Ab Initio SCF Treatment of Allyl Anion and Distorted Propenyl Anions[1]

Donald W. Boerth and Andrew Streitwieser, Jr.*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received April 15, 1977

Abstract: Ab initio SCF calculations have been performed on the allyl anion and distorted propenyl anions. The structure of allyl anion has been clarified by partial optimization of geometry. The carbanion has a CCC skeletal angle of 132.5° which is much larger than the normal sp[2] bond angle. In addition, calculations with the STO-3G basis set indicate that both pyramidal and planar structures are of essentially equal energy with no apparent inversion barrier. The calculations on distorted propenyl anions provide a simple model for acidity effects found in cyclic olefins. Allyl protons are predicted to be more acidic in larger rings (i.e., large CCC angle), whereas vinyl protons are predicted to be of greater acidity in small ring systems (i.e., small CCC angle).

Introduction

Allylic systems (cation, radical, and anion) have been the subject of extensive experimental and theoretical investigation. Much of the interest in these systems originated because allylic intermediates are generated in a wide variety of chemical reactions[2-4] and because allylic systems are the simplest of all conjugated π-electron systems. From a theoretical point of view, it is little wonder that the allyl cation, anion, and radical have been studied at considerable length in the π-electron approximation. These studies encompass molecular orbital,[5] valence bond,[6] and Linnett's nonpairing[7] treatments. Several other semiempirical ($\sigma + \pi$) calculations on allyl systems have been reported.[8]

In terms of ab initio SCF treatments the allyl cation and radical are well-understood species. These systems have been studied with a variety of different basis sets, with and without configuration interaction.[9-17] The geometry of the cation has been optimized in work by Pople,[10] Clark and Armstrong,[13] and Peyerimhoff and Buenker.[9] Similar rigorous studies of the geometry of the radical appear to be lacking, except for the work of Peyerimhoff and Buenker,[9] who extended their structural calculations on the cation to the radical via Koopmans' theorem. Considerable interest in the calculations on the radical has been focused on proton coupling constants.[14] In addition, the potential surfaces related to conrotatory and disrotatory ring openings of the corresponding cyclopropyl systems have been studied for both cation[10,13,16,17] and radical.[16,17]

In contrast to the cation and radical, the allyl anion has been only minimally characterized by ab initio treatments.[9,11,16-18] A large part of the earlier consideration of the allyl anion stemmed from interest in the potential energy surfaces for electrocyclic transformation of cyclopropyl to allyl anion.[16-18] In two studies[9,17] the primary concern was the allyl cation. In these, the anion results were obtained indirectly by extrapolation via Koopmans' theorem. In none of these cases has an allyl anion with fully optimized geometry been described.

The present theoretical investigation of the allyl anion derives chiefly from the fact that allyl anion in one form or another is believed to be a transition state or intermediate in a number of reactions,[4] some of which have been studied experimentally in our group.[19] For example, some marked differences in kinetic acidities of allylic hydrogens in cyclic alkenes have been observed that are believed to be the result of conformational effects imposed by the ring system.

Our present objectives are twofold: (1) to ascertain the structure of the allyl anion and to explore the effects of deformation of the CCC angle on the total energy; (2) to understand the effects on energy of CCC angle perturbations in propylene and the corresponding propenyl anions. From these calculations we hope to obtain semiquantitatively the proton affinities of various allyl and vinyl carbanions derived from distorted propylenes. In this type of approach the calculated absolute proton affinities are, of course, less significant than the relative trends introduced by variations in the CCC angle.

Allyl Anion

Calculations performed on the allyl anion were carried out chiefly at the STO-3G level.[20] Significant conclusions from these calculations were reexamined with the 4-31G basis set.[21] The exponents for the STO-3G calculations were the standard exponents described previously for neutral species.[20] Although exponents optimized for anions have been recommended for minimum-basis sets,[22,23] the computation with the more flexible basis set revealed only minor differences in the results. All calculations were performed with the SCF program GAUSSIAN 70.[24]

As regards the structure of allyl anion attention was focused on the carbon–carbon bond length, the CCC skeletal internuclear angle (θ), and methylene deformation from the nodal plane; i.e., the question of a planar or pyramidal anion. Other geometrical parameters could have been optimized, but these were not deemed of sufficient importance to warrant the expense of the calculation. In addition, optimization of some parameters might have led to unrealistic results, especially in the case of CH bonds. Minimum basis sets applied to anions are known to give abnormally long CH bonds.[23,25] In this part of the study all CH bond lengths were set at 1.08 Å and HCH angles were fixed at 120° as in a number of other calculations.[12,16,18] The 2 hydrogen was positioned on the bisector of the CCC angle.

CC Bond Length

Separate optimization of the C_1C_2 and C_2C_3 bond lengths confirmed that the structure with equal CC bonds (to within ±0.001 Å) is energetically preferred. An optimized CC bond length of 1.378 Å for the anion was obtained in close agreement with the result of Clark and Armstrong.[18] Calculations at the 4-31G level reveal an only slightly longer bond length of 1.390 Å. A lengthening upon proceeding from a minimum-basis set to a double-ζ basis has been observed for other systems.[23] Compared to the published STO-3G results for the cation,[10] the anion CC bonds are slightly shorter (Figure 1).[26]

CCC Bond Angles

The potential surface for CCC skeletal deformation (Table I and Figure 2) shows, not unexpectedly, that an increase in
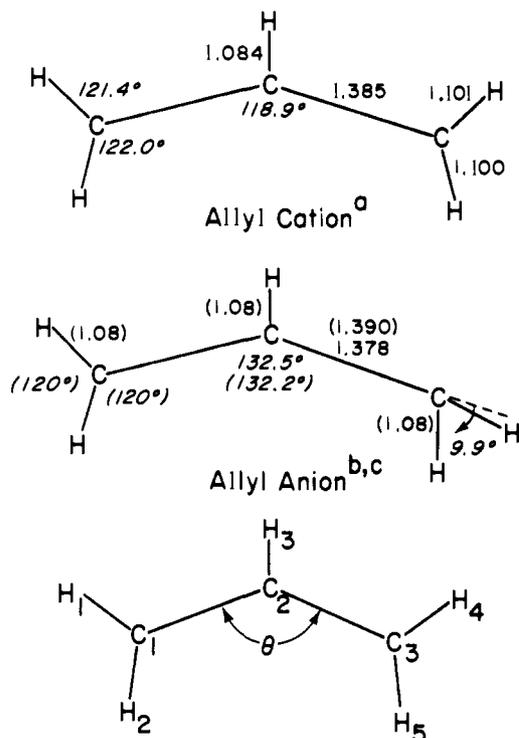
Figure 1. Structure of allylic systems. (a) STO-3G structure of allyl cation from ref 10. (b) Present STO-3G results for allyl anion. (c) Assumed values are in parentheses; 4-31G results are in brackets.

Table I. Energies of Distorted Allyl Anions (Symmetric)

θCCC,	Total energy, au	
deg	4-31G (CC = 1.390 Å)^a	STO-3G (CC = 1.378 Å)^a
110	−116.1974	
115	−116.2095	−114.8206
120	−116.2178	−114.8291
125	−116.2231	−114.8343
130	−116.2256	−114.8366
135	−116.2257	−114.8365
140		−114.8341

^{a} Optimized bond lengths (with $C_1C_2 = C_2C_3$); CH = 1.08 Å, HCH = 120°.

the energy of the anion follows contraction of the CCC angle. In appearance, the potential curves are qualitatively similar to those for the cation and radical.[9] The distinguishing feature for the anion is the value of the equilibrium angle of 132.5°. This value is substantially larger than that published for the cation (123°[9] and 118.9°[10]) and for the radical (127°).[9] An expansion of the normal sp² angle appears to compensate for the repulsion of electrons in the terminal p orbitals of the radical and anion; that is, antiaromatic character of the allyl anion, similar to that of cyclopropenyl anion, results in expansion of the CCC angle from the equilibrium angle of propene (125°) (vide infra). In contrast, homoaromatic behavior of the allyl cation, like that of cyclopropenyl cation, accounts for contraction of the CCC angle in the cation. The CCC angle value for allyl anion obtained in the present work is in reasonably close agreement to that (134°) estimated by application of Koopmans' theorem to the cation results.[9] Although understandably lower in energy, the 4-31G potential curve is similar to that calculated at the minimum-basis set level. The optimum angle of 132.2° is within 0.30° of the STO-3G value. This comparison provides added evidence for the reliability of the minimum-basis results for characterization of these systems.

Considerable insight into the cause of the instability of de-
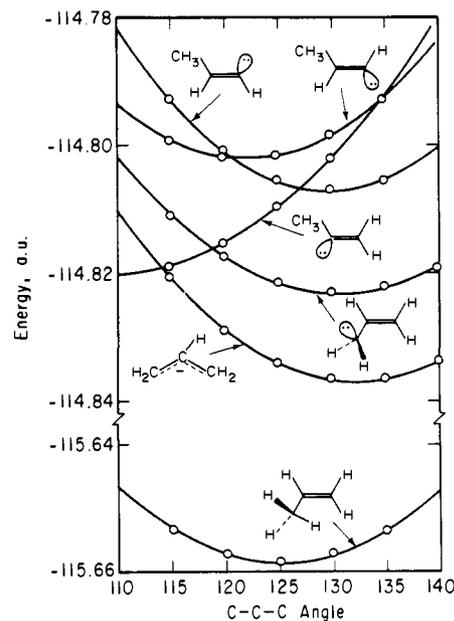
Figure 2. Energies of allyl and propenyl anions and of propylene as a function of CCC bond angle.

Table II. Total Overlap Populations

θ, deg	H_2H_5	C_1C_2	C_1C_3	E anion, au
115	−4.431 × 10⁻⁴	1.0489	−0.1044	−114.8206
120	8.691 × 10⁻⁴	1.0508	−0.0881	−114.8291
125	1.389 × 10⁻³	1.0520	−0.0748	−114.8343
130	1.494 × 10⁻³	1.0524	−0.0640	−114.8366

formed allyl anions can be gained by investigation of the bond overlap populations (Table II). The C_1C_3 overlap population reflects a substantial degree of antiaromaticity in the allyl anion with a CCC angle of 115°. Here the absolute value of the overlap population is already as much as 15% of that for a normal bond. Examination of H_2H_5 overlap populations reveals that the repulsion of terminal hydrogens is negligible even at small angles; hence, "steric hindrance" between terminal hydrogens does not appear to contribute significantly to the instability of contracted allyl anions.

The diagram of energies of valence molecular orbitals (Figure 3) emphasizes factors contributing to the relative stability of allyl anions. The unbound, highest occupied molecular orbital (1a₂) is of significantly lower energy at larger CCC skeletal angles. This result is not surprising since this is π_2 of the allyl system, and from the nodal properties of this MO one would expect antiaromatic behavior between the terminal p_π orbitals. The stabilization of MOs 2b₂ and 4b₂ at larger angles also contributes to an expansion of the CCC angle. It is interesting to note that the terminal hydrogens, 2-H and 5-H, do not have large coefficients in the wave functions for these MOs. These findings substantiate the conclusions based on the overlap populations.

It is doubtless significant that the molecular orbital diagrams derived from the 4-31G and STO-3G calculations are qualitatively alike. Although the HOMO is lower in energy in the 4-31G calculation, it is still unbound. The only significant differences between the STO-3G and 4-31G diagrams occur in the virtual orbitals. In the 4-31G results, the MO 2b₁ (π_3) crosses the MO 7a₁ (σ^*), whereas with the STO-3G basis these MOs do not cross each other. This discrepancy does not cause a problem here because only the ground state is considered.

The resulting structure for allyl anion is similar to that found in the symmetrical allyllithium ion pair structure calculated recently by Bongini et al.[27] The CC bond length of 1.39 Å
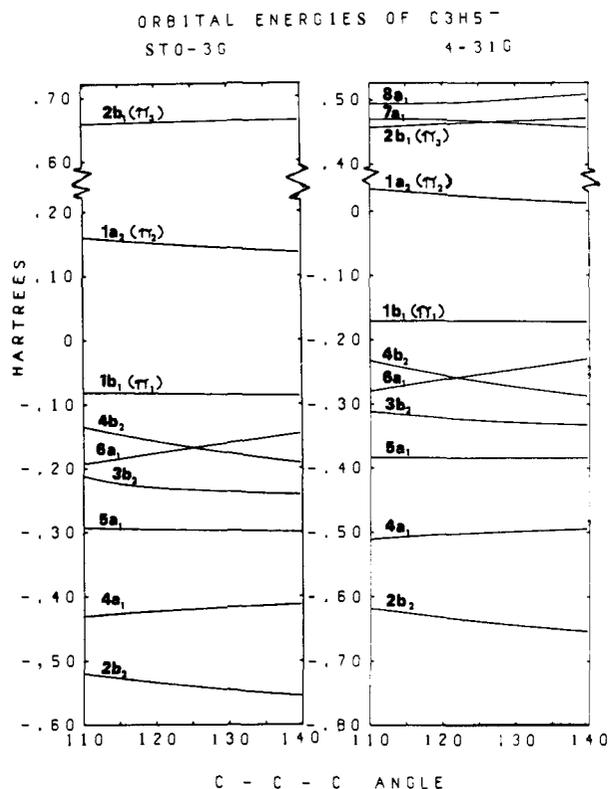
Figure 3. A comparison of STO-3G and 4-31G MO energy levels for allyl anion as a function of CCC bond angle.

Figure 4. Allyl anion inversion potential calculated by STO-3G.

Table III. Energies for Allyl Anion with Out-of-Plane Deformation of Methylene

	Energy,[b] au	Energy,[b] au
ϕ,[a] deg	$C_1C_2 = C_2C_3 = 1.378$[c]	$C_1C_2 = 1.368, C_2C_3 = 1.388$[c]
0	−114.836 87 (0.015)	−114.836 68 (0.134)
5	−114.836 88 (0.008)	−114.836 69 (0.128)
9.9	−114.836 89 (0.000)	
10	−114.836 89 (0.000)	−114.836 73 (0.103)
15	−114.836 86 (0.021)	−114.836 74 (0.096)
20	−114.836 66 (0.147)	−114.836 62 (0.172)
25	−114.836 10 (0.498)	−114.836 15 (0.463)

[a] Out-of-plane angle; angle of methylene plane compared to molecular plane. [b] Energy in kcal/mol in parentheses relative to optimum energy at ϕ = 9.9°. [c] CCC = 132.5°, HC_1H = 120°, HC_3H = 120°, CH = 1.08°, C_2C_3H = 120°.

found in their STO-3G study agrees well with our finding for the free carbanion whereas their CCC bond angle of 127° is significantly less than that for the free anion. The Coulombic effect of the lithium cation provides an additional force that promotes contraction of the bond angle from that in the free anion.

From all indications, the limited-basis set (STO-3G) with "standard" exponents gives reasonable results for the allyl anion. The calculations at the 4-31G level demonstrate that ab initio SCF methods, even at the minimum-basis set level, provide a satisfactory theoretical model which confirms our earlier expectations for this system. Further computations on propene and allyl and other propenyl anions were, therefore, conducted only at the STO-3G level.

Allyl Anion: Planar or Pyramidal?

Both Shanshal[8b] and Gründler,[8a] using semiempirical methods, found the pyramidal anion to be more stable than the planar form by 16–17 kcal mol⁻¹. In the present calculation, this finding was tested by ab initio methods. The energetics of inversion were followed by incrementally depressing one set of terminal methylene hydrogens out of the nodal plane by an angle ϕ (Table III). Although these computations agree qualitatively with the semiempirical results, the difference at the STO-3G level between planar and pyramidal forms is hardly significant (less than 0.1 kcal mol⁻¹). Further optimization of geometry and use of larger basis sets with polarization functions may increase this difference, but the inversion barrier is likely to remain relatively small.

Inspection of the results summarized in Figure 4 reveals a long, flat valley in the region of the inversion potential surface for an allyl anion with equal carbon–carbon bonds. The qualitative conclusion based on the STO-3G results is that the terminal methylene group is not at all rigidly held in either the planar or pyramidal geometry; i.e., methylene wagging motion is quite unhindered.

It is a bit surprising that at the STO-3G level the pyramidal

allyl anion (no longer of C_{2v} symmetry) prefers equal CC bonds (to within ±0.001 Å). Contrary to chemical intuition, a less stable anion is generated by shortening the C_1C_2 bond and lengthening the C_2C_3 bond. This result obtains for both pyramidal and planar allyl anions. For the asymmetric anion the same general features appear in the inversion potential surface. However, the minimum energy pyramidal geometry is now shifted to larger deviations from planarity.

Propene and Propenyl Anions

Distorted propenes and propenyl anions derived therefrom were considered as models for studies of the acidities of cycloalkenes. Complete ab initio calculations on the cycloalkenes and their anions would require considerable optimization of geometry. As a consequence, such computations would be prohibitively expensive even at the minimum-basis set level. Propene, however, is a small system for which such calculations are practical. Furthermore, the STO-3G basis set has been shown to be adequate for both propene[28] and allyl anion (vide supra). Standard exponents were again used for both propene and the propenyl anions. Standard hydrocarbon geometries[21] were employed for propene, except for the CCC angle, θ. The methyl hydrogens were positioned in accord with both experimental[29] and theoretical[28] geometries; i.e., one CH bond of a tetrahedral methyl eclipses the C=C double bond. For the carbanions the "subtract" procedure[23,25] was employed to arrive at the geometries. Thus, the reference structure for each anion is that of the neutral parent from which a proton is removed without further alteration of geometry. In some cases, it was found useful to permit one additional degree of freedom, rotation about the carbon–carbon single bond. These have been

Table IV. Total Energies (au) of Distorted Propenes and Propenyl Anions[a]

θ, deg	Propene $\alpha = \beta = 60°$	"Rotated subtract" 3-propenyl anion[b]	"Subtract" 3-propenyl anion[c] ($\alpha = 60°, \beta = 60°$)	2-Propenyl anion	cis-1-Propenyl anion	trans-1-Propenyl anion
110	−115.6464	−114.8009	−114.7930	−114.8199	−114.7932	−114.7808
115	−115.6537	−114.8110	−114.8040	−114.8193	−114.7993	−114.7930
120	−115.6575	−114.8177	−114.8113	−114.8156	−114.8019	−114.8010
125	−115.6585	−114.8216	−114.8156	−114.8096	−114.8015	−114.8054
130	−115.6572	−114.8231	−114.8173	−114.8019	−114.7985	−114.8070
135	−115.6538	−114.8223	−114.8168	−114.7929	−114.7930	−114.8058

[a] $C_1C_2 = 1.33$, $C_2C_3 = 1.531$, $C_1H_1 = C_1H_2 = C_2H_3 = 1.076$, $C_3H_4 = 1.099$ Å, $H_1C_1C_2 = 121.7$, $C_2C_3H = 109.5$, $H_4C_3H_5 = 109.5°$. [b] Corresponds to ref 19, Figure 5, for $\alpha = 90°, \beta = \gamma = 30°$. [c] Corresponds to ref 19, Figure 5, for $\alpha = \beta = 60°, \gamma = 0°$.

Table V. Proton Affinities for Propenyl Anions (au)

θ, deg	"Rotated substract" 3-propenyl anion[a]	"Subtract" 3-propenyl anion[b] ($\alpha = 60°$)	2-Propenyl anion	cis-1-Propenyl anion	trans-1-Propenyl anion
110	0.8455	0.8534	0.8265	0.8532	0.8657
115	0.8427	0.8497	0.8344	0.8544	0.8607
120	0.8397₅	0.8462	0.8419	0.8556	0.8565
125	0.8369	0.8429	0.8489	0.8570	0.8531
130	0.8341	0.8399	0.8553	0.8587	0.8502
135	0.8315	0.8370	0.8608	0.8607	0.8480

[a] See Table IV, footnote b. [b] See Table IV, footnote c.

designated "rotated subtract" ions for convenience of notation. Results are summarized in Tables IV and V.

Potential Surfaces for CCC Skeletal Deformations

Although an optimum CCC angle of 124.7° for propene was previously calculated by Radom and Pople,[28a] a portion of the CCC potential surface was required here for computation of the acidities of the various hydrogens in distorted propenes. The potential surface presented in Figure 2 appears symmetric over a wide range of angle deformation. The angle corresponding to minimum energy is 125.0°, in reasonable agreement with that of Radom and Pople[28a] and with experiment.[29,30]

Removal of one of the two nonplanar methyl protons from propene generates a "subtract" pyramidal allyl anion with the lone pair oriented 60° from the nodal plane. This is, however, not the preferred orientation for the lone pair. Rotation by 30° about the carbon–carbon single bond leads to an anion with the lone pair eclipsing the neighboring p_π and with methylene CCCH dihedral angles of 30°; this is the most stable "rotated subtract" ion. The potential surfaces for these allyl anions appear to be almost indistinguishable. Not surprisingly, these are also similar to the surfaces for the planar symmetric (C_{2v}) allyl anion studied at the STO-3G and 4-31G levels. The anticipated expansion of the propene CCC angle upon methyl proton removal is also observed for these two "subtract" ions. The CCC angle minima for the "subtract" and "rotated subtract" carbanions occur at 131.6 and 131.2°, respectively.

Loss of one of the vinylic protons to produce either the cis-1-propenyl, trans-1-propenyl, or 2-propenyl anion provides an interesting theoretical backdrop against which a number of experimental findings[4d,19,31,32] can be compared. We consider first the anions themselves and later the predicted acidities. Removal of the proton from the 2 position yields the most stable vinyl anion; furthermore, a decrease in angle results in a decrease in the energy of the anion formed. The optimum angle for 2-propenyl anion is predicted to be ≲110°. The potential surfaces for cis- and trans-1-propenyl anions are similar to those of the allyl anions in that a decrease in angle destabi-
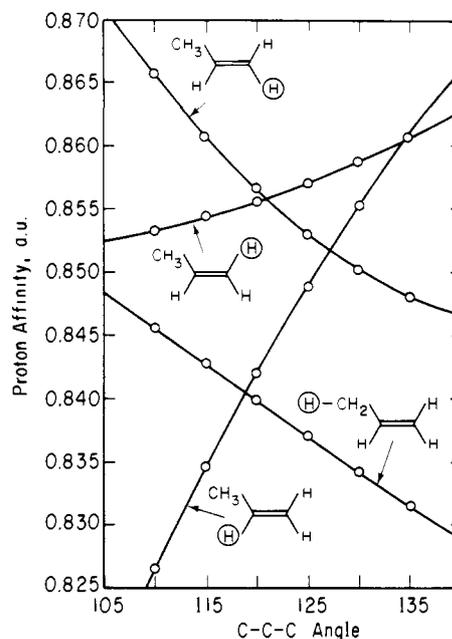
Figure 5. Proton affinities as a function of the CCC bond angle of allyl and propenyl anions derived from the indicated propenes.

lizes the anion. The minimum energy conformations, however, occur at somewhat smaller angles than for the allyl anions (122.0° for trans, 130.7° for cis).

The ab initio results represented here demonstrate that the vinylic anions are generally less stable than the allylic anions. The only exception is that of the 2-propenyl anion where at small angles (<119°) it is predicted to be the most stable of the subtract anions. These ab initio results stand in contrast to the semiempirical work of Gründler.[8a] In that study (presumably with an sp² angle of 120°), the 2-propenyl anion was predicted to be more stable than both the symmetric planar and the pyramidal allyl anions. Both sets of calculations agree in placing cis- and trans-1-propenyl anions at the end of the stability series.

Relative Acidities of Distorted Propenes

In this portion of the study, proton affinities (PA) for the various anions were calculated as a function of the CCC internuclear angle. The energy difference between the "subtract" or "rotated subtract" ion and the parent distorted propene defines the proton affinity.[22] Figure 5 presents plots of proton affinities for the various propenyl anions. Note that these results pertain to having the CCC angle fixed in both the hydrocarbon and its anion—the results are intended to model more complex rigid systems that do not possess the mobility of the propylene system itself.

The conclusions made earlier about the stabilities of the

various propenyl anions are corroborated by the acidities of the different protons of propene. At the normal sp^2 bond angle, the allyl protons are predicted to be more acidic than the vinylic protons. This result contrasts to the semiempirical calculations of Gründler who found the following order for the acidities of protons in propene: 2-H > 3-H > *E*-1-H > *Z*-1-H.[33] Both the present ab initio and semiempirical results show that the vinyl hydrogens at the 1 position are the least acidic.

For allyl anions, the proton affinity increases monotonically with reduction of the CCC angle and corresponds to a decrease in acidity of corresponding protons at small CCC angles. This result would appear to correspond to the experimental reactivity in base-catalyzed isomerization of cyclopentene, cyclohexene, and cycloheptene as shown by Tjan, Steinberg, and de Boer.[4d] However, in a subsequent discussion[19] we will demonstrate that the CCC skeletal angle is not the only factor that governs the kinetic acidity of cycloalkenes.

The vinylic protons (except for the *E*-1 proton[33]) display increased acidity as the CCC angle is contracted. This increased acidity would seem to coincide with greater s character of the vinyl CH bonds.[31] It is interesting to note that the 2 proton undergoes a dramatic increase in acidity at smaller angles so that the calculated acidity for this proton becomes greater than for the allylic protons. This result is completely consistent with experiment. Schröder[31] reported that vinylic protons are much more acidic than allyl protons in cyclopropene and cyclobutene as measured by their susceptibility to deuterium exchange in the ROK/ROD system. In addition, Schröder found that vinyl protons of cyclopropene are qualitatively more acidic than those of cyclobutene. Such a conclusion might have been reached by extrapolating the theoretical acidity curves. Experimentally, at cyclopentene in the cycloalkene series, exchange of allyl protons is substantial and rivals or exceeds that of vinyl protons.[4d,19,31] We must, however, interject a note of caution. The calculations described here represent predictions of behavior in the gas phase whereas all of the experimental results that we have cited were derived from solution phase measurements. One must recognize that there can be marked differences in solution and gas phase acidities, as in the cases of amines[34] and alcohols,[35] for example.

Summary and Conclusions

The present work constitutes an extension of our attempts to understand carbanion chemistry from an ab initio point of view. The allyl anion has been characterized by comparison to the allyl cation. Allyl anion has a larger CCC skeletal angle than allyl cation apparently to minimize the antiaromatic character of interactions between electrons in terminal p_π orbitals. In addition, at the STO-3G level, the anion displays no particular preference for a planar geometry as opposed to a pyramidal carbanion structure. The calculated acidities of the various propene hydrogens and the calculated energies of the corresponding anions conform well in a qualitative sense to what is known experimentally about cyclic olefins; that is, the allyl hydrogens show diminished acidity and the vinyl hydrogens display enhanced acidity as the CCC angle is decreased. As will be demonstrated later, the CCC angle is not the only factor operating to determine cycloalkene acidity. It is, nonetheless, a significant feature which accounts for *general* trends in the series from cyclopropene to cycloheptene.

References and Notes

(1) Acknowledgment is made to the U.S. Public Health Service, Grant GP-12855 of the National Institutes of Health, for partial support of this research. Additional computer time was donated by the Computer Center, University of California, Berkeley.
(2) (a) R. H. De Wolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1965); (b) K. Wiberg and T. Nakahira, *Tetrahedron Lett.*, 1773 (1974); (c) P. de la Mare, "Molecular Rearrangements", Vol. 1, Interscience, New York, N.Y., 1963, p 27.
(3) D. Ruzicka and W. Bryce, *Can. J. Chem.*, **38**, 827 (1960); (b) W. Bryce and M. Hardiman, *ibid.*, **40**, 1031 (1962); (c) C. A. Heller and A. Gordon, *J. Chem. Phys.*, **42**, 1262 (1965); (d) R. Cvetanovic, *Prog. React. Kinet.*, **2**, 39 (1964); (e) C. L. Currie and D. Ramsay, *J. Chem. Phys.*, **45**, 488 (1966).
(4) (a) S. Ela and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 5777 (1966); (b) A. Schriesheim, R. Muller, and C. Rowe, *ibid.*, **84**, 3164 (1962); (c) A. Schriesheim, C. Rowe, and L. Naslund, *ibid.*, **85**, 2111 (1963); (d) S. Tjan, H. Steinberg, and T. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **88**, 680, 690 (1969).
(5) (a) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954); (b) I. Amos and M. Woodward, *J. Chem. Phys.*, **50**, 119 (1969); (c) I. Cooper and R. McWeeny, *ibid.*, **49**, 3223 (1968); (d) J. Tino, *Collect. Czech. Chem. Commun.*, **36**, 3382 (1971); (e) J. E. Harriman and K. M. Sando, *J. Chem. Phys.*, **48**, 5138 (1968); (f) P. Carsky and R. Zahradnik, *J. Phys. Chem.*, **74**, 1249 (1970).
(6) (a) H. Looyenga, *Mol. Phys.*, **11**, 337 (1966); (b) M. Simonetta, E. Gianinetti, and I. Vandoni, *J. Chem. Phys.*, **48**, 1579 (1968); (c) M. Simonetta and E. Heilbronner, *Theor. Chim. Acta*, **2**, 228 (1964).
(7) (a) D. M. Hirst and J. W. Linnett, *J. Chem. Soc.*, 1035 (1962); (b) J. W. Linnett and O. Sovers, *Discuss. Faraday Soc.*, **35**, 58 (1963); (c) D. P. Choong and J. W. Linnett, *Mol. Phys.*, **8**, 151, 541 (1964).
(8) (a) W. Gründler, *Tetrahedron*, **26**, 2291 (1970); (b) M. Schanshal, *Z. Naturforsch. B*, **25**, 1065 (1970); (c) D. H. Lo and M. A. Whitehead, *J. Chem. Soc. A*, 463 (1971); (d) T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, *Bull. Chem. Soc. Jpn.*, **42**, 2437 (1969).
(9) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **51**, 2528 (1969); *Theor. Chim. Acta*, **24**, 132 (1972).
(10) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 6531 (1973).
(11) P. T. Van Duijene and D. Cook, *Mol. Phys.*, **21**, 475 (1971).
(12) D. Cook, P. Dacre, J. Doods, and M. Elder, *Theor. Chim. Acta*, **22**, 167 (1971).
(13) D. T. Clark and D. Armstrong, *Theor. Chim. Acta*, **13**, 365 (1969).
(14) A. Hincliffe, *Chem. Phys. Lett.*, **11**, 131 (1971); *Theor. Chim. Acta*, **25**, 138 (1972).
(15) J. McKelvey and W. Hehre, *Mol. Phys.*, **25**, 983 (1973).
(16) L. Farnell and W. G. Richards, *J. Chem. Soc., Chem. Commun.*, 334 (1973).
(17) P. Merlet, S. Peyerimhoff, R. Buenker, and S. Shih, *J. Am. Chem. Soc.*, **96**, 959 (1974).
(18) D. T. Clark and D. Armstrong, *Theor. Chim. Acta*, **14**, 370 (1969).
(19) A. Streitwieser, Jr., and D. W. Boerth, *J. Am. Chem. Soc.*, following paper in this issue.
(20) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(21) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(22) A. Streitwieser, Jr., P. H. Owens, R. Wolf, and J. Williams, *J. Am. Chem. Soc.*, **96**, 5448 (1974).
(23) J. Williams and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **97**, 2634 (1975).
(24) W. J. Hehre, W. Lathan, R. Ditchfield, M. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., No. 236.
(25) P. H. Owens and A. Streitwieser, Jr., *Tetrahedron*, **27**, 4471 (1971).
(26) Clark and Armstrong,[13] however, report a shorter cation bond.
(27) A. Bongini, G. Cainelli, G. Cardillo, P. Palmieri, and A. Umani-Ronchi, *J. Organomet. Chem.*, **110**, 1 (1976).
(28) (a) L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4786 (1970); (b) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *ibid.*, **92**, 4796 (1970); (c) L. Radom, W. Lathan, W. Hehre, and J. A. Pople, *ibid.*, **93**, 5339 (1971); (d) E. Scarzafava and L. C. Allen, *ibid.*, **93**, 311 (1971); (e) P. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, **16**, 217 (1972); (f) A. D. English and W. E. Palke, *J. Am. Chem. Soc.*, **95**, 8536 (1973).
(29) (a) D. R. Herschbach and L. C. Krisher, *J. Chem. Phys.*, **28**, 728 (1958); (b) D. R. Lide and D. E. Mann, *ibid.*, **27**, 868, 874 (1957); (c) V. W. Laurie, *ibid.*, **34**, 1516 (1961).
(30) D. R. Lide and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).
(31) G. Schröder, *Chem. Ber.*, **96**, 3178 (1963).
(32) M.J. Maskornick, Dissertation, University of California, 1969.
(33) Note: Removal of the *E*-1 proton or *Z*-1 proton generates the *trans*-1-propenyl or *cis*-1-propenyl anion, respectively.
(34) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **93**, 3911 (1971).
(35) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **92**, 5986 (1970); J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952).