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Ab Initio SCF Calculations of the Acidity of Distorted Ethanes and Ethylenes¹

Andrew Streitwieser, Jr.,* Peter H. Owens,^{2a} Richard A. Wolf,^{2b} and James E. Williams, Jr.

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received October 3, 1973

Abstract: *Ab initio* SCF calculations are presented for ethane, ethyl anion, ethylene, and vinyl anion in which the β H-C-H angles are distorted from their normal values. The results provide a simple model for the effect of small or strained rings on the acidity of adjacent bonds. The results are also consistent with changes in the s character of bonds as determined either by overlap populations or by localized molecular orbitals.

Recent kinetic acidity studies have demonstrated a general effect of ring strain in enhancing the acidity of an adjacent C-H bond. The 1 position of biphenylene, adjacent to a four-membered ring, is 79 times more reactive toward lithium cyclohexylamide than is the 2 hydrogen.³ Even in the aryl positions of triptycene, the 1 position, adjacent to the strained bridgehead, is 7.5 times more reactive than the 2 hydrogen in kinetic acidity toward cesium cyclohexylamide. The generality that a hydrogen adjacent to a small or strained ring has enhanced acidity extends to other kinds of systems as well; for example, cyclopropylamine has reduced basicity compared to alkylamines.⁴ The explanation has been advanced that the bond orbital exocyclic to a small ring has higher s character and, hence, greater electronegativity that enhances the acidity of an adjacent bond to hydrogen.³ However, attempts to model the effect by appropriate semiempirical SCF calculations (CNDO, INDO, MINDO) have not given an adequate accounting of this phenomenon.⁵ Since semiempirical MO methods are generally parameterized with nonstrained systems, this result is neither surprising nor useful. In the present study we demonstrate that *ab initio* SCF methods, even at the minimum basis set level, provide a satisfying theoretical model that confirms the earlier interpretation. The calculations were made on ethanes and ethylenes in which the β CH₃ and CH₂ groups, respec-

tively, were given varying HCH bond angles and on the corresponding carbanions generated by removing a proton from the α carbon. In this type of approach the calculated absolute proton affinity of the carbanions is of less significance than the changes produced by the β HCH angle perturbations.

Ethane and Ethyl Anion

Calculations on this system used the STO-4G basis set⁶ with optimized geometry and exponents. The isotropic sp (iso/sp)⁷ basis was used in which the 2s and 2p exponents are constrained to be equal. All calculations were made with the modified IBMOLIV program described previously.⁷ The values obtained are summarized in Table I. Ethane has been examined

Table I. Optimized Exponents and Geometry of Ethane and Ethyl Anion

	Ethane ^a	Ethyl anion
C (1s)	5.67	(5.67) ^a
C (2s, 2p) β	1.75	1.775
C (2s, 2p) α	1.75	1.551
H (1s) β	1.17	1.117
H (1s) α	1.17	1.111
$r(\text{CC})$, Å	1.524	1.551
$r(\text{CH})$ β , Å	1.094	1.128, ^b 1.126 ^c
$r(\text{CH})$ α , Å	1.094	1.179 ^d
Energy, au	-78.8708	-78.0688

^a Assumed value; ethane exponents from ref 6. ^b Anti to lone pair; C α -C β -H_{anti} = 116.0°. ^c Gauche to lone pair; H_{gauche}-C-H_{gauche} = 106.3°. C α -C β -H_{gauche} = 111.0°. ^d H-C α -H = 99.6°; C β -C α -H = 107.0°.

previously by the STO-NG method;⁶ our optimized geometry and orbital exponents as determined by

(6) W. J. Hehre, F. R. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(7) P. H. Owens and A. Streitwieser, Jr., *Tetrahedron*, **27**, 4471 (1971).

(1) Acknowledgment is made to National Science Foundation, Grant no. 29383, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Additional computer time was donated by the Computer Center, University of California, Berkeley.

(2) (a) U. S. Public Health Predoctoral Fellow, 1968-1970; (b) National Institutes of Health Postdoctoral Fellow, 1968-1969.

(3) A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, **90**, 1357 (1968).

(4) J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5030 (1951).

(5) P. C. Mowery, Dissertation, University of California, Berkeley, 1971.

steepest descents agree well with the different optimization procedures of the previous studies and with experiment.

The optimized structure of ethyl anion is that of a staggered pyramidal C_s system. The methyl group is slightly distorted from C_3 symmetry with the hydrogen anti to the carbanion lone pair having a slightly longer CH bond distance than the two gauche hydrogens. All CH bonds in ethyl anion are longer than in alkanes with the α CH's having a calculated length of 1.179 Å. Minimum basis set calculations of methyl anion also give long C-H bonds.⁷ In both systems this result is an artifact of minimum basis sets. Extended basis sets give CH bond lengths that are similar to normal hydrocarbon values; the results of our extensive study of SCF calculations of various carbanions with different basis sets will be presented separately.⁸ For this reason, other calculated minimum basis set properties will not be discussed here but are available elsewhere.⁹

For the calculations of the effect of methyl group distortion the ethane geometry used had C-C and C-H bond lengths of 1.54 and 1.09 Å, respectively, and the undistorted methyl group was given tetrahedral bond angles. The distorted methyl group retained C_3 symmetry. For ethyl anion the C-C, C_β -H, and C_α -H bond distances were taken as 1.551, 1.127, and 1.17 Å, respectively, with bond angles about the α carbon of C-C-H = 107° and H-C-H = 99.6°. The distorted β methyl group was constrained to C_3 symmetry. Orbital exponents used are those in Table I. The calculated energies are summarized in Table II and Figure

Table II. Energies of Distorted Ethane and Ethyl Anion

β H-C-H angle, deg	Total energy, au		Proton affinity of ethyl anion, kcal/mol
	Ethane	Ethyl anion	
90.4	-78.8300	-78.0404	493
97.2	-78.8539	-78.0591	497
103.4	-78.8668	-78.0664	500
108.9	-78.8697	-78.0638	504
113.5	-78.8640	-78.0525	507

1. The energy minimum corresponds to a different β H-C-H bond angle in ethane than in ethyl anion, but the calculated proton affinity of the ethyl anion decreases monotonically as the β H-C-H bond angle is reduced.

Ethylene and Vinyl Anion

STO-3G calculations of ethylene have been reported previously for the iso/sp basis.⁶ Our independent optimizations agree closely with the previous results except that the optimized exponent for C (1s), 5.70, differs slightly from the atomic Slater value, 5.67, assumed in the previous study. Relaxation of the constraint that orbital exponents be the same for all 2s and 2p orbitals causes significant changes. The aniso results in Table III show that the $2p_z$ orbital of the π system becomes more diffuse. The 2s orbital is essen-

(8) J. E. Williams and A. Streitwieser, Jr., to be submitted for publication.

(9) P. H. Owens, Dissertation, University of California, Berkeley, 1973.

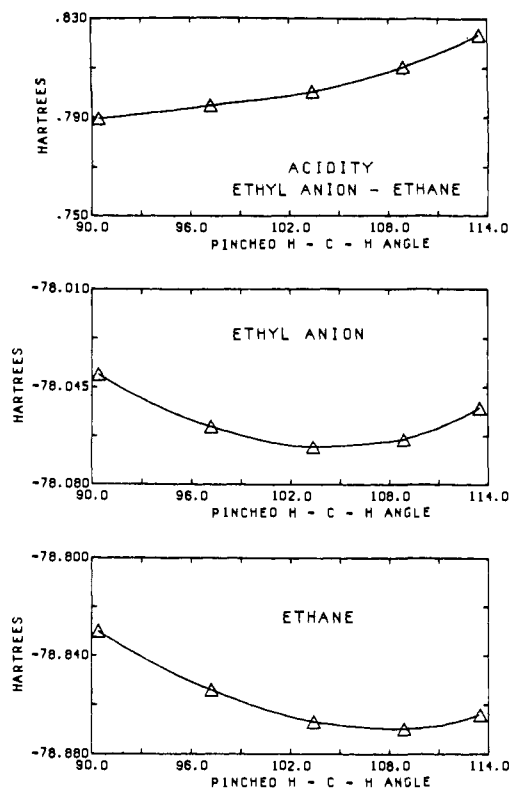


Figure 1. Calculated energies of distorted ethanes and ethyl anions and the corresponding energy differences (proton affinities).

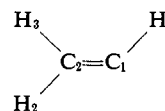
Table III. Optimized Exponents and Geometry of Ethylene

	STO-4G ^a (ref 6)	STO-3G iso/sp	STO-3G ^a aniso/p
C (1s)	(5.67)	5.703	(5.703)
C (2s)	1.70	1.697	1.756
C (2p _x , 2p _y)	1.70	1.697	1.843
C (2p _z)	1.70	1.697	1.493
H (1s)	1.22	1.225	1.169
r(CC), Å		1.317	(1.317)
r(CH), Å		1.090	(1.090)
HCH		115.85°	(115.85°)
Total energy, au (STO-4G)		-77.6306	-77.6782

^a Values in parentheses are assumed.

tially the same as in ethane whereas the in-plane $2p_x$ and $2p_y$ orbitals are even more contracted, perhaps because of reduced screening by the more diffuse $2p_z$ electron density.¹⁰

Vinyl anion was optimized using the iso/p basis set in which all 2p orbitals are given the same exponent which is optimized independently from the 2s orbital. The results are summarized in Table IV for the following structure.



(10) Anisotropic p functions in minimum basis set calculations have been used previously (cf. E. Switkes, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, **51**, 5229 (1969); R. M. Stevens, *ibid.*, **52**, 1397 (1970)). The use of such functions requires extensive optimization of orbital exponents and cannot be recommended. The results reported here happen to have been carried out before we were able to use extended basis sets but the nature of the conclusions does not depend on this feature.

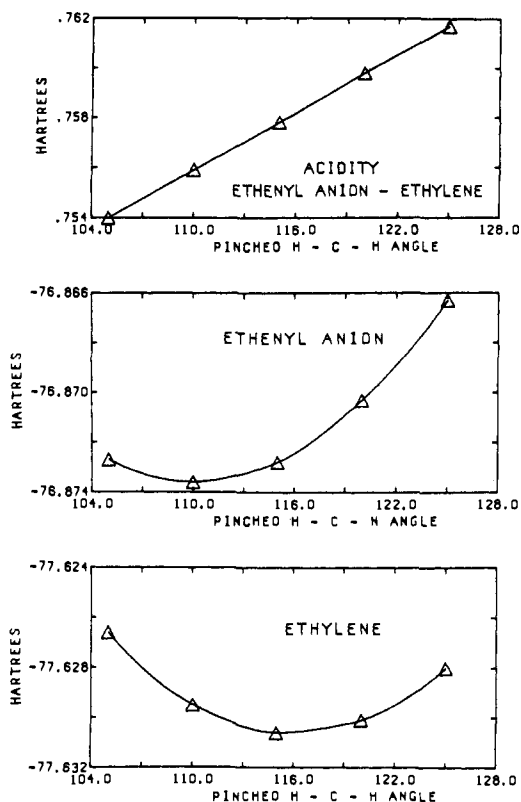


Figure 2. Calculated energies of distorted ethylenes and vinyl anions and the corresponding energy differences (proton affinities).

Table IV. Optimized Exponents and Geometry for Vinyl Anion with the Iso/p Basis Set

C ₁ (1s)	5.70	C-C, Å	1.381
C ₁ (2s)	1.56	C ₁ -H ₁ , Å	1.214
C ₁ (2p)	1.56	C ₂ -H ₂ , Å	1.133
C ₂ (1s)	5.70	C ₂ -H ₃ , Å	1.145
C ₂ (2s)	1.76	H ₂ C ₂ H ₃	109.5°
C ₂ (2p)	1.60	H ₁ C ₁ C ₂	104.0°
H ₁	1.08	H ₂ C ₂ C ₁	122.1°
H ₂	1.12	H ₃ C ₂ C ₁	128.4°
H ₃	1.10	Total energy, au (STO-4G)	-76.8736

Again, all bond distances are lengthened compared to ethylene with the C₁-H₁ bond lengthened to an exceptional degree. Extended basis set calculations show similar bond lengthenings but to much reduced extents.⁸

To calculate the effects of distortion on acidity the β HCH bond angle of ethylene was allowed to vary while retaining all bond distances and the α HCH constant at the optimized values. Similarly, for each corresponding vinyl anion these optimized values for geometry and exponents were used except that the H₂-C₂-H₃ bond angle was allowed to change symmetrically. The results are summarized in Table V and Figure 2. In this system also there is a monotonic decrease in proton affinity, corresponding to an increase in acidity, as the methylene group from which the proton is not removed is decreased in angle.

s and p Character in Bonds. Our original explanation of the effect of adjacent small rings on acidity was based on the s- and p-character of bonds (*vide supra*). This qualitative but simple description can also be modeled in the present SCF-MO context. We earlier

Table V. Effect of Distortion on Proton Affinity of Vinyl Anion

H ₂ -C ₂ -H ₃ angle	Energy, au		Proton affinity, kcal/mol
	Ethylene STO-4G iso/sp	Vinyl anion STO-4G iso/p	
105	-77.6266	-76.8727	473
110	-77.6295	-76.8737	475
116	-77.6306	-76.8728	476
120	-77.6301	-76.8703	477
125	-77.6280	-76.8663	478

proposed a measure of the s character donated by an atom A to a bond A-B in terms of the Mulliken overlap populations, P_{ij} , between atomic orbitals i on atom A and j on B.⁷

$$S(A/A-B) = \frac{\sum_{i=s} P_{ij}}{\sum_{j=s,p} P_{ij}}$$

We expect relative values of this defined quantity to have greater significance than the absolute values. The calculated values for ethane and ethylene are summarized in Tables VI and VII, respectively, as a function of the β H-C-H angle. Both ethane and ethylene show a consistent pattern. As the β H-C-H angle is contracted, the carbon s character in the C_β-H bond is reduced, as expected. The s character contributed by C_β to the C-C bond increases; this is analogous to the enhanced s character of exocyclic bonds in small-membered rings. Conversely, as the s character contributed by C_β increases, that donated by C_α decreases but to a lesser degree. C_α then has additional s character to contribute to C_α-H. The relationship between acidity and s character of the C-H bond is well established.¹¹

Alternatively, s character can be determined by constructing localized MO's from the canonical MO's given by the Hartree-Fock technique and examining directly the s contribution to a localized C-H orbital. We have applied this approach to the distorted ethanes using the Boys localization criterion¹² implemented in our laboratories with a computer routine written by Dr. J. Hashmall. Results of this approach are compared in Table VI with the overlap population definition. Absolute values by the two approaches differ in detail although they are remarkably comparable in magnitude; more important, however, is that in both criteria the changes in s character with perturbation of the ethane structure parallel each other completely.

Extended Basis Set Results

The emphasis in the present work was not on absolute proton affinities of carbanions but on their relative values as a function of remote angle strain. The results described above are in complete qualitative accord with simple orbital concepts of bonding. However, some features of SCF calculations of alkyl anions imply limitations that require further discussion. In particular, the highest occupied MO's of such species are usually of positive energy or antibonding. A detailed discussion of this problem is deferred to another paper in which the electronic properties of several carb-

(11) For example, see A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *J. Amer. Chem. Soc.*, **91**, 529 (1969).

(12) S. F. Boys, "Quantum Theory of Atoms, Molecules and the Solid State," P. Lowdin, Ed., Academic Press, New York, N. Y., 1966, p 253.

Table VI. Bond s Character in Distorted Ethanes

β H-C-H angle, deg	Per cent s character							
	$C_\alpha/C_\alpha-H$		$C_\beta/C_\beta-H$		$C_\alpha/C_\alpha-C_\beta$		$C_\beta-C_\alpha-C_\beta$	
	Overlap	Localization	Overlap	Localizaton	Overlap	Localization	Overlap	Localization
90.4	27.61	27.62	22.94	23.76	26.49	29.68	37.96	40.16
97.2	27.47	27.53	24.20	25.01	28.74	29.93	36.64	37.27
103.4	27.32	27.44	25.53	26.15	29.09	30.21	33.51	34.22
108.9	27.14	27.35	27.14	27.35	29.54	30.56	29.54	30.56
113.5	27.00	27.29	28.58	28.33	29.93	30.87	25.79	27.35

Table VII. Overlap Bond Per Cent s Character in Distorted Ethylenes

β H-C-H angle, deg	$C_\alpha/C_\alpha-H$	$C_\beta/C_\beta-H$	$C_\alpha/C_\alpha-C_\beta$	$C_\beta/C_\alpha-C_\beta$
125	33.26	34.76	24.53	22.44
115.85	33.49	33.49	24.34	24.34
105	33.75	32.13	24.11	26.40

by deleting a proton from the corresponding ethylene. Results are summarized in Table VIII for ethylene and vinyl anion in which the β HCH bond angle is contracted and expanded from the equilibrium value using basis sets of split shell quality and split shell with polarization (d orbitals on carbon). The structure of ethylene used, except for the β angle being varied, is: r

Table VIII. Extended Basis Set Results of Distorted Ethylene and Vinyl Anion

β HCH angle, deg	Split shell ^a			PA, kcal mol ⁻¹	Split shell + polarization		
	$E(C_2H_4)$, au	$E(C_2H_3^-)$, au ^b			$E(C_2H_4)$, au	$E(C_2H_3^-)$, au ^b	PA, kcal mol ⁻¹
109	-78.0012	-77.3039		437.5	-78.0314	-77.3351	436.8
116.7	-78.0028	-77.3033		438.8	-78.0331	-77.3345	438.3
124	-78.0011	-77.2993		440.3	-78.0316	-77.3305	439.8

^a Details of the basis sets used are given in ref 8. ^b These data give an optimized β HCH angle in vinyl anion of 111.7°.

anions are treated.⁸ For the present purpose it is significant that concordant results were obtained for the effects of distortion in two carbanions as different as ethyl and vinyl anions. As a further test a limited study using extended basis sets was made of distorted ethylene and the corresponding vinyl anion obtained by removing a proton without otherwise affecting the molecular structure; that is, vinyl anion was obtained

(C-H) = 1.076 Å, $r(C-C)$ = 1.33 Å, H-C-H = 116.7°. The calculated proton affinities differ in magnitude from the minimum basis set results of Table V, but the trends given by varying the β HCH bond angle are substantially the same. We infer the correctness of the generalization, independent of model or specific compound, that a compression of bond angles results in enhanced acidity of an adjacent C-H bond.