parameters used are collected in Table IV.

The distances taken in the molecular models $MoH_4(SC_nH_m)^{4-}$ and $Mo_2H_6(SC_2H_4)^{6-}$ were respectively Mo–H = 1.80 Å, Mo–S = 2.44 Å, Mo–Mo = 2.72 Å. Ethylene sulfide and trimethylene sulfide were considered to have the same geometry as determined for the free molecules. The two-dimensional molybdenum surface consisted of three layers. The adsorbate coverage was kept at $^1/_4$ throughout all the calculations.

Sets of 6K or 8K points in the irreducible wedge of the oblique unit cell in reciprocal space were used, according to the symmetry of the problem. They were chosen following the geometrical method of Ramirez and Böhm.[23]

Registry No. SC_2H_4, 420-12-2; SC_3H_6, 287-27-4; Mo, 7439-98-7.

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Resonance Interactions in Acyclic Systems. 1. Energies and Charge Distributions in Allyl Anions and Related Compounds

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Abstract: The energies of dissociation of propane to 1-propyl cation and anion and of propene to allyl cation and anion may be satisfactorily reproduced via ab initio calculations at the MP4/6-311++G**//6-31G* level. The reaction of 1-propyl cation with propene to give the unconjugated allyl cation was found to be endothermic, whereas the corresponding reaction of the anion was exothermic. The rotational barrier for allyl cation was 36 kcal/mol, whereas that for the anion was 19 kcal/mol. These data were analyzed in terms of electron delocalization and the electrostatic energies of the ions, and it was concluded that whereas the cation had significant resonance stabilization, the anion had little stabilization. A series of allyl type anions were examined making use of 6-311++G** wave functions calculated at the 6-31G* geometries. Correction for electron correlation at the MP3 level led to calculated proton affinities which agreed well with the experimental values. Electronegative atoms at the central position had little affect on the proton affinities, but when they were at the terminal positions, there was a large change. The changes in electron population among the anions were studied via numerical integration of the charge densities within boundaries which may be assigned to the atoms in the ions. The more stable anions are characterized by a − + − charge distribution for the three atoms in the allylic system, leading to internal coulombic stabilization.

Allyl Anion and Cation

Allyl anion systems such as A=B—C$^-$↔$^-$A—B=C are commonly observed, and generally are considered to be stabilized by electron delocalization.[1] However, recent discussions of the origin of the acidity of carboxylic acids[2,3] and other acids such as nitrous acid[4,5] have suggested that the resonance stabilization of the anions may not be the more important factor in leading to increased acidity. In view of the importance of these species, we have carried out a study of the energies and charge distributions of a number of types of allyl anions.

We shall first examine allyl cation and anion and compare their energies with those for 1-propyl cation and anion, respectively. The cations and anions have received considerable experimental[6,7] and theoretical[8,9] study, but there are important aspects of these systems which have not as yet been explored. The 6-31G* optimized geometries for many of the compounds are available,[10] and we calculated the structures for 1-propyl and allyl anions. The energies were calculated by using the 6-311++G** basis set[11] which is effectively triple-ζ and includes both diffuse functions and polarization functions at all atoms. This was chosen to allow adequate flexibility in describing the charge density distribution. A triple-ζ basis allows the "size" of each atom to be well represented, the diffuse functions allow a better description of lone pairs and anionic sites,[12] and the polarization functions improve the description of the charge density in the region between atoms having different electronegativities. The calculated energies are given in Table I. In addition, the energies of the allyl ions which had been rotated by 90° about one of the C–C bonds to give π-unconjugated ions were obtained and are included in Table I.

The calculated ionization energies of propane and of propene are compared with the experimental data[13] in Table II. The former must be corrected for the charge in zero-point energy caused by breaking one C–H bond. This will involve one C–H stretching vibration and two C–H bending vibrations. The vi-

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Table I. Energies of Hydrocarbons and Ions[b]

compound	6-31G*/6-31G*	6-311++G**//6-31G* RHF	MP2	MP3	MP4
propane	−118.263 65	−118.296 36	−118.770 86	−118.811 11	−118.831 93
propene	−117.071 47	−117.104 93	−117.549 83	−117.582 49	−117.604 65
1-propyl anion	−117.542 39	−117.601 42	−118.092 08	−118.125 67	−118.151 63
1-propyl cation[a]	−117.351 11	−117.383 39	−117.805 86	−117.844 94	−117.865 14
allyl anion (1)	−116.393 49	−116.454 67	−116.912 77	−116.936 78	−116.962 72
allyl anion 90° (1r)	−116.360 94	−116.420 78	−116.879 59	−116.905 88	−116.932 47
allyl cation (2)	−116.193 21	−116.221 64	−116.616 95	−116.646 46	−116.669 35
allyl cation, 90° (2r)	−116.138 99	−116.169 03	−116.558 79	−116.591 68	−116.612 60
hydride ion	−0.422 44	−0.486 96	−0.505 61	−0.510 70	−0.512 85

[a] Classical cation, C_s symmetry. [b] In hartrees.

Table II. Calculated Ionization Energies[b]

reaction	ΔE (kcal/mol) 6-31G*//6-31G*	6-311++G**//6-31G* RHF	MP2	MP3	MP4	ΔH calc	ΔH obs
propane → propyl$^+$ + H$^-$	307.5	267.3	288.3	285.8	284.8	276	274 ± 3[a]
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	417	419 ± 3
propene → allyl$^-$ + H$^+$	425.4	408.0	399.8	405.2	402.8	392	390 ± 3

[a] The value is that for ethane giving the ethyl cation.[15] [b] In kcal/mol.

Table III. Energy Changes for Reactions[a]

reaction	ΔE (kcal/mol) 6-31G*//6-31G*	6-311++G**//6-31G* RHF	MP2	MP3	MP4
propyl$^+$ + propene → unconj allyl$^+$ + propane	+12.5	+14.5	+16.3	+15.5	+15.9
propyl$^-$ + propene → unconj allyl$^-$ + propane	−6.7	−6.8	−5.4	−5.5	−5.1
unconj allyl$^+$ → conj allyl$^+$	−34.0	−33.1	−36.5	−34.4	−35.6
unconj allyl$^-$ → conj allyl$^-$	−20.4	−21.3	−20.8	−19.4	−19.0

[a] Abbreviations: unconj stands for unconjugated and conj stands for conjugated.

brational frequencies were calculated by using the 6-31G* basis set and led to the zero point energies:[14] allyl cation, 41.4; allyl anion, 37.9; propene 48.3, 1-propyl cation, 53.5; 1-propyl anion, 52.1; and propane, 62.4 kcal/mol. These values were used in converting the calculated energy changes to estimated ΔH values. It can be seen that the latter are in very good agreement with the experimental data.[15]

The rotational barriers for allyl anion and cation also were calculated and are summarized in Table III. As previously observed, the barrier for allyl cation was almost independent of basis set,[8] and the same was true for allyl anion. In addition, correction for electron correlation had little effect on the calculated barriers. Therefore one may be confident that they are correct.

An interesting aspect of these data is shown in Figure 1 which gives the energy changes for the processes:

$$\text{propyl}^{+,-} + \text{propene} \rightarrow \text{unconj allyl}^{+,-} + \text{propane}$$

$$\text{unconj allyl}^{+,-} \rightarrow \text{allyl}^{+,-}$$

With the cations, the reaction forming the unconjugated (rotated) allyl ion was found to be endothermic, presumably due to a destabilizing inductive effect of the sp^2 orbital from the C–C double bond.[16] In the case of the anions, the opposite was found, and here the stabilization of the unconjugated allyl anion is again due to the inductive effect of the double bond.

The rotational barrier for the allyl cation was calculated to be 36 kcal/mol, whereas the experimental data suggested a somewhat

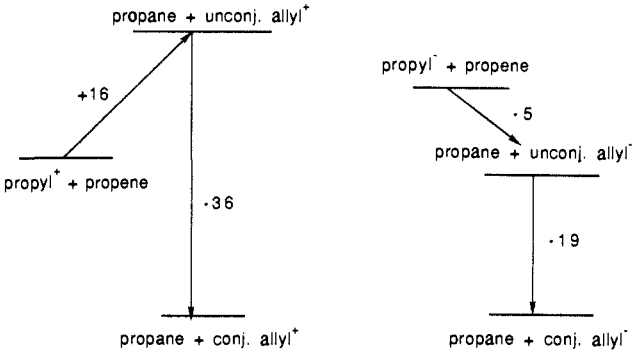

Figure 1. Energy changes for the reaction of propyl ions with propene. The energies are given in kcal/mol.

smaller barrier, 25 kcal/mol.[8a] However, the barrier measured in solution should be smaller than that in the gas phase because of the greater stabilization by the solvent of the rotated form which has the more concentrated charge.[8c] The 36 kcal/mol barrier has been taken as the resonance energy of the allyl cation.[8b] However, it is unreasonably large. Benzene has six π-electrons and six C–C bonds, allowing the π-electrons to be distributed one per bond which will result in reduced π-electron repulsion as compared to ordinary C=C bonds.[17] In the allyl cation, there are two π-electrons and two C–C bonds, and so a simple estimate of the resonance energy of the allyl cation would be about one-third that of benzene. The resonance energy of the latter depends on the model used, and values of 24,[18] 36,[19] and 55 kcal/mol[20] have been

(14) The calculated frequencies are available in the Supplementary Material. They were scaled by the usual factor, 0.90, before calculating the zero-point energies.

(15) The experimental value given for 1-propyl cation is actually that for the ethyl cation. The values should not be much different for the open propyl cation will receive a small stabilization because of its greater size, but the experimentally studied ethyl cation has a small stabilization from bridging.

(16) Lanceloet, C. J.; Harper, J. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 4296.

(17) Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166; **1960**, *11*, 96.

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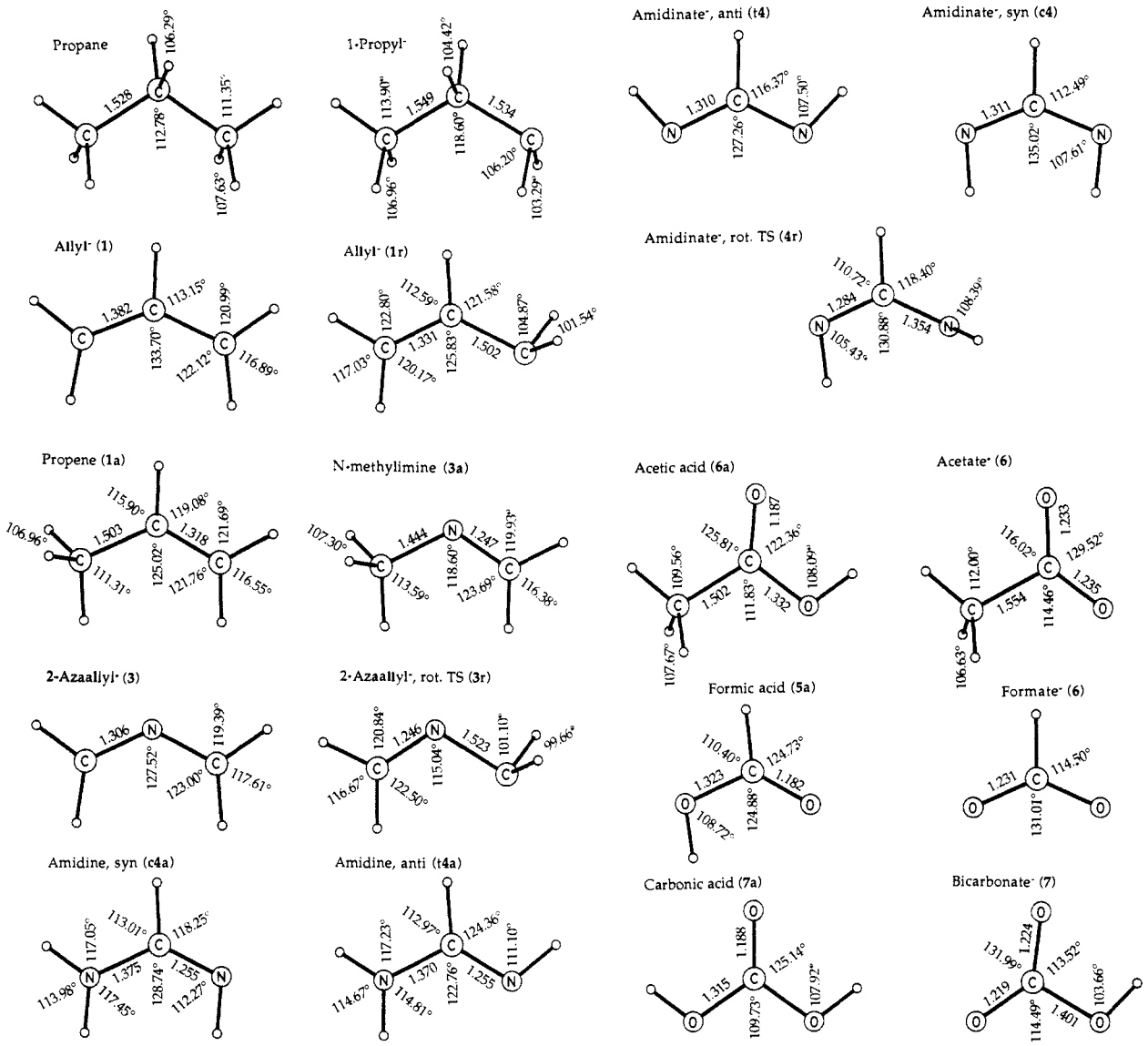

Figure 2. Calculated structures of symmetrical allyl anions and related compounds.

given. So, one might expect the resonance energy of the allyl cation to be in the range of 8–18 kcal/mol.

benzene allyl cation allyl anion

The rotational barrier for the allyl anion was calculated to be 19 kcal/mol, and it is interesting to note that the difference in the rotational barriers of the cation and anion is about 17 kcal/mol, within the range of estimated resonance energy of the allyl cation. Each of the barriers has two components: (a) the decrease in the classical electrostatic energy on going to the planar form and (b) the energy lowering due to electron delocalization. In the "unconjugated" ions, the charge will be to a considerable extent localized on one carbon, but in the planar form, symmetry requires that the charge be equally distributed between the terminal carbons. The change in geometry on rotation (Figure 2) leading to single and double bond lengths, clearly shows the charge localization. The charge will then be relatively concentrated in the unconjugated rotamer, but the charge will be spread over a larger volume element in the planar form, leading to a lower electrostatic energy. An example of this effect is found in a comparison of the relative energies of *tert*-butoxide and methoxide ions in the gas phase.[14,21]

One might make an order of magnitude estimate of the change in electrostatic energy on rotation as follows. The classical energy of a charged sphere is given by $7.2q^2/r$ where r is the radius in Å, and the energy is in eV. The "size" of the localized anion might be taken as about that of methane, or ~2 Å and that of the planar anion might then be on the order of 3 Å. The difference in classical electrostatic energy would then be about 1 eV or 23 kcal/mol. Clearly, the observed difference in energy between the planar and rotated ions is close to this estimate.

One would expect the resonance stabilization of the allyl anion to be much less than for the cation as a result of the greater π-electron repulsion in the anion. In view of the results presented below for other allyl type anions, it would be reasonable to propose that most of the rotation barrier is due to the change in electrostatic energy and that the resonance stabilization is small. Allyl cation should have a similar change in electrostatic energy on rotation, and, as noted above, if one subtracts the anion rotational barrier from that of the cation, the remainder, 17 kcal/mol, is best attributed to resonance stabilization. This is close to the value estimated above by analogy with benzene.

One may then conclude that the resonance stabilization of allyl anion is small and that the barrier to rotation for allyl cation is

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Table IV. Energies of Allyl Type Anions, Their Conjugate Acids, and Related Compounds[a]

ion	6-31G* RHF	6-311++G**//6-31G* RHF	MP2	MP3
2-azaallyl (**3**)	−132.384 12	−132.446 43	−132.940 01	−132.954 29
2-azaally, rot. TS (**3r**)	−132.352 50	−132.415 28	−132.905 61	−132.923 23
amidinate, anti (**a4**)	−148.438 73	−148.509 35	−149.030 37	−149.035 33
amidinate, syn (**s4**)	−148.452 95	−148.519 86	−149.038 95	−149.044 06
amidinate, rot. (**4r**)	−148.416 79	−148.487 82	−149.007 92	−149.013 09
formate (**5**)	−188.182 63	−188.257 58	−188.810 17	−188.796 86
acetate (**6**)	−227.225 06	−227.308 07	−228.011 06	−228.009 19
bicarbonate (**7**)	−263.078 61	−263.179 03	−263.927 62	−263.910 84
nitrite (**8**)	−204.065 67	−204.148 44	−204.744 44	−204.721 13
nitrate (**9**)	−278.912 97	−279.011 28	−279.809 13	−279.779 04
acetaldehyde enolate (**10**)	−152.283 93	−152.351 13	−152.856 52	−279.779 04
acetaldehyde enolate, 90° (**10ra**)	−152.226 57	−152.296 37	−152.800 05	−152.808 43
acetaldehyde enolate, 270° (**10rb**)	−152.226 48	−152.295 90	−152.800 24	−152.808 75
formamide enolate, syn (**s11**)	−168.319 19	−168.390 11	−168.925 73	−168.921 73
formamide enolate, anti (**a11**)	−168.310 76	−168.383 48	−168.920 19	−168.916 06
formamide enolate, rot. TS (**11r**)	−168.269 99	−168.346 00	−168.882 27	−168.877 87
methylimine (**3a**)	−133.061 49	−133.099 16	−133.574 32	−133.598 28
amidine, anti (**a4a**)	−149.075 86	−149.129 65	−149.635 18	−149.649 28
amidine, syn (**s4a**)	−149.073 50	−149.126 47	−149.631 63	−149.645 87
formic acid (**5a**)	−188.762 31	−188.826 02	−189.369 58	−189.365 67
acetic acid (**6a**)	−227.810 65	−227.883 84	−228.576 85	−228.584 00
carbonic acid (**7a**)	−263.647 48	−263.738 38	−264.477 77	−264.469 74
nitrous acid, cis (**c8a**)	−201.639 94	−204.706 78	−205.292 44	−205.281 17
nitrous acid, trans (**t8a**)	−204.637 68	−204.707 02	−205.293 79	−205.282 81
nitric acid (**9a**)	−279.444 26	−279.534 90	−280.335 75	−280.310 67
acetaldehyde (**10a**)	−152.915 96	−152.961 95	−153.454 96	−153.469 13
acetaldehyde enol, syn (**s10e**)	−152.888 88	−152.942 12	−153.435 99	−153.452 48
acetaldehyde enol, anti (**a10e**)	−152.885 39	−152.939 30	−153.433 74	−153.450 47
acetaldehyde enol, 90° C–C (**10er**)	−152.777 68	−152.836 37	−153.332 10	−153.347 06
acetaldehyde enol, 90° C–O	−152.881 52	−152.935 36	−153.427 98	−153.445 52
formamide (**11a**)	−168.930 70	−168.988 47	−169.511 24	−169.514 95
formamide enol, s-HO, a-NH (**11e**)	−168.908 01	−168.968 25	−169.492 87	−169.499 47
formamide enol, s-HO, s-NH	−168.901 94	−168.961 60	−169.486 30	−169.492 98
formamide enol, a-HO, s-NH	−168.900 93	−168.961 20	−169.486 11	−168.493 13
formamide enol, a-HO, a-NH	−168.896 45	−168.957 86	−169.483 27	−169.490 28

[a] Syn refers to a terminal hydrogen being syn to the heavy atom at the other terminal position.

composed of approximately equal contributions from resonance stabilization and changes in electrostatic energy. We are currently attempting to place this hypothesis on a more quantitative basis.

It might be noted that electrostatic terms are frequently important with ions and dipolar species, such as in determining differences in energy among rotamers. For example, with 1,2-dichloroethane,[22] the gauche form, with the higher dipole moment, is 1 kcal/mol less stable than the trans rotamer, having zero dipole moment. When placed in a solvent of high dielectric constant, the difference in energy decreases to essentially zero, presumably because of the decrease in electrostatic energy of the gauche form when placed in solution.

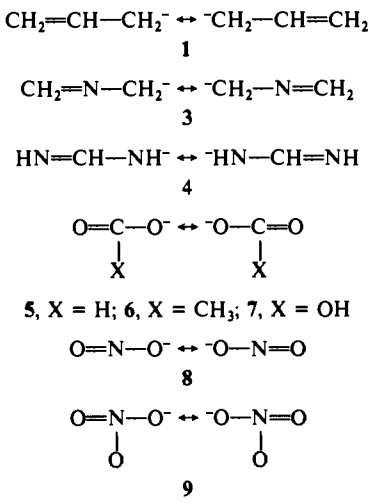
It would be interesting to have experimental values for the rotational barrier of a free allyl anion in the gas phase and in solution. The only experimental data are for solution, and here there are problems of interpretation connected with ion-pair phenomena.[7] The barrier to rotation for allyl cesium was found to be $\Delta G^{\ddagger}$ = 18 kcal/mol, and it was suggested that this was a minimum value for the free ion.[7a] However, subsequent work reported that the barrier was quite low when the ion was initially formed and then increased irreversibly as the ion-paired/aggregated species was produced.[7b] Further experimental studies are needed in order to determine that magnitude of the barrier.

It should be noted that even if the barrier could be measured in a solvent of high dielectric constant, the electrostatic energy component would not be completely eliminated. In a classical sense, many of the electrostatic "lines of force" pass through the molecule rather than the solvent, and only those passing through the solvent would be affected. The problem is similar to that of the interaction of a dipole with a carboxylate ion which has been discussed in detail by Westheimer and Kirkwood.[23]

(22) Wiberg, K. B.; Murcko, M. *J. Phys. Chem.* **1987**, *91*, 3616.

Symmetrical Allyl Anions

In addition to the allyl anion (**1**), the following symmetrical ions were studied in order to see how the electronegativity of the atoms in the system affects the charge distribution. The structures were obtained by using the 6-31G* basis set, and the energies and wave functions were obtained by using the calculated structures



and the 6-311++G** basis set. There may be a relatively large change in the electron correlation energy on going from the parent compound to its anion, and therefore the Møller–Plesset correction was calculated through the third order (MP3), and these values

(23) Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *6*, 506. Westheimer, F. H.; Kirkwood, J. G. *J. Chem. Phys.* **1938**, *6*, 513.

Table V. Calculated Gas-Phase Ionization Energies[a]

reaction	ΔE 6-31G* RHF	ΔE 6-311++G**//6-31G* RHF	ΔE 6-311++G**//6-31G* MP2	ΔE 6-311++G**//6-31G* MP3	ΔH calc	ΔH obs[13]
$CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2^-$	452.6	436.1	425.9	430.1	420	419 ± 3
$CH_3CH{=}CH_2 \rightarrow {}^-CH_2{-}CH{=}CH_2$	425.4	408.0	399.8	405.2	395	390 ± 3
$CH_3N{=}CH_2 \rightarrow {}^-CH_2{-}N{=}CH_2$	425.0	409.6	398.0	404.1	394	
$H_2NCH{=}NH \rightarrow {}^-HN{-}CH{=}NH$ (cis)	399.4	382.6	374.1	379.8	371	
$CH_3CO_2H \rightarrow CH_3CO_2^-$	367.5	361.3	355.0	360.7	352	349 ± 3
$HCO_2H \rightarrow HCO_2^-$	363.7	356.7	351.0	356.9	349	345 ± 3
$HOCO_2H \rightarrow HOCO_2^-$	357.0	351.0	345.2	350.7	342	
$HNO_2 \rightarrow NO_2^-$	360.4	350.4	343.9	351.2	343	338 ± 4
$HNO_3 \rightarrow NO_3^-$	333.4	328.6	330.5	333.6	325	325 ± 3
$CH_3CHO \rightarrow CH_2{=}CHO^-$	396.6	383.3	375.5	381.1	371	366 ± 3
$HCONH_2 \rightarrow HCONH^-$	383.7	375.5	367.4	372.2	363	360 ± 3

[a] In kcal/mol.

also are given in Tables I and IV. As is frequently found, the MP2 calculation overcorrected, and the MP3 values were between those obtained by using RHF and MP2.

We first wished to see if the relative energies of the anions and their parent acids were satisfactorily reproduced by the calculations. The energies of the acids were obtained by using the same basis sets (Table IV), and the calculated energy changes are given in Table V. In the case of formic acid, 6-31G* calculated frequencies suggested a change in zero-point energy of 8.3 kcal/mol on ionization, and this value was used for all of the acids. The ionization of NH bonds was assumed to have a zero-point energy change which was the average of that for CH bonds (10.3 kcal/mol) and OH bonds. These values were used in converting the calculated energy changes into estimated changes in ΔH of ionization. In some cases, the gas-phase proton affinities of the anions have been determined,[13] and these data also are given in the table. The experimental values have an absolute uncertainty of about 3 kcal/mol, although the relative energies are considerably better. The calculated structures of the ions are shown in Figure 2.

The comparison of the calculated and observed ionization energies in Table III shows that the calculated results are in good agreement with experiment, especially considering the uncertainty (~3–4 kcal/mol) in the latter values. Further improvements in the calculated ionization energies might be realized by including the full MP4 correction (cf. Table II). However, the computer time required for these calculations was too long to be practical with this large a group of compounds.

It is clear that the calculated ionization energies change in a manner parallel to the experimental values. Since the latter are not available for some of the systems of interest, in the following discussion the calculated values will be used throughout.

The anion from *N*-methylimine (**3a**) has an electronegative group at the central position, and this should affect the charge distribution. However, the calculated ionization energy of **3a** was essentially the same as for propene. No energetic advantage was found in replacing the central CH of propene by nitrogen. The barrier to rotation about the C–N bond of this ion was found to be essentially the same as for the allyl anion. In this connection, it is interesting to note the similarity of the ionization energies of formic acid and nitrous acid. Again, the central atom has a relatively small effect.

The replacement of the end carbons of allyl anion with nitrogen giving the amidinate ion (**4**) does lead to a relatively large decrease in ionization energy, suggesting that the stabilization of an allyl anion requires that the electronegative atom be placed at the terminal positions.[24] The carboxylic acids continue this trend, with a further decrease in the ionization energy. Here, it is interesting to note that the electronegativity of the substituent at the carboxylate carbon is important, with methyl increasing the ionization energy as compared to hydrogen, and the electronegative hydroxy group decreasing it.

Table VI. Calculated Energy Changes[c]

species	ΔE 6-31G* RHF	ΔE 6-311++G** RHF	ΔE 6-311++G** MP2	ΔE 6-311++G** MP3
a. Rotational Barriers				
allyl (**1**)	20.4	21.3	20.8	19.4
2-azaallyl (**3**)	19.8	19.5	21.6	19.5
amidinate (**4**)	22.7	20.1	19.5	21.1
acetaldehyde enolate (**10**)	36.0	34.4	35.3	33.3
formamide enolate (**11**)	30.9	27.7	27.2	27.5
acetaldehyde enol, about CO	4.6	1.8	1.4	1.4
acetaldehyde enol, about C=O	69.8	66.4	65.2	66.2
b. Keto/Enol Equilibria				
acetaldehyde, keto/enol	17.0	12.4	11.9	10.4
formamide, keto/enol	14.2	12.7	11.5	9.7
c. Syn/Anti Isomerization				
amidinate[a]	8.9	6.6	5.4	5.5
formamide enolate[a]	5.3	4.2	3.5	3.6
amidine[b]	1.5	2.0	2.2	2.1
nitrous acid[b]	−1.4	0.2	0.8	1.0
acetaldehyde enol[a]	2.2	1.8	1.4	1.3
formamide enol (about CO)	4.4	4.4	4.2	4.0
formamide enol (about CN)	3.8	4.2	4.1	4.1

[a] Syn form is the more stable. [b] Anti form is the more stable. [c] In kcal/mol.

With nitrous and nitric acids, the same factors appear important. The additional oxygen attached to the central nitrogen causes a considerable increase in acidity.

The rotational barriers for the ions derived from methylimine and amidine were calculated and are given in Table III. Again the barriers were not much affected by changes in basis set or correction for electron correlation, and the values were very close to those for allyl anion. This is despite the large changes in charge density (see below) and again suggests that the main part of the barrier results from the difference in electrostatic energy between the planar (delocalized) and rotated (localized) charge distributions.

Rotation about a C–C or C–N bond did have an important effect on the bond lengths and angles (Figure 2). In the case of allyl anion (**1** and **1r**), rotation about the C–C bond led to C–C bond lengths which were close to those of propene. The bond angle in **1r** opposite the carbanionic center was considerably smaller than that opposite the other methylene group. The angles commonly respond to differences in electronegativity, and when steric interactions are not dominant, the larger angle is found opposite the more electronegative atom.[25] This is seen to be the case in **1r**. The bond angles at the carbanionic methylene were rather small, indicating high p-character, allowing the unshared pair of electrons to be in an orbital with high s-character. Similar changes

(24) Although the energies of the 2-azaallyl and amidinate ions have not been determined, it is known that 2-azaallyl anions rearrange to 1-azaallyl ions (Pearson, W. H.; Szura, D. P.; Harter, W. G. *Tetrahedron Lett.* **1988**, *29*, 761) in good accord with the present calculations.

(25) Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285.

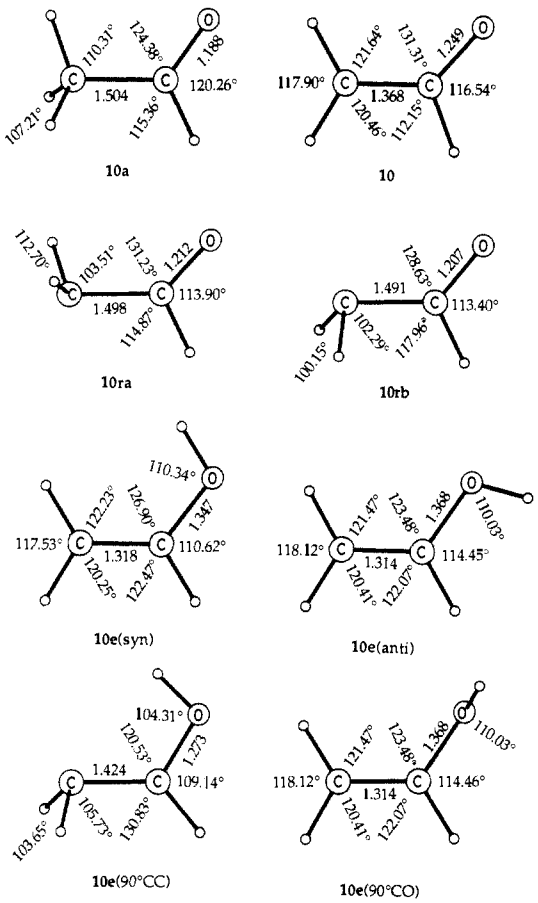


Figure 3. Calculated structures of acetaldehyde (**10e**), its enols and (**10e**), and enolate ions (**10**) using the 6-31G* basis set.

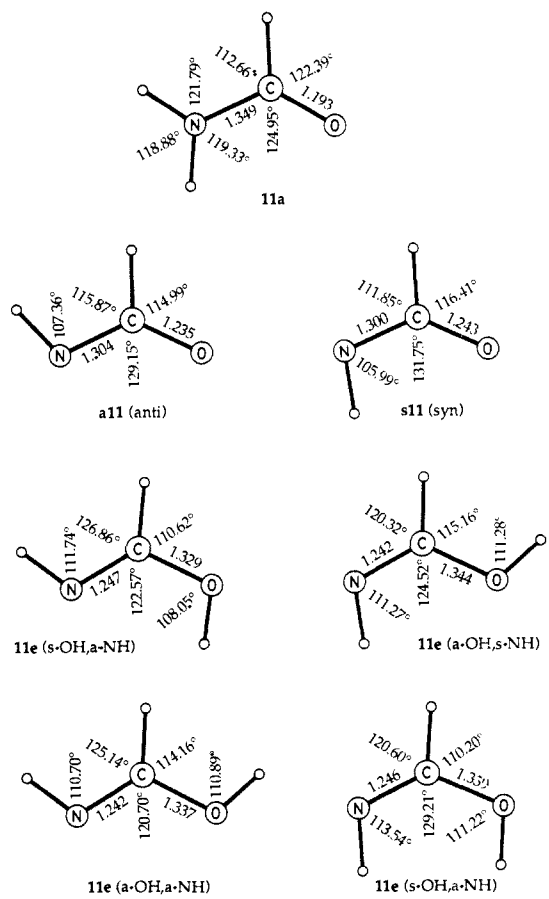


Figure 4. Calculated structures of formamide (**11a**), its enols (**11e**), and enolate ions (**a11**,s11) using the 6-31G* basis set.

in geometry were found with 2-azaallyl and amidinate ions.

Unsymmetrical Allyl Anions

We were interested in seeing the effect of having two different atoms at the termini of an allyl anion, and, therefore, we have studied the enolate ions derived from acetaldehyde (**10**) and formamide (**11**). For comparison, we also have studied acetaldehyde (**10a**), its enols (**10e**), formamide (**11a**), and its enols (**11e**). The energies are summarized in Table V, and the rotational barriers are given in Table VI. The structural data for the compounds related to acetaldehyde are summarized in Figure 3, and those for formamide are in Figure 4. The calculated ionization energies of acetaldehyde and formamide were in reasonable agreement with the experimental values.

It may be noted that the calculated ionization energy of acetaldehyde was close to the average of those for propene and formic acid and that the same comparison may be made between formamide and the average of the ionization energies of amidine and formic acid. For the set of allyl anions, the replacement of one terminal CH_2 by NH reduced the ionization energy by 12 kcal/mol, the replacement of one CH_2 by O reduced the ionization energy by 23 kcal/mol, and the effects were additive. This again emphasizes the importance of the nature of the terminal atoms in determining the stability of an allyl anion.

Acetaldehyde enol may adopt either the syn or anti conformations (Figure 3), and the former was found to have the lower energy as a result of its smaller dipole moment (syn, μ = 1.10 D; anti, μ = 2.04 D). There are four possible conformers for formamide enol (Figure 4), and they are shown with their relative energies in Figure 5. There is a dipole associated with the OH bond and also with the nitrogen lone pair, and they are included in the figure. It can be seen that the lowest energy rotamer has the most favorable dipole–dipole interactions and that the least stable rotamer has the least favorable interaction.

The barriers for rotation about the C–C bond of acetaldehyde enolate and the C–N bond of formamide enolate were significantly

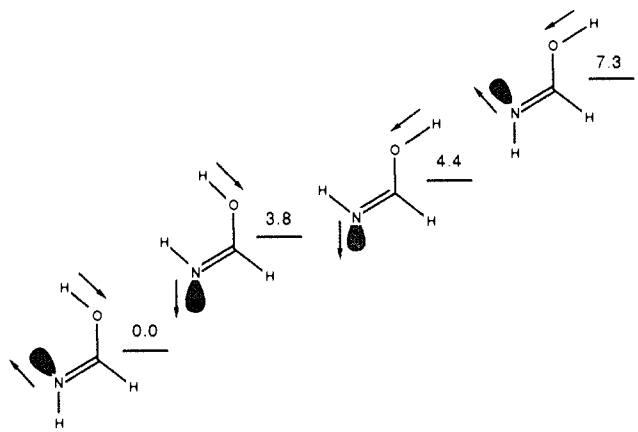


Figure 5. Relative energies of formamide enols.

higher than that for the other compounds which were studied. This is in accord with the generally accepted idea that the negative charge will prefer to be located at the more electronegative atom. It would lead to increased double bond character in the C–C and C–N bonds, respectively, and a larger rotational barrier. For comparison, the barrier for rotation about the C–C bond of acetaldehyde enol also was calculated. The value (66 kcal/mol) was about that for ethylene and was *much* larger than that for the enolate ions. It can be seen that the C=C double bond character in these ions is not much greater than that for allyl anion.

The changes in geometry among the acetaldehyde and formamide related compounds and ion might be noted. On rotation about the C–C bond, the C–O bond length shortened to a value close to that for acetaldehyde. The C–O bond length in the enolate ion was relatively long, but still *much* shorter than that in the enols. There also was a large effect on the C–O bond length in the enols on rotation about the C–C bond where it is 1.35–1.37 Å in the

planar forms and 1.27 Å in the rotated form.

Similar changes were found with formamide. The enolate had a longer C–O bond and a shorter C–N bond than in formamide.

Bond and Atom Properties

A further understanding of the differences among the ions described above requires that we have information on how the structural changes affect the charge density distribution. This distribution is one of the most fundamental characteristics of any molecule, and all of its properties could be calculated if it were known.[26] The charge distribution is found experimentally via X-ray crystallography, and it has been shown that the distribution calculated from the molecular orbital wave functions using basis sets such as those used in this investigation are in very good agreement with the experimental values.[27] Thus, we have carried out a study of the distributions obtained from the 6-311++G** wave functions.

The charge distribution in planar systems such as these may conveniently be visualized by using projection density plots in which all of the charge density above and below the molecular plane is collapsed into that plane.[28] They are shown for some of the anions in Figure 6. It can be seen that as one of the atoms becomes more electronegative, the region of space which might reasonably be assigned to that atom increases.

The changes in atomic "size" suggested by these plots find their counterpart in the bond critical points as defined by Bader.[29] Between any two bonded atoms there is a bond path, which is the path of maximum charge density (ρ) which connects the atoms. Along this path, there is a point having the minimum charge density which is known as the bond critical point. Although a minimum along the path, it is a maximum in all other directions. When one examines a symmetrical bond, such as the C–C bond in ethane, the bond critical point will be at the midpoint of the bond. However, if one of the atoms is more electronegative than the other, it will tend to draw the electrons in the bonding region toward itself and correspondingly move the bond critical point toward the less electronegative atom.

The locations of the bond critical points are given in Table VII. The quantities r_A and r_B are the distances from the atoms forming a bond to the critical point, and R is the ratio of r_A:r_B. The charge density at the critical point is given as ρ_c, and the three curvatures of ρ are given as λ_1 to λ_3. The quantity $\nabla^2\rho$ is the Laplacian of ρ, which is negative for covalent bonds having relatively little ionic character. Finally, ϵ is the ellipticity defined as $\lambda_1/\lambda_2 - 1$ which is a measure of the shape of the charge distribution normal to the bond critical point.

In allyl anion (**1**), the terminal carbons would be expected to bear most of the negative charge, thereby decreasing their electronegativity with respect to the central carbon. Correspondingly, R is less than unity. In the rotated ion (**1r**) the carbons forming the double bond would be expected to have about the same electronegativity, and R for the C=C is close to unity. The carbon bearing the negative charge, C3, should have a decreased electronegativity, and the distance to the critical point is considerably less than that from C2. With 2-azaallyl ion (**3**) the distance from the carbon to the critical point for the C–N bond is about half that from the nitrogen, in accord with the difference in electronegativity. On rotation about the C–N bond, changes in R similar to those found for **1** are observed. Similar values of R are found for the C–N bonds of amidinate ion. In the carboxylate ions, the value of R for the C–O bonds is somewhat smaller than for the above C–N bonds. The change from C–N to C–O bonds is not large. There is a limit to how large R may become. At a point along a bond near the nucleus, the charge density begins to increase rapidly, and it is no longer easy to move the critical point toward the atom.

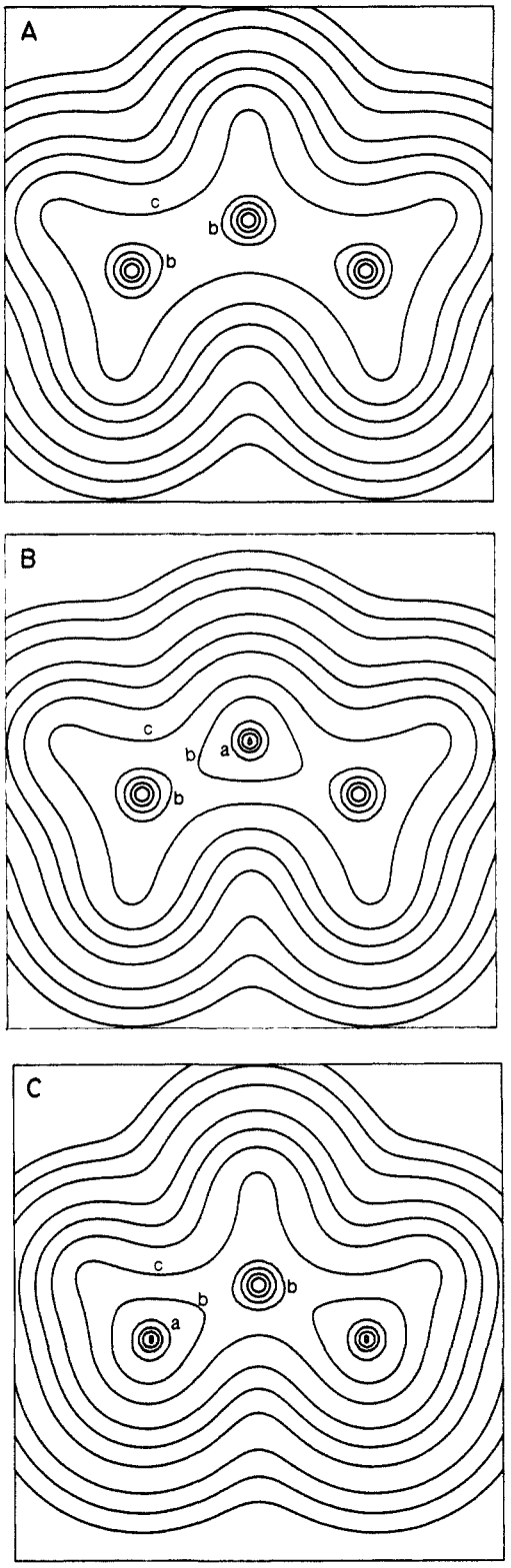


Figure 6. Projection density plots for allyl anion (A), 2-azaallyl anion (B), and amidinate anion (C). The contour levels are a, 0.8 e/au^2; b, 0.4 e/au^2, and c, 0.2 e/au^2.

It has been observed that the charge density at the bond critical point is related to the bond order. It is also related to the bond length. For the C–C bonds in Table VII, ρ_c is linearly related to the bond length with $r^2 = 1.00$ ($\rho_c = 1.128 - 0.583r$(CC)). With the C–N bonds, a similar relationship is found with $r^2 = 0.96$ ($\rho_c = 1.240-0.668r$(CN)).

With nonpolar covalent bonds, such as C–C and C–H, the positive curvature of ρ along the bond (λ_3) is considerably smaller

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Table VII. Bond Critical Points for Allyl Anions and Related Compounds[a]

molecule	bond	r_A	r_B	R	ρ_c	λ_1	λ_2	λ_3	$\nabla^2\rho$	ϵ
allyl (**1**)	C1–C2	0.6369	0.7450	0.855	0.3173	−0.6755	−0.4950	0.2058	−0.9668	0.3687
	C1–Ha	0.6590	0.4207	1.566	0.2751	−0.6882	−0.6167	0.3537	−0.9512	0.1161
	C1–Hb	0.6613	0.4203	1.574	0.2744	−0.6861	−0.6234	0.3578	−0.9517	0.1006
	C2–H	0.6730	0.4185	1.608	0.2811	−0.7062	−0.7018	0.3790	−1.0289	0.0062
allyl, rot. TS (**1r**)	C1–C2	0.6758	0.6555	1.031	0.3547	−0.7949	−0.5710	0.1897	−1.1762	0.3921
	C2–C3	0.8640	0.6378	1.355	0.2540	−0.4662	−0.4235	0.2028	−0.6870	0.1006
	C1–Ha	0.6633	0.4205	1.577	0.2787	−0.6946	−0.6662	0.3591	−1.0017	0.0427
	C1–Hb	0.6766	0.4027	1.680	0.2847	−0.7363	−0.7079	0.4085	−1.0357	0.0401
	C2–H	0.6806	0.4245	1.603	0.2716	−0.6688	−0.6624	0.3715	−0.9598	0.0096
	C3–H	0.6644	0.4479	1.484	0.2525	−0.5811	−0.5331	0.3050	−0.8092	0.0899
2-azaallyl (**3**)	C–N	0.4313	0.8758	0.492	0.3404	−0.8128	−0.5255	1.1540	−0.1843	0.5469
	c–Ha	0.6642	0.4167	1.594	0.2791	−0.7186	−0.6334	0.3715	−0.9805	0.1346
	C–Hb	0.6663	0.4237	1.573	0.2716	−0.6830	−0.6116	0.3589	−0.9357	0.1167
2-azaallyl, rot. TS (**3r**)	C1–N	0.4223	0.8238	0.513	0.4085	−1.0541	−0.8121	1.2972	−0.5690	0.2981
	N–C3	1.0210	0.5043	2.025	0.2189	−0.3408	−0.2701	0.2571	−0.3537	0.2618
	C1–Ha	0.6725	0.4201	1.601	0.2799	−0.7095	−0.6861	0.3738	−1.0217	0.0342
	C1–Hb	0.6919	0.3973	1.742	0.2848	−0.7511	−0.7273	0.4378	−1.0406	0.0342
	C3–H	0.6719	0.4418	1.521	0.2582	−0.6203	−0.5611	0.3255	−0.8559	0.1055
amidinate, anti, (**a4**)	C–N	0.4654	0.8449	0.551	0.3722	−0.8965	−0.7900	0.5023	−1.1842	0.1348
	C–H	0.6853	0.4328	1.584	0.2686	−0.6616	−0.6553	0.3638	−0.9531	0.0096
	N–H	0.7203	0.2890	2.492	0.3454	−1.1770	−1.1505	0.8406	−1.4869	0.0231
amidinate, syn, (**s4**)	C–N	0.4654	0.8464	0.550	0.3697	−0.8694	−0.7909	0.4996	−1.1608	0.0993
	C–H	0.6816	0.4142	1.646	0.2861	−0.7452	−0.7320	0.4023	−1.0748	0.0180
	N–H	0.7240	0.2916	2.483	0.3383	−1.1392	−1.1188	0.8354	−1.4226	0.0183
amidinate, rot. TS (**4r**)	C–Na	0.4406	0.8433	0.523	0.3859	−0.9623	−0.8418	0.9775	−0.9266	0.1432
	C–Nb	0.5470	0.8077	0.677	0.3493	−0.7837	−0.7336	0.2505	−1.2668	0.0683
	C–H	0.6923	0.4199	1.649	0.2754	−0.7033	−0.6912	0.3993	−0.9952	0.0175
	Na–H	0.7335	0.2798	2.621	0.3449	−1.2072	−1.2052	0.8309	−1.5815	0.0017
	Nb–H	0.7230	0.2876	2.514	0.3292	−1.1101	−1.0524	0.8043	−1.3582	0.0541
formate (**5**)	C–O	0.4085	0.8218	0.496	0.3960	−1.0926	−1.0818	2.0535	−0.1209	0.0099
	C–H	0.6973	0.4295	1.623	0.2678	−0.6778	−0.6608	0.3886	−0.9500	0.0258
acetate (**6**)	C–C	0.8061	0.7480	1.078	0.2501	−0.5043	−0.4758	0.2968	−0.6833	0.0598
	C–Ha	0.6721	0.4138	1.624	0.2816	−0.6985	−0.6983	0.3825	−1.0132	0.0017
	C–Hb	0.6719	0.4168	1.612	0.2772	−0.6825	−0.6713	0.3720	−0.9818	0.0167
	C–O	0.4100	0.8233	0.498	0.3946	−1.0860	−1.0666	1.9764	−0.1762	0.0182
	C–O	0.4095	0.8239	0.497	0.3963	−1.0923	−1.0763	1.9941	−0.1744	0.0149
bicarbonate (**7**)	C–O1	0.4125	0.8213	0.502	0.4028	−1.1371	−1.0797	1.8462	−0.3707	0.0532
	C–O2	0.4082	0.8112	0.503	0.4149	−1.2001	−1.1216	2.0057	−0.3160	0.0700
	C–O3	0.4555	0.9460	0.482	0.2623	−0.5964	−0.5127	0.8463	−0.2628	0.1634
	O3–H	0.7693	0.1773	4.340	0.3892	−2.0538	−2.0082	1.1885	−2.8736	0.0227
nitrite (**8**)	N–O	0.5567	0.6726	0.828	0.5124	−1.3930	−1.3098	1.0958	−1.6071	0.0635
nitrate (**9**)	N–O	0.5968	0.6292	0.948	0.5210	−1.4250	−1.2630	1.3005	−1.3874	0.1283
1-propyl	C1–C2	0.6891	0.8452	0.815	0.2423	−0.4484	−0.4078	0.2460	−0.6103	0.0995
	C2–C3	0.7194	0.8293	0.868	0.2416	−0.4495	−0.4447	0.2714	−0.6228	0.0108
	C1–H	0.6627	0.4502	1.472	0.2531	−0.5858	−0.5334	0.3026	−0.8166	0.0982
	C2–H	0.6686	0.4302	1.554	0.2740	−0.6669	−0.6536	0.3514	−0.9691	0.0203
	C3–Ha	0.6685	0.4302	1.554	0.2705	−0.6467	−0.6455	0.3462	−0.9460	0.0020
	C3–Hb	0.6718	0.4183	1.606	0.2782	−0.6852	−0.6791	0.3727	−0.9915	0.0090
acetaldehyde enolate, planar (**10**)	C–C	0.6399	0.7278	0.879	0.3324	−0.7402	−0.5218	0.2056	−1.0564	0.4186
	C–Ha	0.6579	0.4220	1.559	0.2754	−0.6859	−0.6221	0.3489	−0.9592	0.1025
	C–Hb	0.6639	0.4167	1.593	0.2756	−0.6927	−0.6372	0.3661	−0.9637	0.0871
	C–O	0.4154	0.8336	0.498	0.3809	−1.0101	−0.9881	1.7684	−0.2303	0.0228
	C–H	0.6873	0.4291	1.602	0.2706	−0.6790	−0.6668	0.3778	−0.9680	0.0183
acetaldehyde enolate, 90°	C–C	0.6172	0.8812	0.700	0.2617	−0.4774	−0.4405	0.1864	−0.7316	0.0837
	C–H	0.6676	0.4409	1.514	0.2535	−0.5838	−0.5407	0.3145	−0.8100	0.0797
	C–O	0.4001	0.8115	0.493	0.4045	−1.1438	−1.1197	2.5195	0.2561	0.0216
	C–H	0.6984	0.4180	1.671	0.2768	−0.7079	−0.7070	0.4099	−1.0051	0.0013
acetaldehyde enolate, 270°	C–C	0.6164	0.8740	0.705	0.2657	−0.4888	−0.4513	0.1879	−0.7522	0.0831
	C–H	0.7021	0.4274	1.643	0.2663	−0.6648	−0.6611	0.3915	−0.9344	0.0056
	C–O	0.3991	0.8076	0.494	0.4101	−1.1651	−1.1584	2.5756	0.2521	0.0057
	C–H	0.6635	0.4496	1.476	0.2502	−0.5652	−0.5221	0.2967	−0.7906	0.0826
formamide enolate, syn (**s11e**)	C–H	0.6888	0.4221	1.632	0.2770	−0.7125	−0.6951	0.3941	−1.0135	0.0251
	C–O	0.4125	0.8308	0.497	0.3855	−1.0390	−1.0178	1.8790	−0.1778	0.0209
	C–N	0.4559	0.8443	0.540	0.3795	−0.9357	−0.8202	0.6098	−1.1461	0.1408
	N–H	0.7280	0.2859	2.546	0.3407	−1.1672	−1.1536	0.8315	−1.4893	0.0117
formamide enolate, anti (**a11e**)	C–H	0.6914	0.4325	1.598	0.2672	−0.6667	−0.6538	0.3750	−0.9456	0.0197
	C–O	0.4105	0.8248	0.498	0.3933	−1.0681	−1.0660	1.9632	−0.1709	0.0020
	C–N	0.4576	0.8460	0.541	0.3763	−0.9264	−0.8084	0.5901	−1.1447	0.1459
	N–H	0.7215	0.2874	2.510	0.3457	−1.1807	−1.1592	0.8397	−1.5002	0.0185
formamide enolate, rot. TS	C–H	0.7035	0.4274	1.646	0.2661	−0.6707	−0.6597	0.3966	−0.9337	0.0167
	C–O	0.4038	0.8167	0.495	0.4012	−1.1268	−1.1028	2.3010	0.0713	0.0217
	C–N	0.5218	0.8135	0.642	0.3638	−0.8393	−0.7924	0.2545	−1.3773	0.0592
	N–H	0.7236	0.2829	2.558	0.3289	−1.1197	−1.0633	0.7929	−1.3900	0.0530
propene	C1–C2	0.6446	0.6737	0.960	0.3599	−0.8046	−0.5613	0.1741	−1.1918	0.4336
	C2–C3	0.7701	0.7328	1.051	0.2645	−0.5159	−0.5012	0.2710	−0.7460	0.0293
	C1–Ha	0.6795	0.3960	1.716	0.2903	−0.7583	−0.7427	0.4239	−1.0077	0.0210
	C1–Hb	0.6793	0.3979	1.707	0.2889	−0.7509	−0.7365	0.4194	−1.0680	0.0195

Table VII (Continued)

molecule	bond	r_A	r_B	R	ρ_c	λ_1	λ_2	λ_3	$\nabla^2\rho$	ϵ
	C2–H	0.6815	0.3978	1.713	0.2911	−0.7587	−0.7492	0.4245	−1.0834	0.0126
	C3–Ha	0.6791	0.4056	1.675	0.2843	−0.7203	−0.7130	0.4040	−1.0293	0.0102
	C3–Hb	0.6801	0.4067	1.672	0.2820	−0.7108	−0.7027	0.3997	−1.0138	0.0115
methylimine (**3a**)	C1–N	0.4222	0.8251	0.512	0.4018	−1.0212	−0.8200	1.3496	−0.4916	0.2453
	C2–N	0.5014	0.9433	0.532	0.2782	−0.5313	−0.5195	0.2663	−0.7845	0.0228
	C1–Ha	0.6890	0.3903	1.765	0.2954	−0.7945	−0.7768	0.4503	−1.1219	0.0217
	C1–Hb	0.6887	0.3980	1.730	0.2886	−0.7578	−0.7459	0.4321	−1.0716	0.0159
	C3–Ha	0.6815	0.4080	1.670	0.2847	−0.7312	−0.7088	0.4061	−1.0339	0.0316
	C3–Hb	0.6851	0.3991	1.717	0.2886	−0.7568	−0.7315	0.4248	−1.0635	0.0346
amidine, anti (**a4a**)	C–N1	0.4365	0.8187	0.533	0.4094	−1.0504	−0.8557	0.9189	−0.9872	0.2277
	C–N3	0.4663	0.9037	0.516	0.3199	−0.7086	−0.6987	0.5385	−0.8688	0.0142
	C–H	0.6925	0.3915	1.769	0.2961	−0.7985	−0.7842	0.4525	−1.1302	0.0182
	N1–H	0.7356	0.2665	2.760	0.3537	−1.2909	−1.2844	0.8036	−1.7717	0.0051
	N2–Ha	0.7392	0.2560	2.887	0.3558	−1.3744	−1.2956	0.7776	−1.8924	0.0609
	N2–Hb	0.7452	0.2523	2.954	0.3540	−1.3839	−1.3126	0.7680	−1.9284	0.0543
amidine, syn (**s4a**)	C–N1	0.4658	0.9098	0.512	0.3126	−0.6835	−0.6600	0.5458	−0.7977	0.0355
	C–N3	0.4370	0.8186	0.534	0.4092	−1.0490	−0.8503	0.9047	−0.9946	0.2337
	C–H	0.6941	0.3897	1.800	0.3009	−0.8280	−0.8074	0.4688	−1.1667	0.0255
	N1–H	0.7350	0.2724	2.698	0.3489	−1.2521	−1.2410	0.8089	−1.6842	0.0089
	N2–Ha	0.7406	0.2548	2.907	0.3555	−1.3793	−1.2997	0.7753	−1.9036	0.0613
	N2–Hb	0.7406	0.2564	2.889	0.3542	−1.3673	−1.2917	0.7789	−1.8801	0.0586
formic acid (**5a**)	C–H	0.7091	0.3744	1.894	0.3039	−0.8636	−0.8394	0.5053	−1.1977	0.0288
	C=O	0.3944	0.7876	0.501	0.4434	−1.3221	−1.2263	2.7211	0.1728	0.0781
	C–O	0.4282	0.8948	0.479	0.3124	−0.8072	−0.7151	1.4504	−0.0719	0.1288
	O–H	0.7830	0.1703	4.598	0.3752	−2.0554	−2.0218	1.2485	−2.8287	0.0166
acetic acid (**6a**)	C–C	0.6843	0.8176	0.837	0.2735	−0.5548	−0.5210	0.2559	−0.8199	0.0648
	C–Ha	0.6864	0.3930	1.747	0.2898	−0.7546	−0.7457	0.4338	−1.0665	0.0119
	C–Hb	0.6864	0.3975	1.727	0.2838	−0.7261	−0.7168	0.4185	−1.0244	0.0130
	C=O	0.3960	0.7911	0.501	0.4399	−1.3059	−1.2129	2.6226	0.1038	0.0767
	C–O	0.4308	0.9016	0.478	0.3070	−0.7864	−0.6880	1.3662	−0.1082	0.1431
	O–H	0.7819	0.1705	4.586	0.3766	−2.0617	−2.0260	1.2512	−2.8366	0.0176
carbonic acid (**7a**)	C=O	0.3980	0.7901	0.504	0.4460	−1.3212	−1.2043	2.4162	−0.1090	0.0970
	C–O	0.4293	0.8857	0.485	0.3285	−0.8538	−0.8382	1.3895	−0.3026	0.0187
	O–H	0.7830	0.1675	4.675	0.3780	−2.1076	−2.0699	1.3009	−2.8765	0.0182
nitrous acid, trans (**t8a**)	N=O	0.4927	0.6611	0.745	0.6103	−1.7510	−1.5420	0.9130	−2.3800	0.136
	N–O	0.6004	0.7459	0.805	0.3851	−0.9970	−0.9681	1.0237	−0.9414	0.030
	O–H	0.7807	0.1702	4.587	0.3838	−2.1242	−2.0691	1.2818	−2.9115	0.027
nitric acid (**9a**)	N–O	0.5772	0.6106	0.945	0.5663	−1.5363	−1.3469	1.3077	−1.5755	0.1407
	N–O	0.5650	0.6074	0.930	0.5864	−1.6041	−1.3928	1.2853	−1.7115	0.1517
	N–O	0.6276	0.7063	0.889	0.4096	−1.1514	−1.0124	1.1554	−1.0085	0.1374
	O–H	0.7907	0.1647	4.802	0.3758	−2.1538	−2.0939	1.3475	−2.9002	0.0286
acetaldehyde (**10a**)	C–C	0.7215	0.7827	0.922	0.2723	−0.5492	−0.5264	0.2788	−0.7968	0.0433
	C–Ha	0.6869	0.3947	1.741	0.2873	−0.7420	−0.7372	0.4301	−1.0491	0.0064
	C–Hb	0.6833	0.4033	1.694	0.2807	−0.7076	−0.6995	0.4025	−1.0045	0.0116
	C=O	0.3941	0.7936	0.497	0.4296	−1.2424	−1.1811	2.8090	0.3854	0.0519
	C–H	0.7004	0.3949	1.774	0.2901	−0.7824	−0.7763	0.4547	−1.1040	0.0078
acetaldehyde enol, syn (**s10e**)	C–C	0.9017	0.7499	1.203	0.3594	−0.8044	−0.5294	0.1313	−1.2025	0.5196
	C–Ha	0.6762	0.4008	1.687	0.2853	−0.7342	−0.7110	0.4064	−1.0388	0.0327
	C–Hb	0.6796	0.3930	1.729	0.2892	−0.7585	−0.7305	0.4271	−1.0620	0.0383
	C–O	0.4331	0.9144	0.474	0.2903	−0.6756	−0.6049	1.2982	0.0177	0.1169
	C–H	0.6930	0.3806	1.821	0.3028	−0.8436	−0.8106	0.4774	−1.1765	0.0407
	O–H	0.774	0.1743	4.441	0.3830	−2.0511	−2.0095	1.2106	−2.8500	0.0207
acetaldehyde enol, anti (**a10e**)	C–C	0.5629	0.7513	0.749	0.3623	−0.8138	−0.5401	0.1282	−1.2257	0.5068
	C–Ha	0.6832	0.3916	1.745	0.2888	−0.7585	−0.7389	0.4328	−1.0646	0.0264
	C–Hb	0.6798	0.3942	1.725	0.2888	−0.7545	−0.7312	0.4238	−1.0620	0.0319
	C–O	0.4398	0.9284	0.474	0.2784	−0.6117	−0.5623	1.1267	−0.0473	0.0878
	C–H	0.6882	0.3894	1.768	0.2901	−0.8112	−0.7768	0.4518	−1.1362	0.0442
	O–H	0.7736	0.1745	4.434	0.3839	−2.0553	−2.0083	1.2102	−2.8534	0.0234
formamide (**11a**)	C–H	0.7020	0.3890	1.805	0.2963	−0.8125	−0.7952	−0.4693	−1.1384	0.0217
	C–O	0.3983	0.7945	0.501	0.4331	−1.2479	−1.1866	2.5004	0.0659	0.0516
	C–N	0.4538	0.8951	0.507	0.3269	−0.7394	−0.7362	0.7215	−0.7541	0.0043
	N–Ha	0.7479	0.2477	3.019	0.3530	−1.4014	−1.3258	0.7541	−1.9731	0.0570
	N–Hb	0.7430	0.2499	2.974	0.3559	−1.4027	−1.3214	0.7610	−1.9631	0.0615
formamide enol, HO syn NH anti (**11e**)	C–H	0.6996	0.3796	1.843	0.3023	−0.8435	−0.8199	−0.4848	−1.1785	0.0288
	C–O	0.4291	0.8999	0.477	0.3077	−0.7669	−0.6965	1.4123	−0.0511	0.1011
	O–H	0.7816	0.1709	4.575	0.3757	−2.0570	−2.0199	1.2437	−2.8332	0.0184
	C–N	0.4327	0.8139	0.532	0.4176	−1.1058	−0.8752	0.9990	−0.9820	0.2636
	N–H	0.7388	0.3019	2.447	0.3528	−1.3025	−1.2926	0.7909	−1.8042	0.0076

[a] r_A and r_B are the distances from the atoms to the bond critical point, $R = r_A/r_B$, ρ_c is the charge density at the critical point, the λ's are the second derivatives of ρ with respect to the coordinates, $\nabla^2\rho$ is the Laplacian of ρ, and ϵ is the ellipticity.

than the negative curvatures normal to the bond (λ_1 and λ_2), and as a result the Laplacian of ρ ($\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3$) has a large negative value. However, as the bonds become more polar, $\nabla^2\rho$ becomes less negative (such as with the C–N bonds), and with the C–O bonds, it sometimes attains a positive value. This is particularly true with a carbonyl C–O bond, which might best be represented by the dipolar structure.

Although an examination of the bond properties provides useful information, the changes in the atoms on bonding is of more interest. A quantitative description of the electron populations

Table VIII. Atom Properties of Allyl Anions

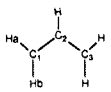
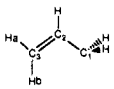
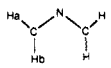
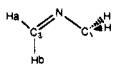
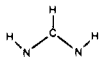
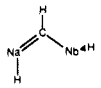
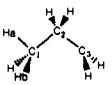
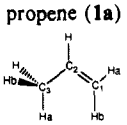
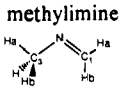
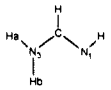
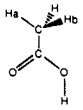
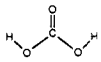
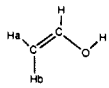
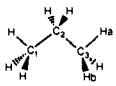
molecule	atom	n_π	n_T	T^a
allyl (**1**)	C1	1.3726	6.1811	37.6761
	C2	0.9136	6.0336	37.8169
	Ha(C1)	0.0800	1.1269	0.6561
	Hb(C1)	0.0712	1.1211	0.6532
	H(C2)	0.0382	1.1087	0.6670
	sum	3.9994	24.0005	116.4547
				(E = −116.4547)
allyl, rot. TS (**1r**)	C1	0.8022	6.2156	37.5316
	C2	0.8184	5.9944	37.7886
	C3	1.1066	6.1096	37.8077
	H(C1)	0.5724	1.1844	0.6680
	H(C2)	0.0358	1.1325	0.6644
	Ha(C3)	0.0494	1.1188	0.6600
	Hb(C3)	0.0424	1.0572	0.6336
	sum	3.9996	23.9969	116.4219
				(E = −116.4208)
2-azaallyl (**3**)	C	1.1834	5.5062	37.2910
	N	1.3494	8.4786	55.2331
	Ha	0.0762	1.1186	0.6581
	Hb	0.0654	1.1362	0.6578
	sum	3.9994	24.0006	132.4469
				(E = −132.4464)
2-azaallyl, rot TS (**3r**)	C1	0.8036	5.9814	37.3847
	N2	1.2746	8.4228	55.1452
	C3	0.7156	5.0889	37.2514
	H(C1)	0.5710	1.1726	0.6722
	Ha(C3)	0.0358	1.1160	0.6648
	Hb(C3)	0.0286	1.0491	0.6275
	sum	4.0002	24.0034	132.4180
				(E = −132.4153)
amidinate (**a4**) (anti)	N	1.6728	8.4369	54.9344
	C	0.5546	4.4565	36.8896
	H(N)	0.0350	0.7542	0.5358
	H(C)	0.0294	1.1605	0.6784
	sum	3.9996	23.9992	148.5084
				(E = −148.5094)
amidinate (**s4**) (syn)	N	1.6870	8.4515	54.9345
	C	0.5354	4.4678	36.9175
	H(N)	0.0312	0.7623	0.5312
	H(C)	0.0276	1.1048	0.6712
	sum	3.9994	24.0002	148.5201
				(E = −148.5199)
amidinate, rot TS (**4r**)	C		4.5618	36.9672
	Na		8.4679	55.0562
	Nb		8.4134	54.78720
	H(Na)		0.7126	0.5100
	H(Nb)		0.7228	0.5072
	H(C)		1.1238	0.6670
	sum		24.0023	148.4893
				(E = −148.4876)
formate (**5**)	C	0.3954	3.9538	36.4804
	H	0.0198	1.1533	0.6726
	O	1.7922	9.4462	75.5522
	sum	3.9996	23.9995	188.2574
				(E = −188.2576)
acetate (**6**)	C(Me)	0.8828	5.9076	37.7425
	Ha	0.0292	1.0785	0.6514
	Hb	0.5400	1.0778	0.6473
	C	0.4118	3.9640	36.4920
	O1	1.7926	9.4462	75.5581
	O2	1.8042	9.4511	75.5697
	sum	6.0006	32.0030	227.3083
				(E = −227.3081)
bicarbonate (**7**)	C	0.3744	3.4112	36.1209
	O1	1.8372	9.4591	75.5870
	O2	1.8172	9.4394	75.6007
	O3	1.9590	9.2885	75.5091
	H	0.0130	0.4021	0.3619
	sum	6.0008	32.0003	263.1796
				(E = −263.1790)
nitrite (**8**)	N	0.7726	6.4129	53.8671
	O	1.6136	8.7933	75.1405
	sum	3.9998	23.9995	204.1481
				(E = −204.1484)
nitrate (**9**)	N	0.9706	5.9776	53.7475
	O	1.6762	8.6726	75.0883
	sum	5.9992	31.9954	279.0124
				(E = −279.0113)
1-propyl	C1	0.7986	6.2682	37.5408
	C2	0.8620	5.8209	37.6492
	C3	0.8802	5.8808	37.7224
	H(C1)	0.5910	1.2089	0.6765
	H(C2)	0.5696	1.1369	0.6788
	Ha(C3)	0.0318	1.1396	0.6656
	Hb(C3)	0.5534	1.1012	0.6566
	sum	6.0006	26.0035	117.6018
				(E = −117.6014)
acetaldehyde enolate (**10**)	C1	1.3380	6.1879	37.7296
	Ha	0.0702	1.1238	0.6562
	Hb	0.0646	1.1038	0.6454
	C2	0.6688	4.9963	37.1666
	H	0.0320	1.1541	0.67654
	O	1.8262	9.4353	75.4796
	sum	3.9998	24.0012	152.3528
				(E = −152.3511)
acetaldehyde enolate 90° (**10r**)	C1	0.8196	6.2610	37.5815
	H	0.5456	1.1432	0.6513
	C2	0.4142	4.9551	37.1404
	H	0.0166	1.1182	0.6678
	O	1.6580	9.3801	75.6051
	sum	6.9996	24.0008	152.2974
				(E = −152.2964)
acetaldehyde enolate, 270°	C1	0.7876	6.2028	37.5628
	H	0.5572	1.1674	0.6611
	C2	0.4336	4.9492	37.1294
	H	0.0192	1.1462	0.6676
	O	1.6454	9.3687	75.6146
	sum	4.0002	24.0017	152.2966
				(E = −152.2959)
formamide enolate, syn (**s11**)	C	0.4676	4.1994	36.6938
	H	0.0248	1.1320	0.6728
	O	1.8224	9.4529	75.5130
	N	1.6566	8.4844	54.9931
	H	0.0286	0.7322	0.5182
	sum	4.0000	24.0009	168.3909
				(E = −168.3901)
formamide enolate, anti (**a11**)	C	0.4724	4.1855	36.6728
	H	0.0254	1.1651	0.6776
	O	1.8116	9.4412	75.5315
	N	1.6578	9.4412	75.5315
	H	0.0330	0.7491	0.5327
	sum	4.0002	24.0019	168.3856
				(E = −168.3835)
formamide enolate, rot 90° (**11r**)	C		4.2758	36.7357
	H		1.1489	0.6684
	O		9.4115	75.5828
	N		8.4660	54.8646
	H		0.6969	0.4936
	sum		23.9991	168.3451
				(E = −168.3460)
propene (**1a**)	C1	0.9730	5.9761	37.7740
	C2	0.9342	6.0184	37.8306
	C3(Me)	0.9138	5.8431	37.7053
	Ha(C1)	0.0346	1.0144	0.6263
	Hb(C1)	0.0340	1.0212	0.6281
	H(C2)	0.0322	1.0242	0.6350
	Ha(C3)	0.0270	1.0354	0.6368
	Hb(C3)	0.5254	1.0337	0.6345
	sum	3.9996	24.0002	117.1051
				(E = −117.1049)
methylimine (**3a**)	C1	0.6266	5.0521	37.2395
	N	1.3650	8.4311	55.2317
	C3	0.8944	5.4045	37.4574
	Ha(C1)	0.0248	0.9970	0.6258
	Hb(C1)	0.0244	1.0266	0.6319
	Ha(C3)	0.0270	1.0563	0.6476
	Hb(C3)	0.5188	1.1053	0.6332
	sum	3.9998	23.9982	133.1003
				(E = −133.0992)

Table VIII (Continued)

molecule	atom	n_π	n_T	T^a
amidine (anti) (**a4a**)	N1	1.5086	8.3944	55.1039
	C	0.5408	4.4525	36.9000
	N3	1.8414	8.3309	55.0949
	H(N1)	0.0238	0.6428	0.4865
	H(C)	0.0224	1.0082	0.6334
	Ha(N3)	0.0332	0.5956	0.4615
	Hb(N3)	0.0298	0.5765	0.4501
	sum	4.0000	24.0009	149.1303
				(E = −149.1297)
formic acid (**5a**)	C	0.3882	4.0863	36.5978
	H	0.0126	0.9414	0.6073
	=O	1.6724	9.3262	75.6738
	O	1.9170	9.2923	75.6174
	H	0.0094	0.3510	0.3264
	sum	3.9996	23.9972	188.8224
				(E = −188.8260)
acetic acid (**6a**)	C(Me)	0.9316	5.8490	37.7398
	Ha	0.0244	0.9844	0.6167
	Hb	0.4998	0.9891	0.6142
	C	0.4202	4.1914	36.6610
	=O	1.6876	9.3458	75.6867
	O	1.9274	9.2982	75.6225
	H	0.0094	0.3528	0.3284
	sum	6.0002	31.9998	227.8835
				(E = −227.8838)
carbonic acid (**7a**)	C	0.3628	3.3703	36.1036
	=O	1.7498	9.3716	75.7021
	O	1.9344	9.2906	75.6453
	H	0.0092	0.3386	0.3213
	sum	5.9998	32.0003	263.7389
				(E = −263.7384)
nitrous acid (**8a**)	N	0.7702	6.2506	53.8136
	O1	1.3472	8.5449	75.2400
	O2	1.8722	8.8443	75.3154
	H	0.0104	0.3586	0.3355
	sum	4.0000	23.9984	204.7045
				(E = −204.7072)
nitric acid (**9a**)	N	1.0066	5.9396	53.7418
	O1	1.5734	8.5179	75.1046
	O2	1.5134	8.4648	75.0982
	O3	1.8978	8.7533	75.2778
	H	0.0086	0.3251	0.3124
	sum	5.9998	32.0007	279.5348
				(E = −279.5349)
acetaldehyde (**10a**)	C(Me)	0.9160	5.8999	37.7654
	Ha	0.0238	0.9890	0.6159
	Hb	0.5084	1.0099	0.6205
	C	0.4446	4.7998	37.0742
	H	0.0156	1.0201	0.6360
	O	1.5824	9.2730	75.6303
	sum	3.9992	24.0016	152.9628
acetaldehyde, enol anti (**a10e**)	C1	0.9842	5.8347	37.6907
	Ha	0.0340	0.9869	0.6112
	Hb	0.0374	0.9985	0.6171
	C2	0.9350	5.5408	37.5294
	H	0.0302	1.0008	0.6311
	O	1.9678	9.2597	75.0991
	H	0.0118	0.3767	0.3478
	sum	4.0004	23.9981	152.9372
				(E = −152.9393)
acetaldehyde, enol syn (**s10e**)	C	1.0308	5.8720	37.6923
	Ha	0.0378	1.0228	0.6249
	Hb	0.0388	0.9936	0.6153
	C	0.8916	5.4964	37.5063
	H	0.0266	0.9684	0.6191
	O	1.9634	9.2696	75.5387
	H	0.0110	0.3776	0.3461
	sum	4.0000	24.0004	152.9427
				(E = −152.9421)
formamide (**11a**)	C	0.4144	4.1588	36.6649
	H(C)	0.0156	0.9998	0.6298
	O	1.6958	9.3324	75.6410
	N	1.8320	8.3901	55.1689
	Ha(N)	0.0204	0.5545	0.4375
	Hb(N)	0.0222	0.5679	0.4467
	sum	4.0004	24.0035	168.9888
				(E = −168.9885)
formamide enol HO syn, NH anti (**11e**)	C	0.5190	4.3513	36.8079
	H(C)	0.0186	0.9627	0.6162
	O	1.9420	9.2915	75.5944
	H(O)	0.0096	0.3556	0.3298
	N	1.4918	8.4170	55.1454
	H(N)	0.0190	0.6238	0.4756
	sum	4.0000	24.0019	168.9693
				(E = −168.9683)
propane	C1	0.8976	5.8498	37.7086
	C2	0.9056	5.8280	37.6958
	Ha(C1)	0.0278	1.0537	0.6442
	Hb(C1)	0.5390	1.0571	0.6453
	H(C2)	0.5438	1.0678	0.6573
	sum	6.0000	25.9990	118.2972
				(E = −118.2964)

[a] The kinetic energies were corrected for the small virial defect found in the RHF calculations by multiplying them by $-V/T - 1$. The values in parentheses are the total energies found in the RHF calculations.

may be obtained by using Bader's theory of atoms in molecules.[29] Atoms are defined by locating the zero-flux surfaces which separate pairs of bonded atoms. These surfaces are obtained by starting at a bond critical point and developing rays which move along paths of most rapid decrease in charge density. A set of these rays formed by starting in different directions from the critical point will produce a surface separating a given pair of atoms. The set of these surfaces, one per pair of bonded atoms, serves to separate the molecule into a set of atomic subregions. This separation is unique, and the usual quantum mechanical quantities, such as the virial theorem, are satisfied within each of the atomic subregions.

Integration of the charge density within each volume element gives the electron population. The kinetic energy may also be calculated at each point, and integration over the volume element will give the kinetic energy associated with each atom, Ω. Since for each atom $E_\Omega = V_\Omega + T_\Omega$, and the virial theorem requires that $V_\Omega = -2T_\Omega$, a corollary of the virial theorem is that the total energy of an atom is given by the negative of its kinetic energy.

The results of the numerical integrations are given in Table VIII. The total electron population for each atom is given by n_T, and that for the out-of-plane orbitals is given by n_π. For ease of comparison, the populations have been converted to atomic charges by subtracting n_T from the atomic number, Z, and are shown in Figure 7. In propene, the sum of the atomic charges for each carbon and its associated hydrogens (group charge) is small. The planar allyl anion has a relatively small group charge at the central carbon, and most of the charge is borne by the terminal carbons. The rotated allyl anion, on the other hand, has a marked difference between the terminal carbons, indicating considerable charge localization.

Whereas the group charges in propene were small, in *N*-methylimine, the group charges become fairly large as a result of the electronegative nitrogen. It bears a large negative charge. A comparison of the 2-azaallyl ion with the imine shows that the charge at nitrogen is unchanged and that the net negative charge in the anion serves to reduce the positive charges at the terminal groups in the imine. In this way, the effect of proton abstraction is similar in propene and *N*-methylimine.

The charges assigned to the atoms may at first appear surprising. An examination of projection density plots (Figure 6) shows the reason for the large charges. In allyl anion, the three carbons have about the same size. However, in 2-azaallyl ion, it can be seen that the nitrogen size is considerably greater than

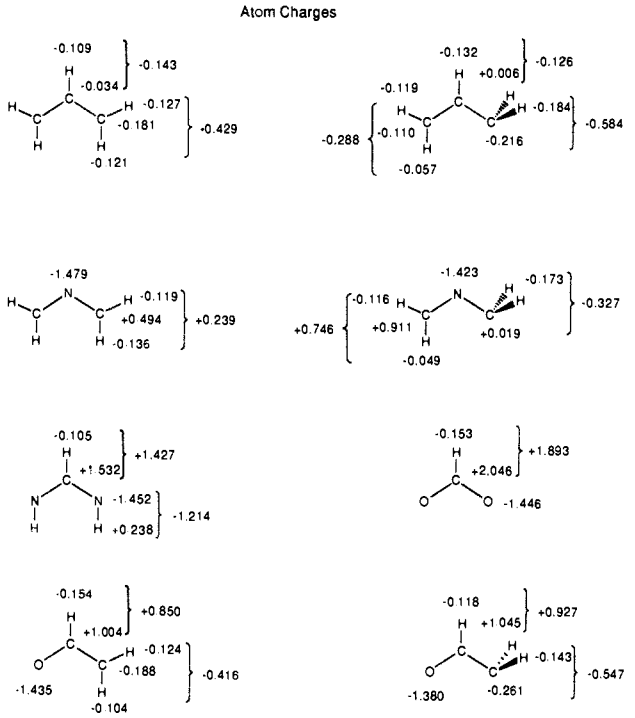


Figure 7. Atomic charges for allyl anions.

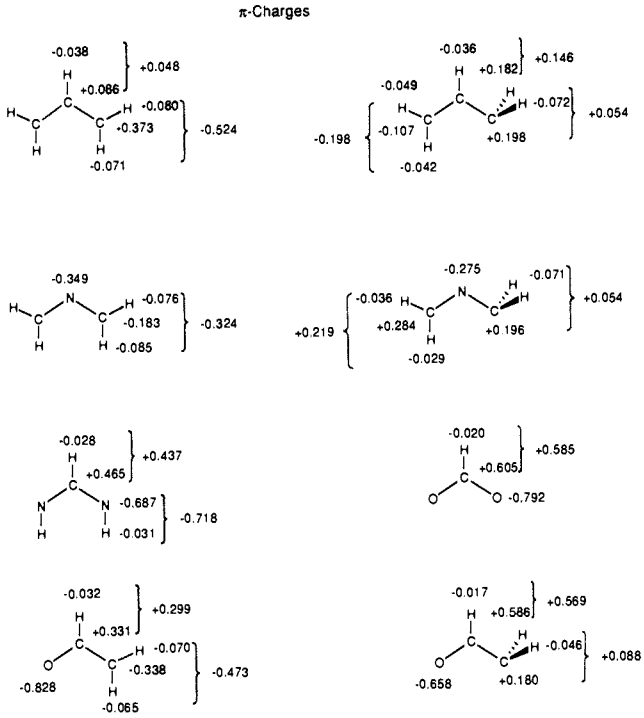


Figure 8. π-Charges for allyl anions.

that for the carbons. This results from the higher electronegativity of nitrogen, leading to a charge shift from carbon to nitrogen and a shift of the bond critical point away from the nitrogen. The large charge at nitrogen then results from a combination of the charge shift toward nitrogen, and the larger volume element for nitrogen resulting from the shift in bond critical point. The same effect is seen in amidinate ion and in formate ion.

It may be noted that a characteristic of the charge distribution for the more stable anions is a $-+-$ pattern for the three atoms which would lead to internal coulombic stabilization. In the case of formate ion, replacement of the carbon bound hydrogen by an electron-releasing methyl group decreases the central carbon's positive charge and decreases the stability of the ion. Conversely, an electron-withdrawing hydroxy group increases its stability.

In conjugated systems, there is interest in examining the charges associated with the π-system, and the values derived from the numerical integration of the charge density are shown in Figure 8. In allyl anion, the charge is largely localized at the terminal carbons, and the central CH group is almost neutral. When the ion is rotated, the charge becomes localized in the σ system, and the π-system is neutral. The carbon bearing most of the negative charge now has a positive π-charge, resulting from the polarization of the π-electrons in the presence of the field of the σ-electrons. In the 2-azaallyl anion, the charge in the π-system is distributed evenly between the nitrogen and the CH_2 groups as a result of the greater electronegativity of nitrogen. On rotation, both methylene groups lose π-electron population to the electronegative nitrogen. When the terminal atoms have the higher electronegativity, as in the 2-azaallyl ion (**4**), they bear a large π-population, and the central carbon now has a positive π-charge. The same type of charge distribution is found with the carboxylate ion.

The atomic and π-charges for acetaldehyde enolate (**10**) and its 90° rotated form (**10r**) also are shown in Figures 7 and 8. The terminal methylene groups have charges which are remarkably similar to those of allyl anion (**1**) showing that the same factors are involved with both ions. This is in accord with the finding that the rotational barrier in **10** is only 50% larger than that in **1**. The C–O bond is strongly polarized as is generally found. The charge distribution found herein is, of course, only appropriate to the gas phase where there is strong driving force for spreading the charge over a large volume element. It would be interesting to know how the charge distribution is perturbed by solvent and/or cations. This will be the subject of a later study.

Conclusions

The calculations have shown that it is possible to calculate ionization energies satisfactorily provided a sufficiently large and flexible basis set is used, and correction is made for electron correlation. There is good evidence for stabilization due to electron delocalization in allyl cation, but relatively little stabilization was found with the anion. This appears to be generally true for allyl anions. These anions are stabilized by electronegative atoms at the terminal positions, which leads to a $-+-$ charge distribution for the atoms of the allyl system. This will lead to internal coulombic stabilization. The stabilizing effects of electronegative terminal atoms are approximately additive, so that the ionization energy of acetaldehyde is close to the average of that of propene and formic acid.

Calculations

The SCF calculations were carried out by using GAUSSIAN 86 and 88,[30] and the analysis of the wave functions was done with a modified version of PROAIMS.[31] The calculations were carried out by using either a VAX-GPX workstation or a TRACE 7/200 computer, both of which were provided via NIH grants. The numerical integrations of the charge density was carried out by using a CSPI array processor which was provided by a DOE instrument grant.

Acknowledgment. This investigation was supported by a grant from the National Institutes of Health.

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Supplementary Material Available: Vibrational frequencies (unscaled) for propane, 1-propyl cation, 1-propyl anion, propene, allyl cation, allyl anion, formic acid, and formate ion that were calculated with the 6-31G* basis set (2 pages). Ordering information is given on any current masthead page.

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