned to the methyl group of propene have shifted to higher frequencies for the allyl radical.

The considerable changes in CC bond length noted upon inspection of the calculated structures of allyl and propene result in characteristic shifts of the stretching frequencies. In propene the double bond CC stretching frequency is 1770 cm^{-1}, the single bond CC stretching is at 946 cm^{-1}. In allyl there are two equivalent CC bonds not as strong as a CC double bond but stronger than a CC single bond. The asymmetric combination of CC stretches has a frequency of 1204 cm^{-1}. This is the deformation mode responsible for the symmetry breaking of the HF model. In light of the frequency of the CC symmetric stretch assigned to be 1093 cm^{-1}, the magnitude of the CC asymmetric stretch frequency is surprisingly high. Note that both the 1093-cm^{-1} and the 1370-cm^{-1} modes contain a significant mixture of CC symmetric stretch and asymmetric CH_2 bends. The former mode is described as the CC symmetric stretch because of its larger contribution to the 1093-cm^{-1} vibrational mode.

The weaker CC bonds in allyl (compared to the C=C double bond in propene) result in a softer out-of-plane bending motion of the terminal CH_2 group in allyl than in propene. Indeed, the out-of-plane CH_2 bending frequency in propene is 958 cm^{-1}, while the same mode frequencies of allyl are 786 and 761 cm^{-1}. Alternatively, the CC bond in the allyl radical is stronger than the CC bond in the ethyl radical for which the pyramidal CH_2 bending motion has a frequency of 540 cm^{-1}. The pyramidal bending motion in the ethyl radical, and the out-of-plane bending motion in ethylene give rise to very intense characteristic bands of the IR spectra. The same vibrational mode in the allyl is also predicted to be responsible for a very intense band.

Similarly, the twisting motions of the CH_2 groups in allyl (596 and 562 cm^{-1}) are slightly "softer" than the same twisting motion in propene (603 cm^{-1}) and in ethylene. However, the barrier to

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Table III. Harmonic Frequencies (cm^{-1}) of the Allyl Radical and of Some Deuterium-Substituted Analogues

		radical			
symmetry	mode	CH_2-CH-CH_2	CH_2-CD-CH_2	CD_2-CH-CD_2	CD_2-CD-CD_2
a_1	CH stretch	3412	3409	2541	2543
b_2	CH stretch	3407	3407	2538	2538
a_1	·CH stretch	3327	2456	3328	2459
a_1	CH stretch	3318	3320	2414	2409
b_2	CH stretch	3314	3314	2400	2401
a_1	sym CH_2 bend (sym)	1661	1660	1367	1351
b_2	sym CH_2 bend (asym)	1632	1628	1271	1193
b_2	·CH bend	1556	1374	1543	1361
a_1	asym CH_2 bend (sym)	1370	1345	1162	1148
b_2	CC stretch (asym)	1204	1096	1110	1003
a_1	CC stretch (sym)	1093	1090	920	920
b_1	·CH out-of-plane bend	1051	844	1016	804
b_2	asym CH_2 bend (asym)	1040	947	803	779
b_1	CH_2 out-of-plane bend (sym)	786	785	649	640
a_2	CH_2 out-of-plane bend (asym)	761	761	601	601
a_2	CH_2 twist (asym)	596	596	424	424
b_1	CH_2 twist (sym)	562	561	434	433
a_1	CCC bend	476	471	392	389

Table IV. Vibrational Frequencies (cm^{-1}) of the Propene Molecule

		CH_3-CH=CH_2		CH_3-CD=CH_2		CH_3-CH=CD_2		CD_3-CH=CH_2	
group	mode	calcd	obsd[a]	calcd	obsd	calcd	obsd	calcd	obsd
CH_2	stretch	3383	3091	3380	3090	2519	2318	3383	3093
CH	stretch	3337	3017	2463	2246	3340	3020	3336	3020
CH_2	stretch	3298	2991	3298	3000	2413	2225	3298	2988
CH_3	stretch	3260	2973	3260	2974	3260	2972	2417	2221
CH_3	stretch	3245	2953	3245	2952	3245	2952	2401	2200
CH_3	stretch	3190	2932	3190	2924	3190	2928	2291	2120
C=C	stretch	1770	1653	1751	1635	1718	1614	1763	1645
CH_3	sym bend	1669	1459	1668	1453	1657	1452	1207	1060
CH_3	asym bend	1664	1443	1663	1443	1664	1449	1200	1055
CH_2	sym bend	1598	1420	1571	1412	1177	1053	1596	1419
CH_3	sym bend	1583	1378	1584	1390	1584	1380	1201	1046
CH	in-plane bend	1441	1298	1195	830	1440	1303	1442	1300
CH_2	asym bend + CH_3 sym rock	1307	1179	1320	1186	1260	1057	1266	1163
CH_3	asym rock	1176	1045	1175	1040	1172	1045	951	868
CH_2	asym bend − CH_3 sym rock	1070	935	969		981	786	935	769
CH	out-of-plane bend	1063	990	907	846	973	909	1061	995
CH_2	out-of-plane bend	958	912	958	913	760	728	966	916
C−C	stretch	946	919	914	918	857	906	853	860
CH_2	twist	603	575	567	549	493	470	561	521
CCC	bend	469	428	465	422	424	380	430	392
CH_3	rotation	217	188	215	185	215	184	163	149

[a] Observed frequencies from ref 15.

rotation about the CC bond in allyl is expected to be much lower than in ethylene.

The motions associated with the hydrogen atom on the central carbon have nearly identical frequencies in allyl and in propene: (CH stretch is 3327 cm^{-1} in allyl, 3336 cm^{-1} in propene; CH in-plane bend is 1556 cm^{-1} in allyl, 1598 cm^{-1} in propene; CH out-of-plane wag is 1051 cm^{-1} in allyl, 1063 cm^{-1} in propene). Furthermore, the CCC bending motion has a frequency of 476 cm^{-1} in allyl and 469 cm^{-1} in propene.

The vibrational frequencies previously reported for the cyclopropyl radical[4] are given in Table V. Compared to the cyclopropyl radical, the allyl radical has several vibrational modes with lower frequency than any of the cyclopropyl frequencies. The most obvious change involves the β-CC stretch of the cyclopropyl radical (916 cm^{-1}) which becomes the CCC bend of the allyl radical (476 cm^{-1}). The other low-frequency modes of the allyl radical involve the CH_2 groups. The corresponding modes in the cyclopropyl radical have higher frequencies presumably due to the more restricted structure of the cyclic radical. The bending motion with frequency 713 cm^{-1} of the α-CH bond in cyclopropyl becomes the wagging motion with frequency 1051 cm^{-1} in allyl. The wagging motion of the α-CH bond at 1208 cm^{-1} in cyclopropyl becomes the bending motion at 1556 cm^{-1} in allyl. No significant differences exist between the CH stretches of the cyclopropyl radical and those of the allyl radical.

Table V. Computed Vibrational Frequencies (cm^{-1}) of the Cyclopropyl Radical[a]

α-CH	stretch	3418
β-CH	stretch	3373
β-CH	stretch	3358
β-CH	stretch	3293
β-CH	stretch	3286
CH_2	bend	1646
CH_2	bend	1623
α-CC	sym stretch	1314
CH_2	asym twist	1301
CH_2	asym wag	1268
CH_2	sym rock + α CH rock	1241
α-CH	wag	1208
CH_2	sym wag	1204
α-CC	asym stretch	995
β-CC	stretch	916
CH_2	asym rock + α CH wag	893
CH_2	sym twist	870
α-CH	sym bend	713

[a] See ref 4.

V. Conclusion

We have determined the structure of the allyl radical. It is characterized by five ethylenic CH bonds and two CC bonds intermediate between a single and double bond. The lowest frequency mode corresponds to the CCC bend (476 cm^{-1}). The out-of-plane bending modes of the CH_2 group in the allyl radical have lower frequencies (786 and 761 cm^{-1}) than the same mode in propene (959 cm^{-1}) but higher frequency than the pyramidal motion of the radical center in the ethyl radical. These out-of-plane bending motions are predicted to be responsible for a very intense band near 770 cm^{-1} characteristic of the IR spectrum of the allyl radical. Previously, we had reported that the lowest frequency mode in the cyclopropyl radical was the α CH bending model (713 cm^{-1}). The allyl radical has several vibrational modes with lower or similar frequency. The present study should be valuable for the identification of the spectra of the allyl radical and of the cyclopropyl radical.

Acknowledgment. We gratefully acknowledge many stimulating discussions with Dr. J. Pacansky (IBM Research Laboratory).

Registry No. CH_2CHCH_2 radical, 1981-80-2; CH_2CDCH_2 radical, 78370-41-9; CD_2CHCD_2 radical, 84752-87-4; CD_2CDCD_2 radical, 84752-88-5; $CH_3CH{=}CH_2$, 115-07-1; $CH_3CD{=}CH_2$, 1184-59-4; $CH_3CH{=}CD_2$, 1517-49-3; $CD_3CH{=}CH_2$, 1517-51-7.

Treatment of Electrostatic Effects within the Molecular Mechanics Method.[1] 1

Ljiljana Došen-Mićović, Dragoslav Jeremić, and Norman L. Allinger*

Contribution from the Faculty of Science, Belgrade University, and Institute of Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia, and the Department of Chemistry, University of Georgia, Athens, Georgia 30602. Received January 26, 1982

Abstract: A model of intramolecular electrostatic effects (called the induced dipole moment and energy (IDME) method) was derived by extending the method originally proposed by Del Re for calculating dipole moments and charge distributions. The IDME procedure consists of taking bond dipoles, calculated by the Del Re procedure, and allowing for nonadjacent dipole interactions by taking all components of bond polarizabilities into account. The method is applied to some simple halides, ketones, and ethers. The total dipole moments are well calculated and charge distributions reproduce many known trends. The calculated energies agree better with experiment overall than those calculated earlier by the modified Smith-Eyring method.

Molecular mechanics calculations have been developed to a high degree of sophistication for hydrocarbons.[2] Similar reasonably accurate and detailed studies have also been carried out for monofunctional polar compounds.[3-8] While the results here are less accurate than for hydrocarbons, they are sufficiently good as to show promise for the general method.

With molecules containing two or more neighboring polar groups, believable molecular mechanics calculations necessitate that electrostatic interactions be considered in addition to what is done with more simple molecules. The differences between predicted and observed equilibrium constants have often been used to estimate the magnitude of such interactions[9] and suggest important effects in 4-hydroxy-[10] and 4-chlorocyclohexanone,[11] for instance. The importance of electrostatic interactions is also evidenced by the strong phase and solvent dependence of conformational equilibria for a number of compounds. Hydrocarbons are known as nonpolar and quite insensitive to phase and solvent as far as their structural properties and conformational energies are concerned.[12] On the other hand, for molecules containing neighboring polar groups, conformational energies may be very sensitive to phase and solvent. 1,2-Dichloroethane, for example, is a mixture of gauche and anti conformations.[13] The composition of the mixture is strongly dependent upon phase and solvent. In the 5-heterosubstituted 1,3-dioxanes,[14] the ΔG for the axial vs. equatorial position of the 5-substituent varies by about 1 kcal/mol on going from the slightly polar carbon tetrachloride to the highly polar acetonitrile. Therefore, in order to apply molecular mechanics to polyfunctional polar compounds in a useful way, electrostatic and solvation interactions must somehow be taken into account.

Previously the electrostatics of the system has been treated in terms of either point dipoles or point charges, utilizing a medium of effective dielectric constant in a standard way.[2] Such models are approximations that we expect to be accurate if the distance between charges (dipoles) in different bonds is large, or at least large compared to the diameters of the atoms or to the effective distance between charges in the same bond. With a few significant exceptions, the two methods (charges or dipoles) give results that are substantially the same. Neither was able to explain, for instance, the high experimental value of the dipole moment of $2\beta,3\alpha$-dichloro-5-cholestane[15] and of a number of other 1,2-diaxial dihalides.

A method for treating the problem of induction, dealing with charges on the classical level, was long ago developed by Smith

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*Address correspondence to this author at the University of Georgia.

(1) The work was supported in part by the Republic Research Fund, SR Serbia. Abstracted from the Ph.D. thesis of L.D.-M. submitted to the University of Belgrade, 1979.

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