Resonance interactions in acyclic systems

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<u>Abstract</u>   The role of resonance in the stabilization of allyl ions has been studied via ab initio molecular orbital calculations using the 6-311++G** basis set and correction for electron correlation. The rotational barrier in allyl cation (35 kcal/mol) is composed of electron delocalization and electrostatic effects whereas the barrier in allyl anion (20 kcal/mol) appear to largely result from electrostatic terms. Allyl anions are stabilized by electronegative groups at the terminal positions, but not at the central position. The changes in atom energies on ionization were calculated and the change in energy of the hydrogen accounts for about half of the difference in gas phase acidity between alcohols and carboxylic acids. The conformations of butadiene were studied, and evidence was obtained for the second rotamer being gauche with a torsional angle on the order of 35°. The origin of the rotational barriers in butadiene and acrolein are discussed.

INTRODUCTION

Many of the explanations of phenomena in organic chemistry are presented in terms of "effects" such as inductive effects, steric effects, anomeric effects and resonance effects. Of these, the resonance effects are probably the more widely applied. Some of the phenomena which have been discussed in terms of resonance interactions include:[1]

1.   The acidity of carboxylic acids as compared to alcohols. Here, carboxylate resonance is thought to stabilize the anion leading to increased acidity:

2.   The decreased acidity of esters as compared to ketones. It is assumed that esters are stabilized by resonance:

Formation of the anion would disrupt the ester resonance, leading to reduced acidity.

3.   The barrier to rotation in acrolein, butadiene and similar compounds:

The double bond character at the C2-C3 bond will lead to an increased rotational barrier.

4.   Larger formation constants for oximes than imines. The former may be prepared in the presence of water whereas imines are readily hydrolyzed in the presence of water. Resonance stabilization of oximes has been proposed as the origin of this difference:

If resonance provides an explanation for these and many other phenomena in organic chemistry, is there any need for further study? There are some recent observations which raise questions about the importance of resonance. In a study of the rotational barrier in formamide, which is believed to result from the C-N double bond character introduced by resonance:

we found that the changes in structure and electron populations on rotation were not in accord with the resonance picture.[2] The C-N bond length changed considerably on rotation (0.08Å), but the C-O bond changed only slightly (0.01Å). The electron population at nitrogen was found to decrease on rotation from the planar form, rather than increasing as predicted by the resonance formulation. We have begun a general study of resonance interactions in acyclic systems in order to gain a better understanding of the phenomena of the type listed above. In the following we will discuss three aspects of these questions: the factors which stabilize allyl anions; the acidity of carboxylic acids; and the origin of the rotational barrier in butadiene and acrolein.

ALLYL IONS

Since only a limited amount of information may be obtained directly via experiments, we have used ab initio molecular orbital theory as a tool for obtaining additional information. There are two approximations inherent in the use of this theory. The first is the choice of basis set, or the set of orbitals assigned to the atoms in the molecule. Ideally, one should use an infinitely large set, but this is of course not possible with finite computational resources. The minimum basis set which is useful for the calculations of interest is, in Pople's nomenclature, 6-31G*.[3] Here, each atomic orbital is represented by a set of Gaussian functions, 6 for the inner orbitals (such as 1s on carbon) and 4 for the valence orbitals. The 4 are taken as a group of 3 of one "size" and 1 of a larger "size" ("split valence" basis set) and the calculation will choose the appropriate linear combination of the two. In addition, the asterisk indicates that polarization functions are to be added to each of the non-hydrogen atoms. In the case of a p-orbital, the polarization function is a d-type orbital. When the latter is added to a p-orbital, it will deform it in a fashion appropriate to the effect of an electrical field.

This basis set is still fairly small, and in some cases we have found it necessary to use a more flexible basis such as 6-311++G**. Here, 5 Gaussian functions are used to represent each valence orbital, taken as a set of three, and two single Gaussians, each of a different "size" (triple zeta basis set). In addition, diffuse functions (denoted by +) are added to each atom. They are simply relatively large atomic orbitals which may be important for the proper representation of anions.[4] The two asterisks indicate that polarization functions are added to all atoms.

The other approximation is the degree of correction for electron correlation. In the standard (RHF) calculation, the repulsion between a pair of electrons is taken as the repulsion between the average distribution for each of the electrons. However, the motions of electrons are correlated to some extent, so that the probability of both being simultaneously in the high repulsion region is low. As a result, the standard procedure finds too large a repulsion energy. The calculation may be corrected for the effects of electron correlation in different ways. We shall make use of the perturbation method developed by Møller and Plesset (MP).[5]

With this introduction, let us see how well the experimental data for simple systems such as the allyl cation and allyl anion are reproduced.[6] The results of the calculations are summarized in Table I. It can be seen that there is a fairly large change in relative energies of propene and its ions as well as for propane and its ions on going from 6-31G* to 6-31++G**, and a further change on correcting for electron correlation. The gas phase ionization energies of propene and propane are known, but before the computed values may be compared with experiment, they must be corrected for the zero-point energy change on ionization. This corresponds to the loss of one C-H stretching mode and two C-H bending modes, and is approximately 7 kcal/mol. The corrected values are given in Table I along with the experimental energies, and it can be seen that there is a very good agreement, showing that the level of theory used is satisfactory.

Table I
Calculated Ionization Energies

| Reaction | ΔE(kcal/mol) | | | | | ΔH calc | ΔH obs |
| | 6-31G* | 6-311++G**//6-31G* | | | | | |
	6-31G*	RHF	MP2	MP3	MP4		
Propane → Propyl$^+$ + H$^-$	307.5	267.3	288.3	285.8	284.8	278	274±3
Propene → Allyl$^+$ + H$^-$	286.0	248.7	268.1	266.9	265.1	258	256±3
Propane → Propyl$^-$ + H$^+$	452.6	436.1	425.9	430.1	426.9	420	419±3
Propene → Allyl$^-$ + H$^+$	425.4	408.0	399.8	405.2	402.8	396	390±3

There are some interesting aspects to these ionization reactions. The barrier to rotation also was calculated at the 6-311++G** level with correction for electron correlation, and the changes in energy for the reaction of a 1-propyl ion with propene to give an allyl ion are shown diagrammatically in Figure 1. This leads to the interesting conclusion that the reaction of 1-propyl cation with propene to give the unconjugated (rotated) allyl cation is endothermic by 16 kcal/mol, whereas the corresponding reaction of the anions is exothermic by 5 kcal/mol. This must be attributed to the inductive effect of the double bond, destabilizing a cationic center, and stabilizing an anionic center.

Figure 1. Energy changes in the reaction of propyl ions with propene

The barrier to rotation for allyl cation has been equated to the resonance stabilization in the planar ion.[7] However, the calculated barrier (36 kcal/mol) is as large as the resonance stabilization of benzene, and much too large to be attributed to resonance alone. A convenient way in which to think about electron delocalization in benzene is in terms of a structure in which there is one π electron per C-C bond.[8] This reduces the electron repulsion associated with the π-electrons in ordinary double bonds, and leads to stabilization:

In the case of the allyl cation, there is a similar situation, but with the allyl anion, two π electrons must be distributed per C-C bond. A simple estimate of the delocalization energy for the allyl cation would be about one-third that of benzene (or possibly somewhat higher because of the positive charge). The benzene delocalization energy is between 24-55 kcal/mol depending on the model used,[9] with 36 kcal/mol being the simple thermochemical estimate.[10] The delocalization energy of allyl cation should then be on the order of 12-18 kcal/mol.

It is interesting that the difference in rotational barrier between allyl anion and allyl cation is 15 kcal/mol, just about what was estimated as the delocalization energy of the latter. The allyl anion should, in terms of the picture given above, have a relatively small delocalization energy because of the repulsive interaction of pairs of π-electrons. One way in which to rationalize all of the data is to propose that allyl anion has a small or negligible delocalization energy, and that the rotational barrier is just the result of a change in electrostatic energy on rotation. In the planar form, the charge is required by symmetry to be distributed between the terminal carbons and hence over a large volume element. In the rotated form, it will largely be localized on one carbon. The electrostatic energy of a charged species in the gas phase is a function of its volume; the large the volume, the lower the energy. Thus, the planar ion will have the lower electrostatic energy. This proposal is currently being tested via additional calculations which should provide a more quantitative estimate of the difference in electrostatic energies.

The allyl cation would be expected to have similar changes in electrostatic energy on rotation. Here, the barrier will be the sum of the delocalization energy and the electrostatic energy.

We may now turn to other allyl anions and see what factors are important in determining their stability. The results of a set of calculations using the 6-311++G** basis set are summarized in Table II. Again, it is possible to compare some of the calculated energy changes with experimental data[6] after correcting for changes in zero-point energies. The comparison is given in the Table. The results are quite satisfactory, especially considering that the experimental data have significant errors.

The introduction of a nitrogen as the central atom in an allyl anion has no significant affect on the energy of ionization. However, terminal nitrogens have a very large effect, and the effect is even greater with terminal oxygens. It is clear from these results that the major factor which determines the ionization energies is the electronegativity of the terminal atoms. Another significant observation is that an electron releasing group (methyl) decreases the acidity of acetic acid whereas an electron withdrawing group (hydroxy) increases its acidity.

Table II.
Calculated Gas Phase Ionization Energies

Reaction		6-31G* RHF	ΔE 6-311++G**//6-31G* RHF	MP2	MP3	ΔH calc	ΔH obs
$CH_3CH_2CH_3$ →	$CH_3CH_2CH_2^-$	452.6	436.1	425.9	430.1	423	419±3
$CH_3CH=CH_2$ →	$^-CH_2-CH=CH_2$	425.4	408.0	399.8	405.2	398	390±3
$CH_3N=CH_2$ →	$^-CH_2-N=CH_2$	425.0	409.6	398.0	404.1	397	----
$H_2NCH=NH$ →	$^-HN-CH=NH$ (cis)	399.4	382.6	374.1	379.8	372	----
HN_3 →	N_3^-	362.4	356.0				355±3
CH_3CO_2H →	$CH_3CO_2^-$	367.5	361.3	355.0	360.7	352	349±3
HCO_2H →	HCO_2^-	363.7	356.7	351.0	356.9	348	345±3
$HOCO_2H$ →	$HOCO_2^-$	357.0	351.0	345.2	350.7	342	----
HNO_2 →	NO_2^-	360.4	350.4	343.9	351.2	342	338±4
HNO_3 →	NO_3^-	333.4	328.6	330.5	333.6	325	325±3
CH_3CHO →	$CH_2=CHO^-$	396.6	383.3	375.5	381.1	374	366±3
$HCONH_2$ →	$HCONH^-$	383.7	375.5	367.4	372.2	363	360±3

A further analysis of the problem requires that the wave functions be examined. Here, we wish to make use of a method which takes all of the electrons into account, rather than just those which are in high lying molecular orbitals. Therefore, we have chosen to analyze the wave function in terms of charge density, making use of Bader's theory of atoms in molecules.[11] Between any pair of bonded atoms, there is a path of maximum charge density known as the bond path. Along this path, there is a point of minimum charge density known as a bond critical point. This is a minimum in charge density along the path, but is a maximum in directions perpendicular to the path. Starting at a bond critical point, we may develop rays for which the charge density decreases most rapidly. If this is done for many directions, the rays will form a surface, known as a zero-flux surface.

The set of these surfaces, one for each bonded pair of atoms, will serve to separate a molecule into a set of volume elements, one for each atom. Within each of these atomic regions we may integrate the charge density to obtain the electron population, and we may in a similar manner calculate the kinetic energy of the electrons associated with each atom. The volume elements thus defined satisfy all of the usual quantum chemical requirements such as the virial theorem. Thus, for each atom, Ω, the relationship between the kinetic energy (T_Ω) and the potential energy (V_Ω) is

$$V_\Omega = -2\,T_\Omega$$

Since the total energy is given by the sum of the kinetic and potential energies,

$$E_\Omega = T_\Omega + V_\Omega = -T_\Omega$$

Thus, the negative of the kinetic energy which may be calculated for each atom is equal to the total energy of that atom. The sum of these atom energies is equal to the calculated total energy of the molecule.

The atomic charges derived from the calculated electron populations are shown in Figure 2. In allyl anion, the charge is mainly distributed between the terminal carbons, and the central carbon is close to neutral. When the terminal CH_2's are replaced by NH's leading to a more stable ion, there is a marked change in electron populations. The terminal atoms have a relatively large negative charge, and the central carbon now assumes a positive charge. This trend is continued with the even more electronegative oxygens replacing the CH_2's leading to the carboxylate ions.

Figure 2. Atom charges for allyl anions

The unique feature of the charge distribution in the more stable ions is the - + - pattern of charges for the three atoms forming the allyl system. Introduction of an electron releasing group (methyl) decreases the positive charge at the central carbon of the carboxylate ions, and raises its energy. Similarly, the electron withdrawing hydroxy group increases the positive charge and increases the acidity. This charge pattern spreads out the charge to reduce the electrostatic energy, and places the higher electron populations at the more electronegative atoms where their kinetic energies will be the largest, leading to the lowest total energies. The coulombic interaction between the central atom and the terminal atoms also would help stabilize the ion.

The calculations for the allyl anions have a relationship to the charge distribution for formamide.[2] Here, in the more stable planar form the nitrogen gained charge density at the expense of the carbonyl carbon:

This leads to the - + - charge pattern found for the allyl anions. Again, it places the electron population on the more electronegative atoms via both the σ and π systems, and leads to a coulombic attraction between the C and N which results in a shorter bond.

ALKOXIDE IONS

Since information on acetic acid and acetate ion was available, it was of interest to compare them with ethanol and ethoxide ion in connection with the question of the origin of the difference in acidity.[2,12] Calculations have been carried out for these species as well as for methanol, methoxide ion, fluoromethanol, fluoromethoxide ion, trifluoromethanol and trifluoromethoxide ion. Using the 6-311++G** basis set and correcting for electron correlation (MP3), the calculated ionization energies were found to be in good agreement with the experimental gas phase values. An interesting observation was that the calculated C-O bond lengths decreased in the order: methanol, 1.400Å. fluoromethanol, 1.361Å and trifluoromethanol, 1.328Å. This appears to be related to the corresponding change in the C-F bond lengths of the fluorinated methanes: CH_3F, 1.383Å, CH_2F_2, 1.338Å, CHF_3, 1.317Å and CF_4, 1.319Å.[13] The fluoromethanol length has been attributed to the anomeric effect[14] whereas the fluoromethane bond length changes have been attributed to negative hyperconjugation.[15]

The bond length changes may be accommodated by considering changes in hybridization. In methyl fluoride, the electronegative fluorine will prefer a carbon orbital with high p-character.[16] This may be seen in the bond angles.[17] On going to difluoromethane, the fluorines will compete for p-character, and each will have less leading to shorter bonds. Finally, with carbon tetrafluoride, symmetry requires that each C-F bond use a carbon orbital with only 75% p-character, leading to the shortest bonds of the group. The same factor will be involved with fluoromethanol compared to methanol.

All of the alkoxide ions have short C-O bonds. The bond shortening with respect to the corresponding alcohol are: methanol, 0.07Å; ethanol, 0.08Å, t-butyl alcohol, 0.09Å, fluoromethanol, 0.10Å and trifluoromethanol,[18] 0.11Å. There is a trend toward a greater decrease with increasing acidity, but it is not a marked trend. The α-CH bond lengths increase by about 0.03Å, α-CC bonds increase by 0.03-0.04Å, and in fluoromethanol, the C-F bond lengthens by 0.08Å on ionization. The only unusual change in bond length was found with trifluoromethanol where the C-F bonds lengthen by 0.16Å on ionization.

The atom charges have been calculated from the wave functions in the fashion described above. They are summarized in Figure 3 for some alcohol/alkoxide ion pairs. In each case, the formation of the alkoxide ion increases the negative charge at oxygen, makes the α-carbons assume a larger positive charge, and places a negative charge at the atoms attached to the carbon. It appears that the charge at oxygen repels the electrons at the adjacent bonds, spreading the charge over a large volume element, and decreasing the electrostatic energy. The polar C-O bond leads to an attractive coulombic interaction and a shorter C-O bond.

Figure 3. Atomic charges for alcohols and alkoxide ions

Although the acetic acid/ethanol acidity difference has been discussed in terms of electrostatic potentials and electron populations,[2,12] it would appear more appropriate to examine the changes in energy on ionization. Some alcohols are compared with acetic acid in Figure 4. It can be seen that a major part of the ionization energy is the loss of the hydroxy proton energy on being converted to H^+ with a zero energy. Fully half of the difference in ionization energy between ethanol and acetic acid is found in the difference in the energies of their hydroxy protons.

Figure 4. Energy changes (kcal/mol) on ionization

BUTADIENE

We may now turn to the next question, the origin of the rotational barrier in butadiene and related compounds such as acrolein. With butadiene, there are two problems: a. the structure of the second (higher energy) rotamer - is it s-cis or s-gauche? and b. what is the origin of the barrier which separates the two forms? We have examined both questions.

The experimental studies have supported the cis structure[19] whereas the theoretical studies have always found the gauche form (with a C=C-C=C torsional angle of about 35°) to have the lower energy.[20] This disagreement needed to be clarified before the second problem could be addressed. An examination of the calculated structure of the cis-rotamer shows that the C-C-C bond angles have become larger indicating a steric repulsion between the terminal methylene groups. This repulsion might be affected by the bond shortening characteristic of the RHF calculations. In order to see if the better geometries that can be obtained at the MP2/6-31G* level of theory might cause a change in relative energies, geometry optimizations were carried out for a number of torsional angles. The effect of electron correlation is shown in Figure 5, and it can be seen that the effect is quite small.

Figure 5. Change in energy for butadiene with the torsional angle. The upper line is for the 6-31G* basis set and the lower line is for MP2/6-31G*.

Figure 6. Calculated change in λ_{max} for butadiene as a function of the torsional angle.

An important experimental datum is the infrared spectrum of the second rotamer which has been obtained by generating mixtures relatively high in its concentration at high temperature, and then rapidly freezing the mixture.[21] In order to be able to make better use of this datum, we have carried out a detailed study of the vibrational modes of trans-butadiene making use of infrared intensity data and theoretical calculations of the force field. The parameters obtain in this study were transferred to the theoretically calculated spectra of both cis- and gauche-butadiene and allowed us to predict their spectra. The principal difference was found with a mode at 732 cm^{-1} which was calculated to be allowed in the gauche form and forbidden in the cis. This band has been observed in the spectrum of the higher energy rotamer,[22] and on deuteration it is found to shift to 594 cm^{-1} in d4 and 583 cm^{-1} in d6.[23] The calculated values were 592 and 583 cm^{-1}, in excellent agreement. These data clearly show that the higher energy form is not cis. However, it does not serve to define the torsional angle.

It is known that the ultraviolet spectrum of the second form is shifted slightly to the red of the trans form.[24]   It is generally found that cisoid dienes have their band shifted strongly to the red. Therefore, we have calculated the shift in the UV band as a function of the torsional angle using the 6-311+G* basis set, and allowing all singly excited configurations to mix (CIS). The predicted shifts are shown in Figure 6. The 38° torsional angle found in the ab initio calculations is in good accord with the calculated spectrum.

There are additional data which support the gauche structure for the higher energy rotamer. 1,3-Cycloheptadiene has λ_{max} = 248 nm[22] and cyclooctadiene has λ_{max} = 228 nm.[23] Using Fieser's rules to correct for the terminal alkyl substitution,[24] the λ_{max} would be 238 and 218 nm respectively. Both have non-zero C=C-C=C torsional angles. The angles have not been determined experimentally, but ab initio calculations using the 6-31G* basis set gave τ=9° for cycloheptadiene and τ=57° for cyclooctadiene (Allinger estimated 54° for the latter via MM1P calculations[25]). Although one might question the ability of the calculations to correctly identify the angle for the 7-membered ring, there is no doubt that the torsional angle is large in the 8-membered ring. The red shift for cycloheptadiene compared to butadiene (λ_{max} = 212nm) agrees well with the calculations discussed above. The torsional angle for cyclooctadiene is greater than that for gauche butadiene, and still its band is to the red of butadiene! Clearly, the torsional angle in the second rotamer of butadiene cannot be near 0°, and a value on the order of 35° would fit the infrared spectrum, the ultraviolet spectrum and the theoretical calculations.

What can be said about the origin of the rotational barrier? One of the attractive proposals for explaining the barrier is the "resonance force" model of Simpson.[26] This involves a dynamic interaction of the electrons in the two double bonds, and as such should not be reproduced by the RHF calculations since they include only static interactions. Figure 5 compares the relative energies obtained using 6-31G*//6-31G* and MP2/6-31G*//MP2/6-31G*. The barrier is unaffected by including electron correlation in both the geometry optimization and in calculating the relative energies. This shows that the origin of the barrier does not involve dynamic interactions of the electrons. Although the C2-C3 bond energy may have a component due to hybridization, this also cannot affect the barrier since it is not changed during rotation.

Since other candidates for an explanation appear to have been eliminated, it must be concluded that the barrier results from delocalizing some of the π charge density in the region between the two central carbons. The amount of p character in the C2-C3 bond may be determined by integrating the π charge density in a series of planes perpendicular to the bond. For trans-butadiene, the value is 0.192 e/au at the center of the bond, and for 90° rotated butadiene it is 0.107 e/au. Thus, trans-butadiene has about two time the π-charge density found in the rotated form. For comparison, the value at the center of one of the C=C bonds is 0.395 e/au.

It is interesting to compare acrolein with butadiene. Whereas the barrier in butadiene might be considered to involve leakage of the π electron into the single bond region, with acrolein, a more direct mechanism appears possible, involving zwitterionic resonance structures. Whereas these structures appear unlikely with butadiene, the polar carbonyl group would make them more reasonable with the aldehyde.

However, the rotational barrier in acrolein is not much larger than that for butadiene. A better comparison might be in terms of electron populations, for the zwitterionic structures, if important, should lead to a shift in charge density during rotation. The changes in population are shown in Figure 7. It can be seen that the population changes are essentially the same for the two compounds, and that the population at the terminal carbon changes in the opposite sense to that expected for a contribution by the zwitterionic structure. It may be concluded that the stabilization of planar acrolein has the same origin as that for butadiene.

Figure 7. Electron populations at the C=C of butadiene and acrolein

CONCLUSIONS

Electron delocalization clearly results in energetic stabilization for allyl cation. The stabilization for allyl anion appears to be much smaller, and may be negligible. Allyl anions are strongly stabilized by electronegative atoms at the terminal positions, leading to a + - + charge distribution for the allyl system. Alkoxide ions are stabilized by moving charge density to the atoms attached to the carbon of the C-O bond, and have short C-O bonds which result from coulombic attraction between the oppositely charged atoms. A comparison of the energetic changes on ionization of ethanol and acetic acid shows that fully half of the difference in ionization energy results from the difference in the energies of the hydroxy protons. Butadiene is found to have a gauche conformation for the higher energy form. The rotational barrier in butadiene results from π-electron transfer into the C2-C3 bonding region. There is little difference between butadiene and acrolein with regard to changes in electron population on rotation, showing that the zwitterionic cannonical structures do not contribute significantly to the stabilization of acrolein.

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