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AB INITIO QUANTUM ORGANIC CHEMISTRY—I

STO–NG CALCULATIONS OF METHANE AND METHYL ANION[1]

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Abstract—We report *ab initio* SCF calculations on methane and Me anion using Pople's STO-4G basis set. Optimization of exponents and geometry gives good agreement with previous calculations and with experiment for bond distances and force constants. The carbanion is more difficult to treat and various isotropic and anisotropic basis sets are compared with extended basis set calculations. The minimum basis set calculations with optimized exponents produce abnormally long C—H bonds. Inversion barriers and population analyses are compared and a series of electron density and MO contours and 3D diagrams is presented. We conclude that minimum basis set calculations of carbanions may be useful in comparing related sets of compounds but it is better to assume geometry in such treatments.

INTRODUCTION

IN THE last few years there have been reported[3] many *ab initio* calculations of small inorganic and organic molecules. Most of these calculations have used either Gaussian type functions (GTO) or Slater type functions (STO) with extended basis sets. Although many of the extended basis set calculations have produced total energies close to estimated Hartree–Fock limits, the difficulty of interpreting electronic properties of the eigenvectors have limited the usefulness of such methods for organic chemists; in particular, population analyses from extended basis set calculations are almost meaningless whereas those from appropriate minimum basis set calculations generally agree well with the type of qualitative electron density considerations that form an important part of physical organic arguments. Nevertheless, total energies from minimum basis set STO calculations are generally no better than one atomic unit from the Hartree–Fock limit.

In a recent series of papers, Pople[4] has proposed several methods of performing minimum basis set calculations that make molecules as large as toluene feasible with third-generation computers. The method used in the present work is his so-called STO–NG method in which N is the number of gaussians used in a linear combination that represents an STO. Although the results of such calculations reflect those of actual STO calculations, all of the mathematical operations are performed on gaussian functions leading to a large saving in computational time. Each atomic orbital has associated with it a "Slater exponent" which in practice is a scaling factor that is applied to each gaussian in the expansion for that atomic orbital.

Expansion of STO's are available in from two to six gaussians. Pople's group makes extensive use of the 3G level whereas much of our work has been at the 4G level (*vide infra*). In Fig 1 we show the STO-4G expansion of a hydrogen 1s STO atomic orbital with a Slater exponent of unity. All of the contributing gaussians, the STO function being fitted and the STO–NG linear combination are shown up to 6·0 A.U. from the nucleus. Excellent agreement is evident from 0·5 to 6·0 A.U. between the actual STO and STO-4G orbital. Only the region either very close to or very far from the nucleus is improved in using an expansion of more than 4 gaussians.

Many properties of interest to the organic chemist, such as energy differences dipole moments and molecular geometry, show little change beyond the STO-4G level. An example is shown in Table 1 where the deprotiation of methane is presented using different STO–NG basis sets, whereas the total energies of methane and methyl anion converge slowly to those of a minimum STO calculation, the energy of deprotiation at the STO-4G level has converged to within 0·07 kcal/mole of the STO-6G result.

The key to successful minimum basis set calculations has been demonstrated to be the use of optimized Slater exponents.[5] In the present work we demonstrate the limits of applicability of such minimum basis set STO calculations with optimized

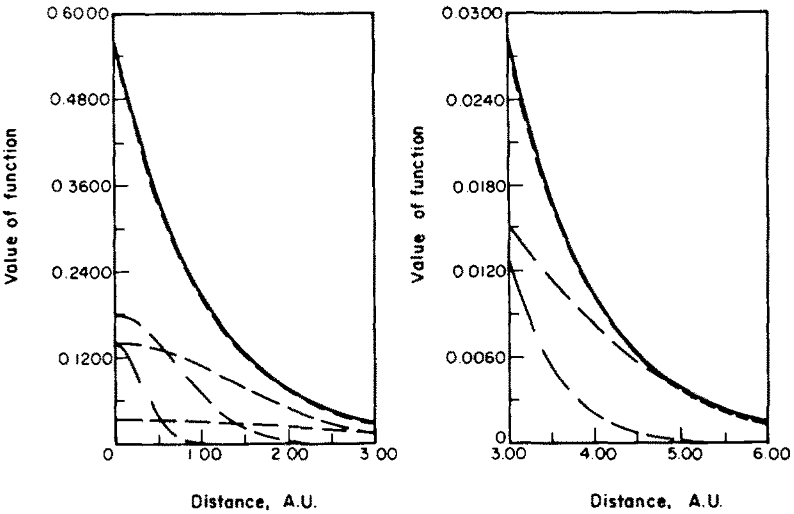


FIG 1. Comparison of Hydrogen 1s Slater orbital with STO-4G showing the component gaussians

TABLE 1. DEPROTIATION OF METHANE USING "STANDARD EXPONENTS"[a] AND FIXED GEOMETRY

Basis set	Energy of methane, a.u.	Energy of methyl anion a.u.	ΔE, a.u.	% Diff. from STO-6G
STO-2G	−38·252005	−37·357978	−0·894027	0·574
STO-3G	−39·726494	−38·825029	−0·901465	0·243
STO-4G	−40·007099	−39·107798	−0·899301	0·012
STO-5G	−40·085688	−39·186515	−0·899173	0·002
STO-6G	−40·109915	−39·210723	−0·899192	

[a] "Standard exponents" of Pople. Ref. 4*a*

[b] C—H bond distance equals 1·094 A and H—C—H angle equals 109·47°

exponents in the treatment of Me anion and its lone pair as a prelude to more extensive work with larger carbanions to be reported subsequently. When determining either the optimum Slater exponents or the molecular geometry for a molecule, a steepest descent procedure was used in which a function of several independent variables (total energy) in minimized by simultaneously varying all of the variables in the direction of maximum gradient.[6] Calculations in both our group and Pople's group have demonstrated that exponent and geometry parameters determined by optimization at the STO-3G level are generally within 1·0% of those determined at the STO-4G level. Therefore, we adopted the general procedure of performing all optimization at the STO-3G level followed by a final calculation at the STO-4G level using the final optimized parameters; however, in the present paper, all optimization is at the STO-4G level. Optimization was performed until all variable parameters changed by less than 0·2% between successive steepest decent cycles; usually three cycles were required.

CALCULATIONS

All calculations were performed using a version of IBMOL4[7] modified to run on a CDC 6400 with extended core storage (ECS). The transformation and SCF sections of the program were only slightly modified with regards to changed logic but extensive changes were made that involved writing key routines in assembly language (COMPASS), redimensioning arrays, changing the program from double to single precision and eliminating external tape files by utilizing central memory and ECS space. Single precision on the CDC 6400 involves using 60 bit words and retains 15 decimal significant figures.

The integral section of IBMOL4 was restructured so as to incorporate both molecular and local symmetry. This version of the integral section can only be used in STO–NG calculations and involves searching the integrals from a fast "dummy calculation" for all unique non-zero values and using the result of this search in a later calculation. The integrals needed by the transformation section are not those over the primitive gaussians but those over the contracted gaussians; i.e., the simulated STO functions. Therefore, while there are many more integrals over gaussian functions in a STO-4G calculation than in a STO-2G calculation, the number of integrals over contracted gaussians is independent of N for the same molecule. Each integral over contracted gaussians is a linear combination of n^4 integrals over primitive gaussians. It can be shown that the simplest basis set that incorporates all of the symmetry of a STO–NG basis set calculation is not a STO-1G basis set but a mixed basis set where all s type gaussians are represented by a STO-2G expansion and all p type gaussians are represented by a STO-1G expansion.[8] A dummy basis set calculation of this sort can be performed from 16 to 256 times as fast as a STO-4G calculation depending on the ratio of s to p type gaussians in the molecule.

The new integral section for IBMOL4 starts with a dummy basis set calculation as described above. The integrals over contracted gaussians from this calculation are then searched for zero values and equalities with both same and opposite sign using "hash code" search techniques.[9] Whereas a linear search time is proportional to the square of the number of items being searched, a hash table search using a "hashing" procedure generating a random hash code has a search time proportional to the number of items being searched so long as the total number of items is less than about two-thirds of the capacity of the hash table.

This technique automatically detects both local and molecular symmetry. The results of this search are then used to prepare the integrals over the full STO–NG basis set. This new version of IBMOL4 can reduce the integral evaluation time by as much as a factor of 10 for molecules having a large number of symmetry elements. For example, total calculation times in minutes at the 4G level for the new and old programs with various molecules are, respectively: methyl anion, 0·71, 2; methane, 0·28, 3; ethane, 5·32, 26; cyclopropane, 15·30, 79. Clearly such calculations become feasible even for molecules of substantial size.

Methane

The Hartree–Fock (H.F.) limit for methane has been estimated by Hollister and Sinanoglu[10] to be −40·22 A.U. and by Ritchie and King[11] to be −40·23 A.U. Krauss,[12] using a total of 33 GTO's, calculated an energy for methane of −40·1668 A.U. Later, Ritchie and King[11] using an extended contracted gaussian basis (ECGTO) of 39 CGTO's reported an energy of −40·1983 A.U. Woznick[13] using an extended contracted STO basis (ECSTO) of 27 CSTO's reported an energy of −40·1804 A.U. The best calculation of methane to date is that of Arrighini *et al.*[14] using 39 STO's; they report a value of −40·2045 A.U. Many of these extended basis calculations use polarizing d functions on the carbon[14] and p functions on the hydrogens.[11, 14] No optimization of any of these basis sets has been performed—most of the authors used a basis related to those proposed for free atoms by Huzinaga.[15]

One of the earliest reported minimum basis set calculations was the work of Pitzer and Lipscomb[16] using an STO basis with Slater's Rule exponents and giving a value of −40·1141 A.U. Several minimum basis set calculations where the Slater exponents have been optimized so as to minimize the total energy of methane have recently been reported. Pitzer[5] used an *anisotropic* STO basis in which the 2s and 2p exponents were separately optimized (all three 2p exponents must be equal by symmetry in a tetrahedral molecule) and Pople[4a] used an *isotropic* STO-4G basis where the 2s and 2p exponents are constrained to be equal (*Iso*-sp).

Two sets of calculations have been performed in the present work. First, Pople's STO-4G, *Iso*-sp calculation was repeated using the optimized Slater exponents in his work. The equilibrium C—H distance was determined. Secondly, a calculation was performed using an ECGTO basis as recently proposed by Dunning.[17] This ECGTO basis can be described as a 4s3p/2s basis in which the orbitals before the slash refer to the CGTO's on carbon (4 "s" type CGTO's for the carbon 1s and 2s A.O.'s and 3 "p" type CGTO's for each of the three 2p A.O.'s) and the orbitals after the slash refer to the CGTO's on hydrogen. The GTO set being contracted is a 9s5p/4s basis. The STO-4G basis, therefore, uses 36 GTO's contracted to 9 CGTO's while the ECGTO basis uses 40 GTO's contracted to 21 CGTO's. The energy components of these two calculations are given in Table 2 together with Pitzer's anisotropic STO and Ritchie and King's ECGTO results.

Dunning's basis set is a definite improvement over the other ECGTO and ECSTO basis sets previously mentioned that did not use polarizing functions even though his set is smaller. This is not surprising since, unlike the earlier work using a free atom basis, Dunning's basis set is based on his optimized ECGTO calculations on water. As expected, the STO-4G and STO results show the greatest differences in the total energy and in the $1a_1$ orbital energy. This reflects the inability of the STO-4G basis to represent adequately the behavior of the STO basis near the nucleus. Klessinger[18] has proposed using a mixed STO–NG basis. His value of −40·0009 A.U. for a STO-5G expansion of the carbon 1s A.O. and a STO-3G expansion for all the other A.O.'s in methane is slightly higher than that resulting from the STO-4G basis. Since the reported integral evaluation time for this mixed STO–NG basis is more than 3 times that for the STO-4G basis, there seems little reason to recommend it as a useful basis.

TABLE 2. VARIATION OF METHANE ENERGY COMPONENTS WITH BASIS SET

	STO-4G *Iso*/sp	STO[a] *Aniso*	ECGTO 4s3p/2s	ECGTO[b] 4s5p/4s1p
E_{Total}	−40·01213	−40·12822	−40·18555	−40·1983
E_1	−79·55194		−79·69934	
E_2	26·09222		26·06620	
E_{Nu}	13·44759		13·44759	
MO's				
$1a_1 : \psi_1$	−11·15671	−11·2049	−11·20764	−11·2216
$2a_2 : \psi_2$	−0·92238	−0·9252	−0·94558	−0·9295
$1t_2 : \psi_{3-5}$	−0·53489	−0·5384	−0·54342	−0·5348

[a] Ref 5

[b] Ref 11 with an assumed C—H bond length of 1·122 A.

Comparing the minimum basis STO-4G with the ECGTO 4s3p/2s basis it can be seen that the ECGTO basis causes all of the orbital energies to be lowered with the $1a_1$ orbital energy being stabilized the most. Note that of the various components of the total energy it is the one-electron component (both kinetic and potential) rather than the electron repulsion two-electron component that is lowered substantially in going from a minimum to an extended basis.

The exponents and electronic properties of methane from the STO-4G, STO and ECGTO 4s3p/2s basis sets are compared in Table 3. The fortuitous agreement of the 2s and 2p exponents for the anisotropic STO basis support Pople's isotropic/sp assumption. Mulliken and bond populations for the STO-4G and STO calculations are almost identical as are the optimized exponents. The equilibrium C—H distance, 1·089 Å, determined in the STO-4G calculation differs only slightly from the values obtained by Pitzer, 1·085 Å, for the STO basis and by Newton, *et al.*,[4e] 1·083 Å, for the STO-3G basis. The mean internuclear C—H distance determined by electron diffraction is 1·106 Å with an estimated equilibrium distance of 1·085 Å.[19] a value showing excellent agreement with these calculated results.

The experimental value for the first ionization potential of methane is 0·4774 A.U. or 12·99 e.v.[20] This value is about 0·05 A.U. (1·3 ev or 30 kcal/mole) lower than the highest orbital energy (t_2) for either the minimum or extended basis set calculations shown in Table 2. It is doubtful that the application of Koopman's theorem to H.F. calculations will yield accurate estimates of ionization potentials even for large extensive basis sets.

TABLE 3. EXPONENTS AND PROPERTIES OF METHANE

	STO-4G[a] *Iso*/sp	STO[b] *Aniso*	ECGTO 4s3p/2s	Experimental
Exponents: C1s	5·67	5·68		
C2s	1·76	1·76		
C2p	1·76	1·76		
H1s	1·17	1·17		
C—H distance (Min.)	1·089 A	1·085 A	1·089 A[c]	1·085[e]
Force Constants: k_n (mdyn/A)	6·84	5·88		5·01
k_e (mdyn/A)	1·41			1·38
Mulliken Populations:				
Total: C	0·0798	6·0762	6·7710	
H	0·9800	0·9809	0·8073	
C1s	1·9939	1·9946	1·9941	
C2s	1·1392	1·1312	1·4693	
$C2p_x$. $C2p_y$. $C2p_z$	0·9822	0·9835	1·1025	
Overlap Populations:				
Total: C—H[d]	0·7672	0·7694	0·7460	
C2s—H	0·2260	0·2269	0·1770	
$C2p_x$—H + $C2p_y$—H + $C2p_z$—H	0·5534	0·5549	0·5758	
Overlap %s:[d] C/C—H	27·85		22·83	

[a] Ref. 4a. the C—H bond distance was optimized using the exponents determined by Pople for STO-4G

[b] Ref. 5

[c] Assumed value

[d] Contains C1s contributions to overlap

[e] r_e

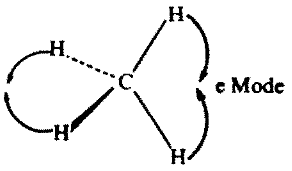
Comparison of the minimum basis set and ECGTO population analyses shows the usual large differences. The ECGTO basis depicts a much more electronegative carbon (−0·77) than the STO-4G basis (−0·08). Both the carbon 2s and 2p A.O.'s become more electron-attracting in going from the STO-4G to ECGTO basis changing from −0·14 to −0·47 and +0·02 to −0·10, respectively. The increased electronegativity of carbon in the ECGTO calculation is accompanied by a decrease in the C—H bond population. Even though the bond population between the H1s and C2p A.O.'s has increased slightly, the large decrease in the bond population between the H1s and C2s A.O.'s leads to a net lowering of the total bond population. This effect of extended basis sets is known to result from an inbalance in the basis sets used. Such inbalance causes regions of electron density near one atom to be "assigned" to the atomic orbital of another atom. On the other hand, the population analyses from the minimum basis sets seems qualitatively correct from organic chemical experience.

Population analyses also provide a useful alternative to localized orbitals in determining the particular orbital composition of a bond. An empirical definition of the fraction of s-character in a bond A—B is given in terms of the overlap populations P_{ij} between A.O.'s i on Atom A and j on B in eq. 1.

$$S(A/A\text{—}B) = \sum_{\substack{i=s \\ j=s+p}} P_{ij} \Big/ \sum_{\substack{i=s+p \\ j=s+p}} P_{ij} \tag{1}$$

The numerator is summed over only s type A.O.'s for atom A while the other sums in the numerator and denominator are over both s and p type A.O.'s. It can be seen that any bond will have two s-characters associated with it—each of the two referring to the contribution of one of the two atoms defining the bond. For C—H bonds only the C/C—H value need be given since the H/C—H value is always 100·0%. This empirical definition can lead to negative contributions and the sum over all of the bonds to a given atom need not equal 100%. Note that this definition includes STO 1s contributions to bonding since some 1s contribution is required to provide the appropriate orthogonality or nodal properties for a STO 2s orbital. Comparing the STO-4G and ECGTO results given in Table 3 it can be seen that the aforementioned changes in bond populations are reflected in a lower percent (C/C—H) value for the ECGTO basis.

A molecule with five atoms in tetrahedral symmetry has four sets of normal vibrations: one of a_1, one of e and two of t_2 symmetry. The a_1 mode involves only bond stretching and the e mode only bond bending whereas the t_2 modes involve both bending and stretching.[21] The force constants for the a_1 and e modes of vibration are easily calculated from a series of STO-4G calculations where either all four C—H bonds are symmetrically stretched while maintaining tetrahedral symmetry or where the C—H bond lengths are kept constant while pairs of the C—H bonds are compressed as shown in I. These compressed methanes belong to the C_{2v} molecular



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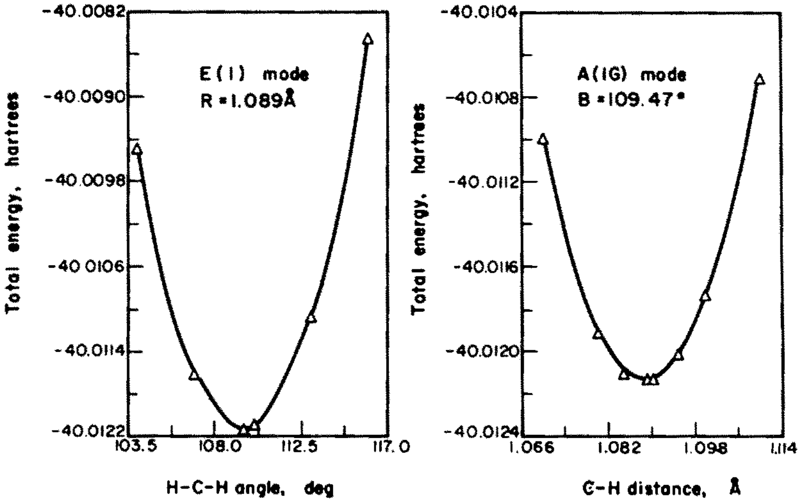

FIG 2. Energies for bending and stretching of methane in E_1 and A_{1g} modes, respectively

point group. The results of these calculations are given in Table 4 and are depicted graphically in Fig 2.

It can be shown[22] that the symmetry coordinates S_{a_1} and S_e for the a and e modes are related to the C—H distance R and the H—C—H angle θ by:

$$S_{a_1} = 2\,\mathrm{R}$$
$$S_e = \sqrt{3/2}\,R\theta$$

The total energy E_T is therefore related to R and θ for the a_1 and e modes by:

$$a_1: E_T = -\tfrac{1}{2}k_{a_1}S_{a_1}{}^2 = -2k_{a_1}R^2$$
$$e: E_T = -\tfrac{1}{2}k_eS_e{}^2 = -\tfrac{3}{4}k_eR^2\theta^2$$

where k_{a_1} and k_e are the force constants in terms of symmetry coordinates for the a_1 and e modes respectively.

By fitting the points near the minimum from Table 4 to a parabola and taking the second derivative of the parabola, k_{a_1} and k_e can be determined; the values obtained are given in Table 3. The experimental values for the a_1 and e mode are 5·01 mdyn/Å and 1·38 mdyn/Å respectively.[22] The value obtained for the e mode for the STO-4G basis is 1·41 mdyn/Å; however, the value of 6·84 mdyn/Å for the a_1 mode is not in as good agreement with the experimental results.

TABLE 4. METHANE—VARIATION OF TOTAL ENERGY WITH GEOMETRY[a]

Symmetrical Stretch A_1 Mode H—C—H Angle = 109·47°		Symmetrical Bend E Mode C—H Bond Distance = 1·089 Å	
C—H Dist (Å)	Energy (A.U.)	H—C—H Angle (deg)	Energy (A.U.)
1·070	−40·010984	104·00	−40·009484
1·080	−40·011886	107·00	−40·011590
1·085	−40·012084	109·47	−40·012126
1·089	−40·012126	110·00	−40·012101
1·090	−40·012120	113·00	−40·011045
1·100	−40·011718	116·00	−40·008443
1·110	−40·010710		

[a] Optimized exponents were used from the equilibrium geometry (Table 3)

One can conclude from the results of these methane calculations that the STO-4G basis when compared to an STO basis show excellent agreement for optimized exponents, equilibrium geometry and Mulliken and bond populations, fair agreement for force constants and orbital energies other than those of the 1s core electrons, and poor agreement with the total energy and 1s core electron orbital energies. In addition to the lower energies obtained by using an ECGTO basis, substantially different electron distribution as reflected by Mulliken and bond overlap populations are obtained from those of a minimum basis set.

Methyl anion

One of the earliest *ab initio* calculations to be reported for methyl anion (CH_3^-) was that of Rutledge and Saturno[23] using the one-center expansion method. Their results indicated that the D_{3h} planar form of CH_3^- is more stable than the pyramidal C_{3v} form and has a total energy of −39·2734 A.U. Kari and Csizmadia[24] in a series of papers report EGTO calculations of CH_3^- with a variety of basis sets ranging in size from 12 to 58 GTO's based on Huzinaga's free atom values.[15] Their work indicates a pyramidal geometry for CH_3^- with the best energy of −39·4972 A.U. obtained for a 10s6p1d/8s (N = 58) EGTO basis. They also have estimated the H.F. limit at −39·525 A.U.

There have been no minimum basis set calculations of CH_3^- reported to date. We here contrast minimum basis STO-4G results with those of EGTO calculations and also determine the sensitivity of these results to assumptions imposing isotropy on the basis set or to fixing certain exponent and geometric parameters. The conclusions drawn from this work on the simplest carbanion system have bearing on related calculations on ethyl and larger carbanion systems.

Optimum exponents and geometry have been determined for three STO-4G basis sets: the previously defined *Iso*/sp basis, the *Iso*/p basis where the three 2p exponents are constrained to be equal but are optimized separately from the 2s exponent; and the anisotropic (*Aniso*) basis where all four valence A.O.'s exponents are optimized separately subject to any symmetry constraints imposed by the point group of the molecule. For a C_{3v} or D_{3h} molecule such as CH_3^-, two of the 2p A.O.'s belong to the "e" irreducible representation and must have the same exponents. Pople[4a] has proposed a set of "standard" exponents based on optimized neutral molecules; the fourth STO-4G basis set calculation performed involved optimizing the geometry of CH_3^- using these assumed standard exponents in the basis set. All steepest descent optimization cycles for this work were performed at the STO-4G level.

Finally, optimized geometry was determined for CH_3^- using the ECGTO basis of Dunning previously mentioned in the section on methane, in order to compare the extended basis set results with those of the various STO-4G sets. The final optimized values of the exponents and geometry parameters for both the pyramidal (C_{3v}) and planar (D_{3h}) forms of CH_3^- for these five different basis sets are given in Table 5. The C_3 symmetry element is taken as coincident with the z axis and one of the hydrogens (H1) lies in the xz plane.

The C2s, 2p exponent of 1·547 obtained for the *Iso*/sp basis for C_{3v} CH_3^- when contrasted to the value of 1·76 obtained for methane reflects the increased screening expected at a negatively charged atom. It is noteworthy that this value is almost exactly the average of the C2s and C2p exponents obtained for the *Iso*/p basis. In the *Iso*/p calculations the C1s exponent was also optimized giving a value of 5·700 which is slightly higher than the value of 5·67 assumed by Pople for carbon. The *Aniso* results show that there is a large difference between the C2p_z and C2p_x, 2p_y exponents with the latter having exponents slightly higher than the C2s value. Thus, the p-orbitals involved in bonding to hydrogen are effectively smaller and less diffuse than the p_z-orbital used principally for the carbanion lone pair. The *Iso*/p value for the C2p exponents is closer to the C2p_z *Aniso* value than to the *Aniso* C2p_x, 2p_y value reflecting the importance of lone pair stabilization to the minimized energy. Quite similar results contrasting STO *Aniso* and *Iso*/p basis sets for water and ammonia were recently reported by Switkes, Stevens and Lipscomb.[25] Unexpectedly low values for the hydrogen exponents were obtained for all of the STO-4G basis sets when compared to that obtained for methane (1·17) or for the standard value (1.24).

TABLE 5. OPTIMUM EXPONENTS AND GEOMETRY FOR METHYL ANION FOR DIFFERENT BASIS SETS

	STO-4G Stand.[a]	STO-4G *Iso*/sp	STO-4G *Iso*/p	STO-4G *Aniso*	ECGTO 4s3p/2s	EGTO[c] N = 58
PYRIMIDAL-C_{3v}						
Exponents: C1s	5·670[b]	5·670[b]	5·700	5·700[b]		
C2s	1·720	1·547	1·600	1·640		
$C2p_x$, $C2p_y$			1·481	1·750		
$C2p_z$				1·303		
H1s	1·240	1·078	1·084	1·062		
Geometry: C—H (Å)	1·109	1·189	1·198	1·160	1·103	1·106
H—C—H angle (deg.)	101·01	97·51	98·74	104·59	107·50	
out of plane angle	26·99	29·75	28·80	24·00	21·38	23·5
PLANAR-D_{3h}						
Exponents: C1s	5·670[b]	5·670[b]	5·698	5·700[b]		
C2s	1·720	1·520	1·703	1·711		
$C2p_x$, $C2p_y$			1·424	1·749		
$C2p_z$				1·215		
H1s	1·240	1·118	1·150	1·093		
Geometry: C—H (A)	1·060	1·130	1·123	1·090	1·080	

[a] Standard exponents of Ref 4*a*
[b] Assumed value
[c] Ref. 24

The equilibrium C—H value obtained for C_{3v} CH_3^- using standard exponents is quite close to the value obtained for the ECGTO basis. The *Iso*/sp and *Iso*/p basis sets produced unusually large C—H distances fully 0·1 Å longer than a normal C—H bond. These long bonds are clearly a result of the lowering of the C and H exponents in the anion. The completely optimized *Aniso* results indicate a slightly shorter C—H bond but one still considerably longer than given by either the ECGTO or standard STO-4G methods. The out-of-plane angle also appears to be extremely sensitive to the type of basis set used with the ECGTO basis giving a smaller angle than any of the STO-4G basis sets.

The results for the D_{3h} form of CH_3^- in all cases indicate a shorter C—H bond than in the C_{3v} structure as expected in a change to a C_{sp^2}—H bond. This change in carbon hybridization is also reflected in higher exponents for all of the carbon and hydrogen exponents except that of the $C2p_z$ A.O. in the *Aniso* basis. In general the same trends between the various basis sets seen for the C_{3v} form are also evident for D_{3h}.

In Table 6 are given the energy components for both the C_{3v} and D_{3h} forms of CH_3^- for these five basis sets together with the results from an *Iso*/sp STO-6G calculation. For comparison the results from the 10s6p/8s EGTO calculation of Kari and Csizmadia are also included. For both C_{3v} and D_{3h} the total energy improves as constraints are removed from the exponents. There seems to be little

TABLE 6. VARIATION OF ENERGY COMPONENTS WITH BASIS SET FOR METHYL ANION (OPTIMUM GEOMETRY)

	STO-4G Stand.	STO-4G *Iso*/sp	STO-4G *Iso*/p	STO-4G *Aniso*	STO-6G[a] *Iso*/p	ECGTO 4s3p/2s	EGTO[b] 10s6p/8s
PYRAMIDAL-C_{3v}							
E_{Total}	−39·11610	−39·21230	−39·21378	−39·24538	−39·31637	−39·47762	−39·4798
E_1	−75·25183	−72·88478	−72·66904	−73·14631	−72·77711	−74·12107	
E_2	26·61934	24·77358	24·63137	24·82474	24·63684	25·11544	
E_{Nu}	9·51639	8·89890	8·82389	9·07670	8·82389	9·52800	
$1a_1$; ψ_1	−10·53724	−10·85335	−10·87108	−10·86226	−10·91469	−10·88945	−10·8840
$2a_1$; ψ_2	−0·46019	−0·52990	−0·53707	−0·54247	−0·53760	−0·59631	−0·6364
$3a_1$; ψ_5	0·15856	0·02286	0·01949	0·03519	0·01808	0·00215	0·0077
1e ; ψ_3, ψ_4	−0·01838	−0·15421	−0·15724	−0·18944	−0·15875	−0·23074	−0·2717
PLANAR-D_{3h}							
E_{Total}	−39·08164	−39·17194	−39·19030	−39·24316	−39·29239	−39·47166	−39·4780
E_1	−76·11458	−73·75962	−73·74791	−74·02212	−73·85237	−74·42793	
E_2	27·18233	25·34728	25·25961	25·19947	25·26198	25·28808	
E_{Nu}	9·85061	9·25040	9·29799	9·57949	9·29799	9·66819	
$1a_1'$; ψ_1	−10·47331	−10·79544	−10·82811	−10·87171	−10·87307	−10·87516	−10·8876
$2a_1'$; ψ_2	−0·41881	−0·48476	−0·51319	−0·55061	−0·51368	−0·57845	−0·6130
$1a_2''$; ψ_5	0·22360	0·09448	0·08516	0·07435	0·08371	0·03049	0·0198
1e ; ψ_3, ψ_4	−0·10322	−0·17340	−0·17910	−0·23182	−0·18058	−0·25138	−0·2819

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[a] The optimum geometry and exponents determined for the STO-4G-*Iso*/p basis set were used in the STO-6G-*Iso*/p calculation without any additional optimization

[b] Ref. 24*b*

justification in using the *Iso*/p basis over the *Iso*/sp basis since the improvement in the total energy in so doing is less than 1 Kcal/mole. As with methane, the ECGTO basis of Dunning gives an energy almost as low as previous calculations using much larger basis sets.

It is interesting to note the positive orbital energy obtained for the $3a_1$ MO in all those reported in the literature. In the best calculations this energy is of the order of 1–5 Kcal and is probably close to the energy of this MO in the H.F. limit. Combined with a pair correlation energy of about 1 volt, this result suggests that methyl radical has an electron affinity of about 20 Kcal.

The inversion barrier for the STO-4G basis sets and selected EGTO basis sets are given in Table 7. For assumed geometries using various EGTO basis sets the inversion barrier in general decreases as the size of the basis set increases whereas for optimized geometries larger inversion barriers are calculated. Polarizing functions on the carbon appear to increase the barrier. The ECGTO results obtained in this work are in the same range as these EGTO results while the inversion barriers obtained for most of the STO-4G basis sets are much higher. The value obtained for the *Aniso* STO-4G basis, however, is quite close to that obtained for some of the smaller EGTO basis sets. It seems clear that any isotropy forced on the exponents destabilizes the D_{3h} form more than the C_{3v} form of CH_3^- causing the inversion barrier to increase accordingly. This result is not unexpected since the splitting of the 2p exponents obtained for the *Aniso* results is much greater for D_{3h} in which the lone pair is pure p_z compared to C_{3v} in which all of the p-orbitals contribute to the lone pair. The much lower total energies obtained for the STO-6G calculations lead, however, to approximately the same inversion barrier; that is, inversion barriers can be added to the list of properties that have essentially converged by the STO-4G level.

TABLE 7. INVERSION BARRIER FOR METHYL ANION COMPARISON OF DIFFERENT BASIS SETS

Basis set		Barrier (kcal/mole)	Ref
STO-4G	Stand.	21·54	this work
	Iso/sp	25·23	this work
	Iso/p	14·68	this work
	Aniso	1·39	this work
STO-6G	*Iso*/p	14·99	this work
ECGTO	4s3p/2s	3·73	this work
EGTO	3s1p/2s. N = 12	4·17[a]	24*b*
	5s2p/3s. N = 20	5·56[a]	24*b*
	7s3p/4s. N = 28	4·38[a]	24*b*
	9s5p/4s. N = 36	1·61[a]	24*b*
	10s6p/4s. N = 40	1·22[a]	24*b*
	10s6p/8s. N = 52	3·50	24*c*
	10 6p1d/8s. N = 58	7·00	24*c*

[a] These calculations used fixed C—H bond lengths

We are not including the complete MO wavefunctions here; they are available by request. Instead, we reproduce one set of MO's in pictorial form for *Iso*/sp D_{3h}

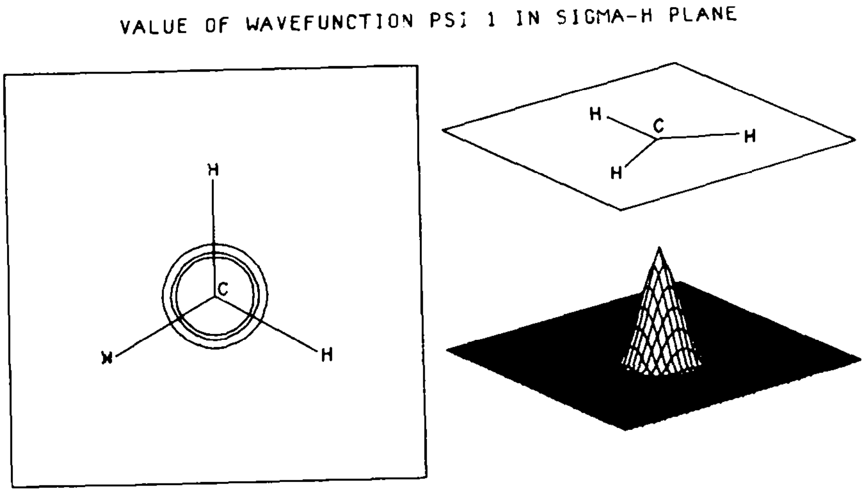
methyl anion in Fig 3. In this figure are shown both contour diagrams and a 3D representation of all of the occupied MO's. In the 3D drawing a modified logarithm scale is used; $\pm \log|\psi|$ is plotted for values of $|\psi|$ greater than some arbitrary small number. the sign being taken as that of ψ. Points for all smaller values of $|\psi|$ are included in the grid plane. This logarithm function was plotted rather than ψ itself in order to emphasize features of relatively low amplitude that are important in the bonding region but would be lost in comparison with the core amplitude. This function is plotted as a vertical axis for points in a given plane as shown to the same scale immediately above each 3D plot. ψ_1 is primarily the C_{1s} orbital. ψ_2 is completely bonding with the orthogonal C_{1s} shown as a negative peak in the center. ψ_3 and ψ_4 are the degenerate MO's showing C—H bonding with a single orthogonal nodal surface each. ψ_5 is the lone pair MO in which the nodal surface is the plane of the molecule.

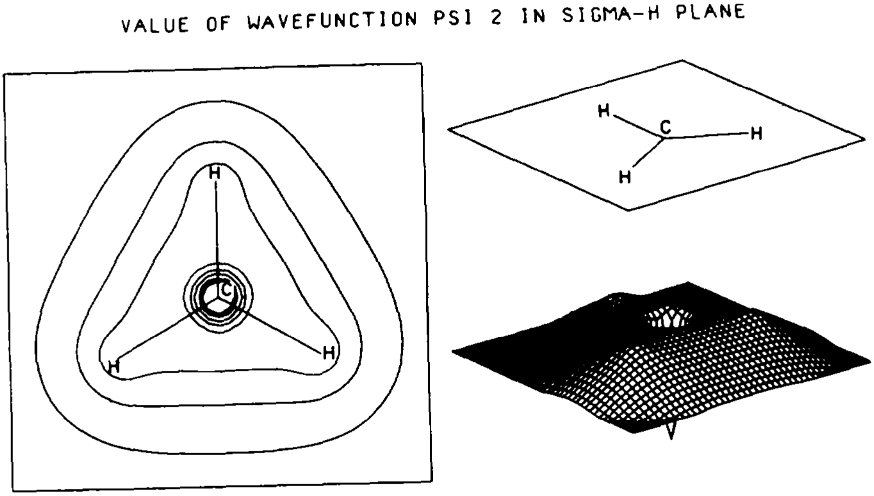
The Mulliken population for the STO-4G basis sets for the atoms and the A.O.'s are given in Table VIII for both C_{3v} and D_{3h} CH_3^- and the overlap populations are given in Table 9. As with methane. large differences are apparent between the ECGTO and minimum basis set results. The ECGTO calculations indicate more than a full negative charge on C ($-$ 1·13) for C_{3v} CH_3^- whereas all of the STO-4G results show some of the negative charge on the hydrogens. The standard exponent results are generally closer to the *Aniso* results than to the *Iso*/sp or *Iso*/p calculations except for the C2p_z C_{3v} CH_3^- population. This outcome is understandable when one recalls that in the *Aniso* case the C2p_x, 2p_y exponent is 1·75 and the C2p_z exponent is 1·303 while the standard C2p exponent is 1·72.

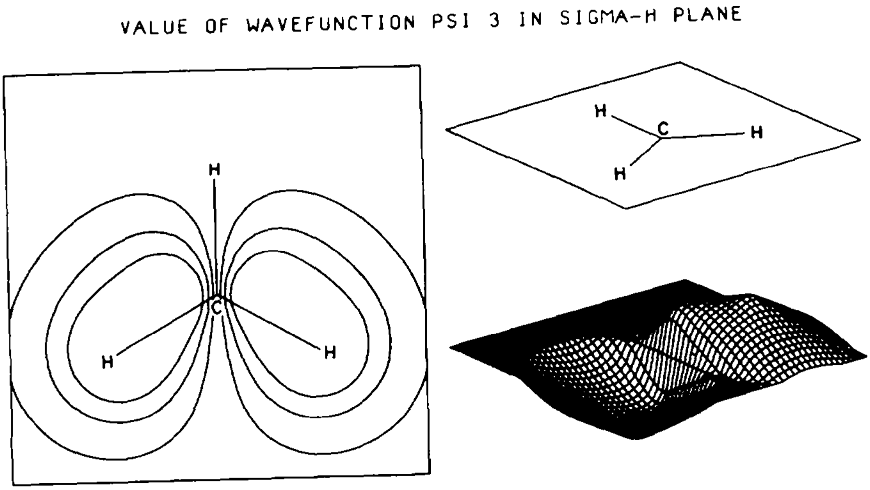
In all cases the more electronegative sp^2 C in $D_{3h}CH_3^-$ has a larger C population. due almost entirely to the increased C2p_z population. In all cases the C2s population decreases and the C2p_x, 2p_y population increases in going from C_{3v} to D_{3h}. Even

TABLE 8. MULLIKEN POPULATIONS FOR FULLY OPTIMIZED METHYL ANION FOR DIFFERENT BASIS SETS

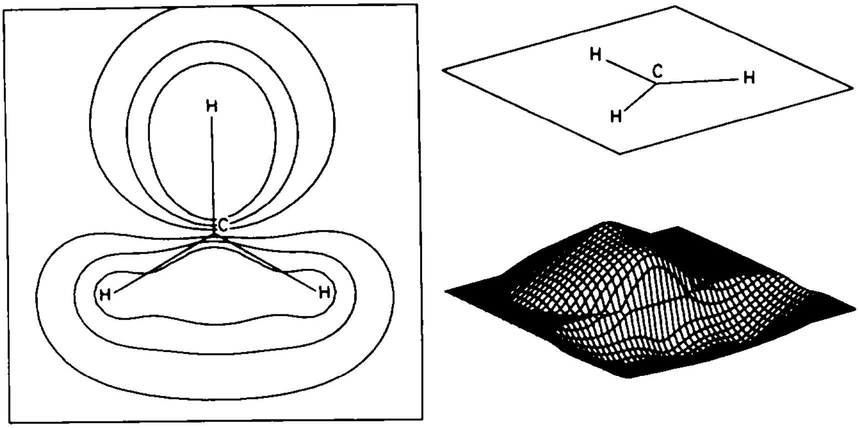
		STO-4G Stand.	STO-4G *Iso*/sp	STO-4G *Iso*/p	STO-4G *Aniso*	ECGTO 4s3p/2s
PYRAMIDAL-C_{2v}						
Total:	C	6·5018	6·7091	6·7816	6·6472	7·1274
	H	1·1661	1·0970	1·0728	1·1178	0·9575
Basis Functions:	C1s	1·9951	1·9971	1·9964	1·9955	1·9943
	C2s	1·3879	1·6039	1·5587	1·4182	1·4014
	C2p_x. C2p_y	0·7789	0·8151	0·8470	0·7668	0·9214
	C2p_z	1·5609	1·4779	1·5325	1·6700	1·8890
	H1s	1·1661	1·0970	1·0728	1·1178	0·9575
PLANAR-D_{3h}						
Total:	C	6·5982	6·9626	7·0640	6·8311	7·2630
	H	1·1339	1·0125	0·9787	1·0563	0·9123
Basis Functions:	C1s	1·9939	1·9964	1·9944	1·9942	1·9944
	C2s	1·0183	1·2065	1·1320	1·1187	1·2888
	C2p_x. C2p_y	0·7930	0·8798	0·9688	0·8591	0·9899
	C2p_z	2·0000	2·0000	2·0000	2·0000	2·0000
	H1s	1·1339	1·0125	0·9787	1·0563	0·9123


VALUE OF WAVEFUNCTION PSI 1 IN SIGMA-H PLANE
H
C
H
H
H
C
H
H


VALUE OF WAVEFUNCTION PSI 2 IN SIGMA-H PLANE
H
C
H
H
H
C
H
H


VALUE OF WAVEFUNCTION PSI 3 IN SIGMA-H PLANE
H
C
H
H
H
C
H
H

VALUE OF WAVEFUNCTION PSI 4 IN SIGMA-H PLANE



VALUE OF WAVEFUNCTION PSI 5 IN SIGMA-V PLANE

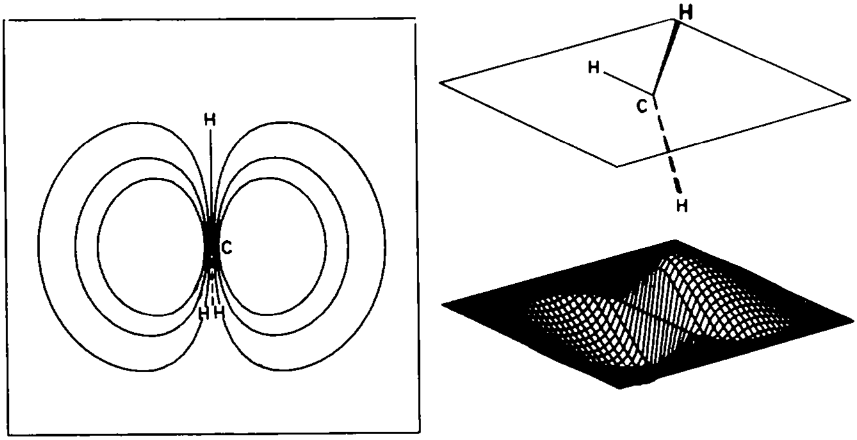


FIG 3. Occupied MO's for D_{3h} methyl anion in the STO-4G *iso*/sp basis. The vertical axis in the 3D plots are of $\pm \log |\psi|$, as discussed in the text, in a plane and scale defined immediately above each 3D plot

though the D_{3h} C is more electronegative than the C_{3v} C, all of the STO-4G calculations with the exception of the *Iso*/p case show some of the negative charge still residing on the hydrogens. The ECGTO results for D_{3h} C indicate a charge of $-1{\cdot}26$, an increase of 0·13 negative charge from C_{3v}. It should be noted, however, that in both forms the H population obtained for the ECGTO basis exceeds that obtained for methane (0·8073) using the same basis.

The C—H overlap populations all show the variation one would expect with different equilibrium C—H distances; the shorter the bond length the larger the overlap population. For these basis sets the overlap C—H population obtained for methane (see Table 3) is considerably larger than even the values for D_{3h} CH_3^- where C—H bond lengths less than that of methane were obtained. This indicates that there

TABLE 9. OVERLAP POPULATIONS FOR FULLY OPTIMIZED METHYL ANION FOR DIFFERENT BASIS SETS

	STO-4G Stand.	STO-4G *Iso*/sp	STO-4G *Iso*/p	STO-4G *Aniso*	ECGTO 4s3p/2s
PYRAMIDAL-C_{3v}					
Total: C—H[a]	0·6750	0·6286	0·6864	0·7036	0·7842
Basis Functions:					
C2s—H1. H2. H3	0·0934	−0·0088	0·0506	0·1560	0·2474
C2p_x—H1	0·4592	0·4734	0·4878	0·4488	0·5116
C2p_x—H2. H3	0·1148	0·1184	0·1220	0·1122	0·1280
C2p_y—H2. H3	0·3444	0·3550	0·3658	0·3366	0·3836
C2p_z—H1. H2. H3	0·1314	0·1688	0·1540	0·1080	0·0368
Overlap %s:[a]					
C/C—H	12·50	−2·14	6·50	20·86	30·07
PLANAR-D_{3h}					
Total: C—H[a]	0·7832	0·8106	0·8268	0·7814	0·7980
Basis Functions:					
C2s—H1. H2. H3	0·2998	0·2932	0·2908	0·2974	0·2758
C2p_x—H1	0·5002	0·5288	0·5500	0·4996	0·5358
C2p_x—H2. H3	0·1251	0·1322	0·1375	0·1248	0·1340
C2p_y—H2. H3	0·3751	0·3966	0·4125	0·3748	0·4018
Overlap %s:[a]					
C/C—H	36·15	34·76	33·49	36·07	32·85

[a] Contains C1s contributions to overlap

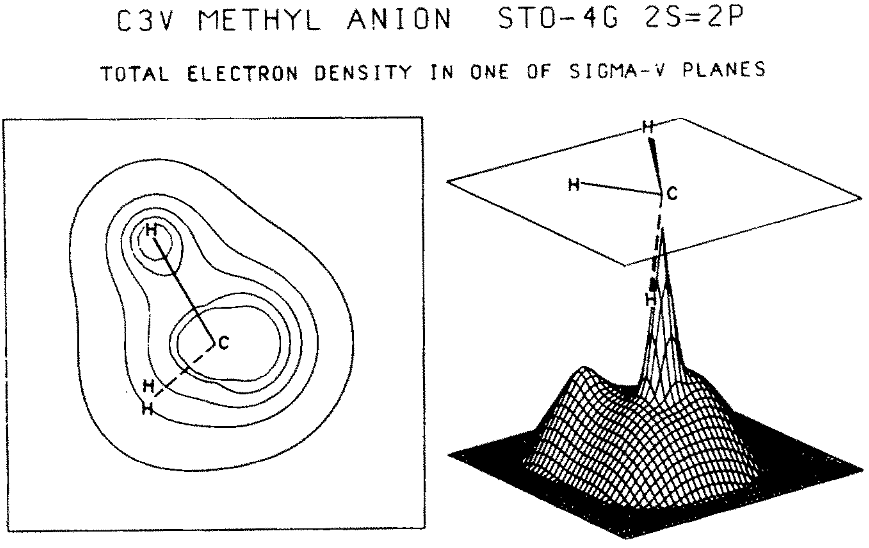
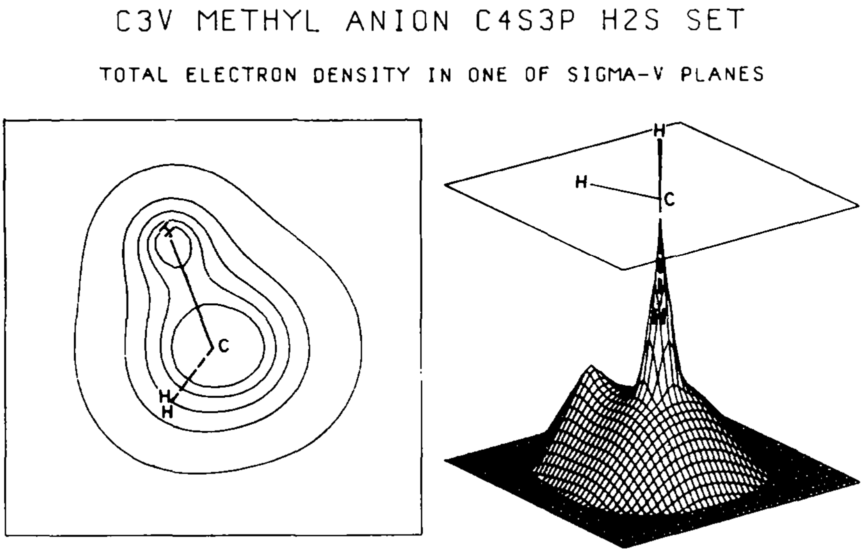


FIG 4. Electron density in one plane as shown for C_{3v} methyl anion in the STO-4G *Iso*/sp basis. Contours on the left are at 0·02, 0·08, 0·14, 0·20 and 0·26, respectively. The 3D plot is of log (electron density) with all values for electron density below an arbitrary small number incorporated in the grid plane


C3V METHYL ANION C4S3P H2S SET

TOTAL ELECTRON DENSITY IN ONE OF SIGMA-V PLANES

FIG 5. Electron density for methyl anion in the 4s3p/2s basis for comparison with Fig 4. Contour values are the same as in Fig 4

must be repulsion of the electrons in the bonding region by the lone pair onto the hydrogens. The ECGTO overlap populations are quite close to those of the STO-4G basis sets in D_{2h} CH_3^- while C_{3v} CH_3^- results show many discrepancies between the extended and minimum basis set overlap populations. While the agreement is not as good as that obtained with Mulliken populations, the standard exponent overlap populations are the closest of the STO-4G results to the *Aniso* basis.

The percent s-character is a sensitive function of the equilibrium C—H distance used. At the long distances given by several of the methods, the amount of s-character is small or negative. Such results are certainly artifacts of the constraints imposed. Some of the effects of these constraints are evident in electron-density plots. Fig 4 shows the electron density function from the *Iso*/sp calculation of C_{3v} CH_3^- in a plane containing one C—H bond and bisecting the other two. Both contour and modified logarithm 3D representations are shown. Fig 5 is a similar plot for the ECGTO calculation. Note the sharper peaks at H and in the C—H bonding region in the latter diagram. The constraint of accommodating a diffuse lone pair with the same minimum basis set as bonding electron pairs gives the latter an artificial diffuseness.

Fig 6 shows similar plots of D_{3h} CH_3^- in the *Iso*/sp approximation for the electron density in the molecular plane. The hydrogens and C—H bonding regions are again sharper and steeper. None of the lone pair electrons in the p_z-orbital appears in this figure, of course. A direct comparison may be made with the H_3 plane of C_{3v} CH_3^- Fig 7. The swelling plateau in the center is the "tail" of the lone pair. This plane does not include the C—H bonding region but it does show clearly the electron density about each hydrogen.

The six normal mode vibrations for a pyramidal C_{3v} molecule with four atoms all involve both bond stretching and bond bending so the exact analysis performed with

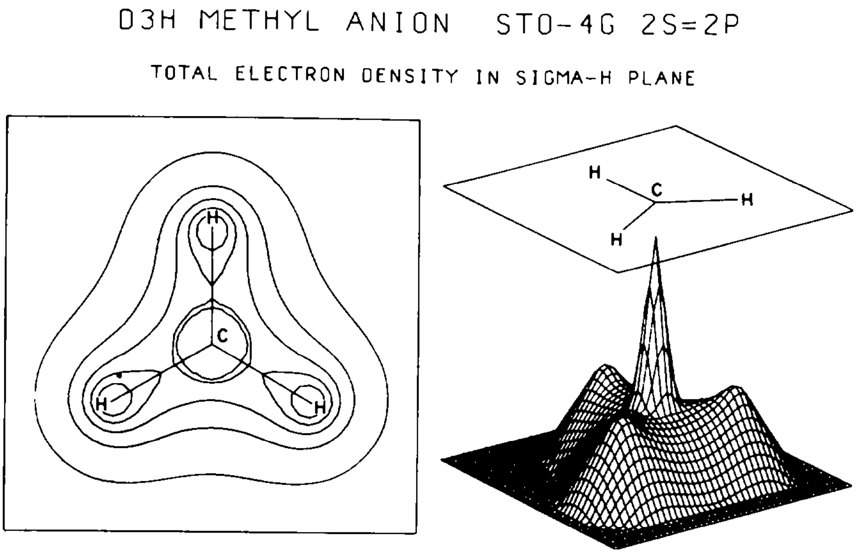


FIG 6. Electron density in the molecular plane of D_{3h} methyl anion in the *Iso*/sp basis. Contours shown are 0·02, 0·08, 0·14, 0·20 and 0·26, respectively. The log plot is defined as above

methane cannot be simply done for CH_3^-. Because of the differences in the C and H masses. however, the two a_1 modes of vibration may be crudely approximated by one involving C—H stretching and one involving out-of-plane bending.[21] In Table 10 are given the results of calculations for these two modes of vibration for the *Iso*/sp, *Iso*/p and *Aniso* STO-4G basis sets. Fig 8 graphically depicts the results for the *Iso*/sp

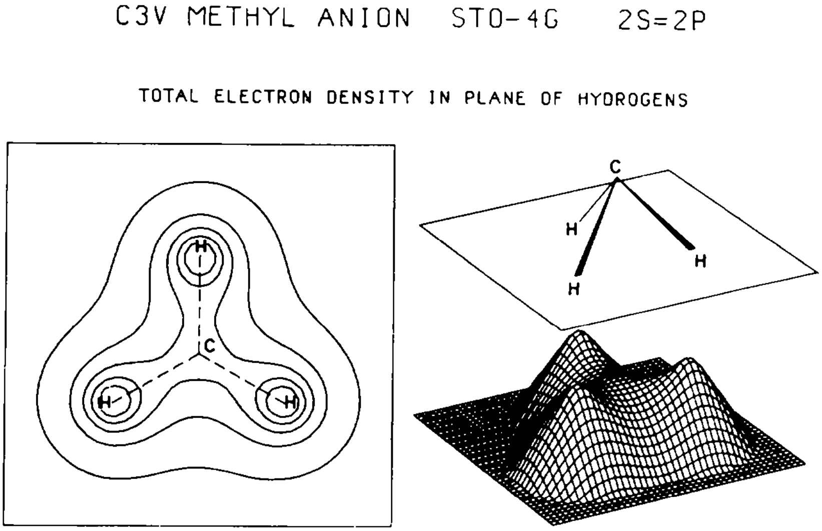


FIG 7. Electron density of 3_{3v} methyl anion *Iso*/sp basis in the plane defined by the three hydrogens. The plots are defined above.

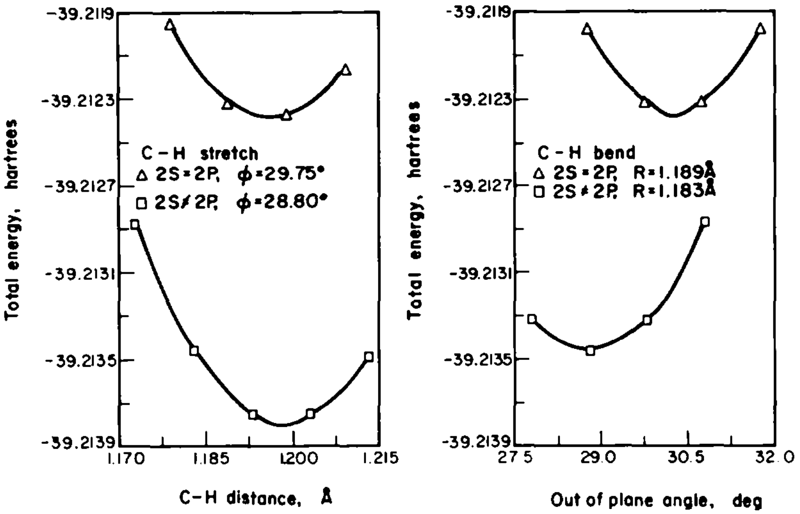


FIG. 8.

and *Iso*/p basis sets. By fitting the change in total energy as a function of either the C—H distance or the out-of-plane angle to a parabola and taking the second derivative the stretching force constant, k_r, and the bending force constant, k_ϕ, can be determined.

In Table 11 are presented the values for these force constants for the three STO-4G

TABLE 10. METHYL ANION—VARIATION OF TOTAL ENERGY WITH GEOMETRY EQUILIBRIUM GEOMETRY AND OPTIMUM EXPONENTS

Symmetrical C—H Stretch Constant out of plane Angle, ϕ					
STO-4G *Iso*/sp $\phi = 29{\cdot}75°$		STO-4G *Iso*/p $\phi = 28{\cdot}80°$		STO-4G *Aniso* $\phi = 24{\cdot}00°$	
C—H Dist (A)	Energy (A.U.)	C—H Dist (A)	Energy (A.U.)	C—H Dist (A)	Energy (A.U.)
1·179	−39·211951	1·173	−39·212862	1·140	−39·245325
1·189	−39·212300	1·183	−39·213455	1·150	−39·245520
1·199	−39·212360	1·193	−39·213746	1·160	−39·245378
1·209	−39·212145	1·203	−39·213752	1·170	−39·244919
		1·213	−39·213488		
Symmetrical Out of Plane Bend Constant C—H Distance, R					
STO-4G *Iso*/sp $R = 1{\cdot}189$ Å		STO-4G *Iso*/p $R = 1{\cdot}183$ Å		STO-4G *Aniso* $R = 1{\cdot}160$ Å	
ϕ (deg.)	Energy (A.U.)	ϕ (deg.)	Energy (A.U.)	ϕ (deg.)	Energy (A.U.)
28·75	−39·211972	27·80	−39·213309	23·00	−39·245364
29·75	−39·212300	28·80	−39·213455	24·00	−39·245378
30·75	−39·212309	29·80	−39·213318	26·00	−39·244725
31·75	−39·211981	30·80	−39·212881		

TABLE 11. METHYL ANION FORCE CONSTANTS FOR DIFERENT BASIS SETS[a]

Basis Set		k_r (mdyn/A)	k_ω (mdyn/A)	Ref.
STO-4G	*Iso*/sp	12·29	7·46	this work
	Iso/p	12·45	6·66	this work
	Aniso	14·25	2·41	this work
EGTO	10s6p/8s. N = 52	6·92	1·25	[24c]
	10s6p1d/8s. N = 58	8·56	2·02	[24c]

[a] All force constants determined at equilibrium geometry

basis sets as well as those reported by Kari and Csizmadia for two of their EGTO calculations. The k_r values appear to vary little with choice of STO-4G basis set all giving values about twice those obtained for the EGTO basis sets. This higher value for k_r is surprising in that the minimum basis set calculations all yielded longer C—H bond lengths than the extended basis sets. The k_ω values obtained reflect the behaviour seen in the inversion barriers; the lower the barrier, the smaller the k_ω value. The k_ω values reported for the EGTO calculations are reasonably close to that obtained for the *Aniso* STO-4G basis as were the respective inversion barriers.

In order to compare the CH_3^- k_r values to the k_{a_1} values obtained for methane. k_r must be converted to the appropriate symmetry coordinate. The S_{a_1} symmetry coordinate for CH_3^- is given by:

$$S_{a_1} = \frac{1}{\sqrt{3}}(R_1 + R_2 + R_3) = \sqrt{3}R$$

where R is the C—H distance. Therefore the two force constants are related by:

$$k_{a_1} = \frac{1}{3} k_r$$

The k_{a_1} value for both the *Aniso* and *Iso*/p basis sets is 5·88 mdyn/Å (the two basis sets must be identical for a tetrahedral molecule) for methane whereas for C_{3v} CH_3^- the values are 4·75 and 4·15 mdyn/Å, respectively, for the two basis sets. Still lower values are given by the extended basis sets for CH_3^-; thus, it seems probable that this mode of vibration would contribute significantly to a k_H/k_D secondary isotope effect of greater than unity in a base-catalyzed deprotiation of methane.

Because of our general interest in the acidity of hydrocarbons, one of the properties we obviously would like to calculate is the proton affinity of anions. Calculated proton affinities for CH_3^- for different basis sets are summarized in Table 12. The same methane value was used for the *Iso*/sp, *Iso*/p and *Aniso* basis sets. The *Iso* sets give virtually identical results much better than the standard set. The *Aniso* basis gives a better result than the *Iso* sets but still substantially higher than the H-F limit. The ECGTO proton affinity is virtually at the H-F limit. However, the H—F proton affinity is considerably above the experimental value. The latter number has substantial uncertainty because of the lack of a sound value for the electron affinity of methyl radical. Nevertheless, the uncertainty is surely not that high and the relatively high H—F value would appear to mean that the correlation energy in

TABLE 12. PROTON AFFINITIES FOR METHYL ANION FOR DIFFERENT BASIS SETS

Basis Set		Proton Affinity	
		Hartrees	Kcal/mole
STO-4G	Stand.	0·89129	557
	Iso/sp	0·79983	500
	Iso/p[a]	0·79834	499
	Aniso[a]	0·76675	479
STO-6G	*Iso*/p[a]	0·79496	486
ECGTO	4s3p/2s	0·70793	442
H-F limit[b]		0·705	441
Experimental			393[c]

[a] Refers to methyl anion basis set only; methane basis set is *Iso*/sp. STO-6G methane has standard exponents. not optimized

[b] For estimated H-F energy of methane see Ritchie and King [11]; for estimated H-F energy of pyramidal methyl anion see Kari and Csizmadia [24b]

[c] Calculated assuming an electron affinity of CH_3^- of 25 Kcal/mole

methyl anion is much higher than in the isoelectronic methane. perhaps in the inter-pair correlation between the lone pair and bonding pairs.

We conclude that lone pairs in carbanions present real problems for *ab initio* calculation. They can apparently be handled satisfactorily by extended basis sets: the separate adjustment of inner and outer parts of atomic orbitals in different molecular orbitals appears to be especially important for lone pairs: but such treatments rapidly become out of reach with larger sized molecules. In minimum basis set treatments. the problem of representing lone pair electrons by the same orbitals as bonding electrons is partially relieved by completely anisotropic optimization of all of the STO exponents but. here also. complete optimization is impractical for larger compounds. With isotropic basis sets the constraint of a single STO exponent imposed on a carbanion leads to unrealistic C—H bond distances. However. the present results show that there is no advantage in the partially isotropic *Iso*/p set.

A reasonable and practical course for subsequent work with larger systems is to use a "standard carbanion exponent" that reflects realities of electron distribution in a *Iso*/sp treatment without optimization of geometry. In Table 13 we summarize some results of calculations with several types of *Iso*/sp basis sets and methane geometry for CH_3^-. The "subtract" case assumes the same exponents for the anion as were obtained for the hydrocarbon. The "Stand" case uses proposed standard anion exponents that we have derived from the results of exponent optimization for several different anions with fixed hydrocarbon geometry; the "opt" case is where the exponents were actually optimized for the fixed hydrocarbon geometry. The fully optimized *Iso*/sp results previously presented are included for comparison. The "stand" and "opt" results are similar and substantially different from the "subtract" results. Comparing the "opt" with the fully optimized case. it is clear that imposing hydrocarbon geometry had little effect on the C2s. 2p exponent; however. the H1s exponent increased by 0·05 units. Also observed is a decrease in the C population and an increase in the H and C—H bond populations.

Iso/sp STO-4G anion calculations using assumed hydrocarbon geometry and either hydrocarbon exponents (subtract) or standard anion exponents are expected to be useful in comparing trends in similar molecules, but the large discrepancies between these calculations and more fully optimized *Iso*/sp and *Aniso* calculations must always be kept in mind. In particular, interpretations based on population analysis will require circumspection in such calculations. Calculations performed on a variety of hydrocarbon anions to be discussed later will make clear which of the three *Iso*/sp basis sets using hydrocarbon geometry ("subtract", "Stand", and "Opt") is best suited for the analysis of a particular molecular property.

TABLE 13. *Iso*/sp STO-4G RESULTS FOR METHYL ANION WITH METHANE GEOMETRY

Basis set[a]	Subtract[b]	Stand.[c]	Opt.[d]	Fully optimized[e]
Exponents: C2s, 2p	1·76	1·56	1·55	1·547
H1s	1·17	1·14	1·13	1·078
Total energy	−39·1104	−39·1884	−39·1891	−39·2123
Mulliken populations				
Total C	6·3352	6·8715	6·8920	6·7091
Total H	1·2216	1·0428	1·0360	1·0970
Total C—H overlap	0·6905	0·7622	0·7638	0·6287
%s overlap, C/C—H	21·71	20·82	20·66	−2·14

[a] C—H distance 1·089 Å, HCH angle 109·471° except for "fully optimized"

[b] Exponents and geometry of optimized methane

[c] Assumed "standard carbanion" exponents

[d] Optimized exponents for methane geometry

[e] Optimized structure and exponents; C—H distance, 1·189 Å, HCH angle 97·51°

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