

lability of the primary and tertiary H atoms makes it possible to evaluate, by a method introduced by Otvos, *et al.*,³⁰ and improved by Wolfgang, *et al.*,³¹ the distribution of the activity in the tritiated *i*-C₄H₁₀. The result obtained, showing that most (>90%) of the ³H activity is contained in the methyl groups, suggests that, unless an extensive reshuffling of the H atom follows the protonation, the attack which causes the tritium atom to remain bound in the isobutyl ion must take place on the methyl groups, while the attack on the tertiary carbon is likely to be followed by the elimination of tritium as hydrogen tritide,³² according to eq 26.

Finally, the difference in CH₄^{*} and C₂H₆^{*} yields from the interaction of the He³H⁺ ions with *n*-C₄H₁₀ and *i*-C₄H₁₀ is again evidence for the absence of a long-lived

(30) J. W. Otvos, D. P. Stevenson, C. D. Wagner, and O. Beek, *J. Am. Chem. Soc.*, **73**, 5741 (1951).

(31) A. Odell, A. Rosenberg, R. D. Fink, and R. Wolfgang, *J. Chem. Phys.*, **40**, 3730 (1964).

(32) This interpretation is supported by a most recent mass spectrometric observation (G. G. Volpi, private communication) that both C₄H₉D⁺ and C₄H₉⁺ ions are formed in the protonation of (CH₃)₃CD with ³H⁺ ions.

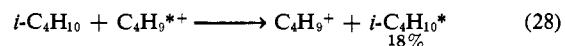
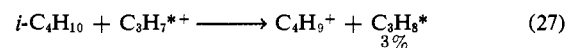
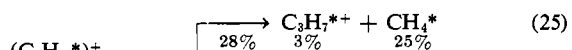
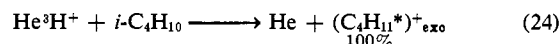


Figure 4. Protonation of isobutane by the He³H⁺ decay ions.

protonated intermediate capable of undergoing rearrangement and qualitatively reflects the trend reported by Aquilanti and Volpi¹¹ for the abundances of the propyl and ethyl ions in the protonation of *n*-C₄H₁₀ and *i*-C₄H₁₀ with H₃⁺.

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Ab Initio Bond-Orbital Calculations. I. Application to Methane, Ethane, Propane, and Propylene

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Abstract: A bond-orbital approach to *ab initio* calculations using a basis set of spherical Gaussians is developed and applied to methane, ethane, propane, and propylene. The method places emphasis on the transferability of nonorthogonalized bond orbitals from molecule to molecule. Several properties of methane and ethane are calculated using two different basis sets. Barriers to internal rotation in ethane, propane, and propylene are also calculated. The results for propane show that there is considerable interaction between the two methyl groups. The correct stable geometry is predicted for propylene, but the computed barrier is too small.

Quantum mechanical calculations, *ab initio*, on rather large molecules of chemical interest are now being carried out by means of the Roothaan LCAO-SCF technique.¹ Thus such molecules as benzene,² pyrrole,³ pyridine,⁴ and pyrazine⁵ have been treated.

An interpretive disadvantage of the LCAO-SCF procedure is that the molecular orbitals (MO's) do not in general correspond to the chemist's intuitive picture of molecules in terms of localized chemical bonds, lone-pair electrons, and the like. This can be overcome by subjecting the MO's to a unitary transformation utilizing the method suggested by Lennard-Jones and Pople⁶ and further developed by Edmiston and Ruedenberg.⁷

This procedure yields a set of localized orbitals which correspond in many cases to bond orbitals or lone pairs.

In this paper we begin by assuming that molecules such as CH₄ or C₂H₆ can be described in terms of 1s core, C-H bond, and C-C bond orbitals, and that these functions, after Löwdin orthogonalization,⁸ are at least a fair description of the localized orbitals which would result from a transformation of the SCF-MO's obtained utilizing the same basis set. We further assume that the nonorthogonalized C-H bond functions in CH₄, C₂H₆, C₃H₈, etc., are identical and can be carried over from molecule to molecule without change.

Atomic Orbitals

The carbon core and the bond orbitals are written as linear combinations of a minimal set of 1s, 2s, and 2p orbitals centered at the carbon atoms and 1s orbitals centered at the hydrogens. Ideally Slater orbitals would be used to represent these functions but the

(1) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(2) J. M. Schulman and J. W. Moskowitz, *J. Chem. Phys.*, **43**, 3287 (1965).

(3) E. Clementi, H. Clementi, and D. R. Davis, *ibid.*, **46**, 4725 (1967).

(4) E. Clementi, *ibid.*, **46**, 4731 (1967).

(5) E. Clementi, *ibid.*, **46**, 4737 (1967).

(6) J. E. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc. (London)*, **A202**, 155 (1950).

(7) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

(8) P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).

necessity of evaluating the resulting large number of three- and four-center electron interaction integrals renders this procedure unsuitable for rapid routine calculations. Therefore, each atomic orbital is expanded in terms of a basis set of spherical Gaussians, $\exp(-\alpha r_j^2)$. The idea of using such a basis originated with Preuss⁹ and has been applied to many molecules with good results.¹⁰

Pitzer¹¹ has carried out minimal basis LCAO-SCF calculations on methane in which the orbital exponents, ζ , of the Slater orbitals used as a basis set have been carefully optimized. The best values of these exponents near the predicted equilibrium C-H bond distance are 5.68 for the carbon 1s, 1.76 for both the carbon 2s and 2p, and 1.17 for the hydrogen 1s. We use these results and the variational methods suggested by McWeeny¹² and elaborated by Huzinaga¹³ to derive the appropriate linear combinations of Gaussians.

The carbon 1s and 2s orbitals were constructed from a basis set of five Gaussians having α values 0.32, 1.6, 8.0, 40.0, and 200.0.¹⁴ After the best variational fit to the Slater 2s was found, it was Schmidt-orthogonalized to that of the 1s, and it is this orthogonalized function which is used in all calculations described in this paper.

The carbon 2p orbitals were obtained by taking linear combinations of pairs of Gaussians centered 0.1 au away from the carbon along the positive and negative x , y , and z axes. Two different bases were considered. The first consisted of three pairs of Gaussians with α values of 0.3054, 0.989, and 4.226 (*i.e.*, each 2p orbital is represented by a linear combination of six spherical Gaussians). The second basis contained two pairs of Gaussians having α values of 0.402 and 1.738. In both cases the α 's were found by minimization of the one-electron energy of the 2p orbital using the appropriate Hamiltonian.

Two basis sets were also used to represent the hydrogen 1s orbital. The first set consisted of three Gaussians with α values of 0.2073, 0.9326, and 6.160. The second set contained two Gaussians having α values of 0.2759 and 1.824. The α 's were found by scaling the results of Huzinaga.¹³

Calculations on Methane

Calculations were carried out on the methane molecule for the dual purpose of establishing the C-H bond function and to compare some computed properties with the results of Pitzer¹¹ in order to ascertain whether or not at least qualitatively reliable values for these can be obtained. It is assumed that the wave function can be written as an antisymmetrized product of five doubly occupied orthogonalized orbitals representing the carbon 1s electrons and the four C-H bonds. These functions are Löwdin-orthogonalized⁸ linear combinations of the carbon 1s orbital and the four C-H bond orbitals, b_1 - b_4 . These latter quantities are written as

$$b_i = N(t_i + \lambda h_i) \quad (1)$$

where N is a normalization factor, t_i is a tetrahedral

(9) H. Preuss, *Z. Naturforsch.*, **11a**, 823 (1956).

(10) For example, see W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967), and reference therein.

(11) R. M. Pitzer, *ibid.*, **46**, 4871 (1967).

(12) R. McWeeny, *Acta Cryst.*, **6**, 631 (1953).

(13) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).

(14) J. W. Moskowitz and M. C. Harrison, *ibid.*, **42**, 1726 (1965).

hybrid directed toward the i th hydrogen, and h_i is a 1s orbital centered at this same hydrogen nucleus.

Methane calculations were carried out using two basis sets denoted by (5,3,3) and (5,2,2). [The first number (5) is the number of Gaussians used to represent the carbon 1s or 2s orbitals, the next (2 or 3) is the number of pairs of Gaussians in the p-orbital representation, and the final number (2 or 3) is the number of Gaussians representing the hydrogen 1s function.] In each calculation, the energy was minimized with respect to λ at various values of the C-H internuclear separation. The results are given in Table I, along with the predicted

Table I. Energy Results for Methane^a

	(5,3,3) basis	(5,2,2) basis
E ($R = 2.00$)	-39.92135	-39.81252
λ ($R = 2.00$)	1.043	1.080
E ($R = 2.06$)	-39.92224	-39.81460
λ ($R = 2.06$)	1.055	1.095
E ($R = 2.08$)	-39.92097	-39.81371
λ ($R = 2.08$)	1.059	1.100
E ($R = 2.10$)	-39.91900	-39.81210
λ ($R = 2.10$)	1.062	1.105
R_{eq}^b	2.038	2.048
k^c	29.8	30.3

^a Energies and distances are in atomic units. ^b Predicted equilibrium C-H distance. ^c Computed breathing mode force constant in mdyne/Å.

values of the C-H equilibrium internuclear distance and the force constant for the breathing mode. The computed energies are about 0.2-0.3 au above the SCF results of Pitzer which in turn are probably about 0.1 au above the true SCF energy. This is expected because of the small basis sets and the fact that the wave functions are not of the SCF type. The predicted equilibrium internuclear separations are in fair agreement with the experimental result¹⁵ of 2.067 au, but the calculated force constants for the breathing mode are in considerable disagreement with the experimental value¹⁶ of 23.47 mdyne/Å.

Table II gives the expectation values of several operators computed at $R = 2.06$ and compares these results with those found by Pitzer with his minimal-basis SCF function. In general, the results found here are in good agreement with the values of

Table II. Expectation Values for Methane^a

Operator	(5,3,3) basis	(5,2,2) basis	Pitzer
$\langle -1/2\nabla^2 \rangle$	39.7694	39.6877	40.162
$\langle 1/r_c \rangle$	16.5559	16.5273	16.682
$\langle r_c^{-2} \rangle$	34.8203	34.3449	35.185
$\langle 1/r_H \rangle$	4.9219	4.9324	4.9582
$\langle \delta_{xyz}^2 \rangle^b$	1.2178	1.1796	0.9354
$\langle eqQ_D/h \rangle^c$	224.7	253.9	224

^a All values in atomic units unless specified otherwise. ^b Octopole moment in units of 10^{-34} esu cm^3 . The results include the nuclear contribution. ^c Deuteron quadrupole coupling constant in CH_3D in kc/sec. The operator q is $(3z_D^2 - r_D^2)/r_D^5$, with the coordinate system such that the deuteron lies on the positive z axis. Q_D is the quadrupole moment of the deuteron, -2.796×10^{-27} cm^2 , taken from H. Narumi and T. Watanabe, *Bull. Am. Phys. Soc.*, **9**, 11 (1964). The results include the nuclear contribution.

(15) K. Kuchitsu and L. S. Bartell, *ibid.*, **36**, 2470 (1962).

(16) L. H. Jones and R. S. McDowell, *J. Mol. Spectry.*, **3**, 632 (1959).

Pitzer. The deuteron quadrupole coupling constant in CH_3D computed from the (5,3,3) wave function is also in excellent agreement with the value of 233 kc/sec computed by Caves and Karplus¹⁷ using the more accurate SCF wave function of Woznick.¹⁸

Calculations on Ethane

It is assumed in all calculations on ethane that the C–C bond length is 2.92 au, the C–H bond length is 2.08 au, and all angles are tetrahedral. The C–H bond function found for methane at a C–H bond distance of 2.08 au is carried over without change. The C–C bond function is written as

$$b_{\text{cc}} = N(t_1 + t_2) \quad (2)$$

where t_1 and t_2 are tetrahedral hybrids on the two carbon atoms directed toward the molecular midpoint. Calculations are carried out using both the (5,3,3) and (5,2,2) basis sets for eclipsed, staggered, and intermediate conformations. The energy results are given in Table III. The barrier to internal rotation is given

Table III. Energy Results for Ethane

Conformation	(5,3,3) basis		(5,2,2) basis	
	E^a	ΔE^b	E^a	ΔE^b
Staggered	-78.679510	0.000	-78.493038	0.000
Intermediate	-78.677271	1.404	-78.490933	1.320
Eclipsed	-78.675009	2.823	-78.488802	2.657

^a Energy in atomic units. ^b Energy minus energy of staggered conformation in kcal/mole.

as 2.823 kcal/mole by the (5,3,3) basis and 2.657 kcal/mole by the (5,2,2) calculation. A comparison of various computed values of the ethane barrier^{19–23} is given in Table IV. The experimental value of the barrier is 2.875 ± 0.125 kcal/mole.²⁴

Table IV. Computed Barriers in Ethane^a

Reference	Energy of staggered conformer		Barrier, kcal/mole	Basis set
	Energy	Barrier		
Pitzer ¹⁹	-78.99115	3.3		16 Slater functions, Slater-rule ζ 's
Pitzer ²³	-79.09797	3.5		16 Slater functions, methane ζ 's
Pedersen ²²	-78.50898	2.88		34 Gaussians
Pedersen ²²	-78.57040	3.45		52 Gaussians
Clementi ²⁰	-79.10824	3.62		86 Gaussians contracted to 32 functions
Fink ²¹	-79.14778	2.52		110 spherical Gaussians contracted to 18 functions
Present result	-78.67951	2.82		64 spherical Gaussians contracted to 9 BO's

^a All calculations except those described in this paper are SCF.

A calculation can also be made of the sixfold component of the internal rotation potential from the data

- (17) T. Caves and M. Karplus, *J. Chem. Phys.*, **45**, 1670 (1966).
- (18) B. J. Woznick, *ibid.*, **40**, 2860 (1964).
- (19) R. M. Pitzer and W. N. Lipscomb, *ibid.*, **39**, 1995 (1963).
- (20) E. Clementi and D. R. Davis, *ibid.*, **45**, 2593 (1966).
- (21) W. H. Fink and L. C. Allen, *ibid.*, **46**, 2261 (1967).
- (22) L. Pedersen and K. Morokuma, *ibid.*, **46**, 3941 (1967).
- (23) R. M. Pitzer, *ibid.*, **47**, 965 (1967).
- (24) K. S. Pitzer, *Discussions Faraday Soc.*, **18**, 66 (1951).

in Table III. Assuming the ninefold and higher terms to be zero, we can write

$$\Delta E(\varphi) = \frac{V_3}{2}(1 - \cos 3\varphi) + \frac{V_6}{2}(1 - \cos 6\varphi) \quad (3)$$

where ΔE is the energy relative to the staggered conformation and $V_3 = \Delta E(60^\circ)$ (*i.e.*, V_3 is the ordinary barrier to internal rotation). For the intermediate conformation ($\varphi = 30^\circ$)

$$\Delta E(30^\circ) = \frac{V_3}{2} + V_6 \quad (4)$$

so that V_6 is just the difference between $\Delta E(30^\circ)$ and one-half the threefold barrier. We obtain $V_6 = -7$ cal/mole for the (5,3,3) calculation and -8 cal/mole from the (5,2,2) basis results. Unfortunately, no experimental data are available for this quantity. Lowe and Parr²⁵ have speculated that for systems such as ethane, V_6 should be negative and about 0.5% of V_3 (-14 cal). This is no more than an educated guess, however, and should only be regarded as such. The data of Fink and Allen²¹ and Pedersen and Morokuma²² allow a calculation to be made of V_6 . Fink and Allen's elaborate calculation gives a V_6 of 190 cal/mole, almost certainly an unreasonable result. Pedersen and Morokuma do not give sufficient significant figures for an accurate estimate, but their results indicate V_6 is negative and greater than -10 kcal/mole. This is in agreement with our results and also the speculation of Lowe and Parr.

Table V is a tabulation of expectation values and properties for eclipsed and staggered ethane as computed from the present wave functions. The only calculation requiring explanation is that of the principal components of the deuteron quadrupole coupling tensor for $\text{C}_2\text{H}_5\text{D}$. Let us choose a coordinate system (x, y, z) which is centered at the deuteron with the z axis parallel to the C–C bond and the two carbons lying in the y – z plane. The operator for the $\mu\nu$ component of the field gradient tensor is

$$q_{\mu\nu} = \sum_N \frac{Z_N [3r_{\mu N} r_{\nu N} - \delta_{\mu\nu} r_N^2]}{r_N^5} - \sum_j \frac{3r_{\mu j} r_{\nu j} - \delta_{\mu\nu} r_j^2}{r_j^5} \quad (5)$$

where the first summation is over all nuclei (except the deuteron), the second over all of the electrons, and Z_N is the charge on nucleus N . In the coordinate system chosen, the expectation value of q_{yz} is nonzero so that a rotation of the coordinate system about the x axis by an angle γ is necessary to bring this quantity to zero. This rotation gives a new coordinate system (x, y', z'), and it is the components of the quadrupole coupling tensor in this coordinate system which are given in Table V. The angle γ is such that the y' axis very nearly lies along the C–D bond. Also given in Table V is the asymmetry parameter defined as

$$\eta = (\langle eq Q_D/h \rangle_{z'z'} - \langle eq Q_D/h \rangle_{xx}) / \langle eq Q_D/h \rangle_{y'y'} \quad (6)$$

No experimental values are available for the properties calculated except the molecular quadrupole moment,²⁶ which is $-0.7 \pm 0.2 \times 10^{-26}$ esu cm². The

- (25) J. P. Lowe and R. G. Parr, *J. Chem. Phys.*, **44**, 3001 (1966).
- (26) A. D. Buckingham, R. L. Disch, and D. A. Dunmar, result quoted by Sovers, Karplus, and Kern.²⁷

Table V. Expectation Values for Ethane^a

Operator	(5,3,3) basis		(5,2,2) basis	
	Staggered	Eclipsed	Staggered	Eclipsed
$\langle -1/2\nabla^2 \rangle$	78.4486	78.4592	78.3639	78.3749
$\langle 1/r_c \rangle$	18.8734	18.8730	18.8544	18.8549
$\langle 1/r_H \rangle$	6.6724	6.6750	6.6696	6.6728
$\langle r_m^2 \rangle^b$	108.8510	108.8489	107.6215	107.6334
$\langle z^2 - x^2 \rangle^c$	-0.6672	-0.7365	-0.5343	-0.5902
$\langle eq Q_D/h \rangle_{y'y'}^d$	207.5	207.2	235.9	235.7
$\langle eq Q_D/h \rangle_{zz}^d$	-105.1	-105.2	-119.1	-119.1
$\langle eq Q_D/h \rangle_{z'z'}^d$	-102.4	-102.0	-116.8	-116.6
γ , deg	19.61	19.63	19.52	19.52
η	0.013	0.015	0.010	0.011

^a All values in atomic units unless noted otherwise. ^b Measured from the molecular midpoint. ^c Molecular quadrupole moment in units of 10^{-26} esu cm². The nuclear contribution is included. ^d Principal components of the deuteron quadrupole coupling tensor in units of kc/sec.

computed values all lie within the experimental limits. The Pitzer-Lipscomb function¹⁹ gives quadrupole moments of -0.893 and -1.066×10^{-26} esu cm² for staggered and eclipsed ethane, respectively, whereas the Pitzer function utilizing the optimized Slater orbitals from methane yields a value of -0.623×10^{-26} esu cm² for staggered ethane.²⁷

Calculations on Propane

The major effort in the calculations on propane was directed toward internal rotation in this molecule. Experimentally, the barrier to internal rotation of each of the methyl groups has been estimated by thermodynamic considerations to be about 3.4 kcal/mole.²⁸ Unfortunately it is necessary to assume that internal rotation of the two methyls is independent in deriving this result. Preliminary theoretical calculations²⁹ have revealed that this assumption is not valid so that little information can be gained from the thermodynamic value.

It is again assumed that the C-C bond length in propane is 2.92 au, all C-H bond lengths are 2.08 au, and all angles are tetrahedral. This is not the true geometry,³⁰ but it is expected that this will have no effect on any qualitative conclusions which can be drawn from the computed results.

The conformations for which calculations were carried out can be most conveniently designated by two angles φ_1 and φ_2 , representing the rotation of the methyl groups. The conformation in which both methyls stagger the methylene has $\varphi_1 = \varphi_2 = 0$. This conformation is experimentally known to be the lowest energy form.³⁰ Calculations were carried out on five conformations using the (5,2,2) basis set and for three conformations with the (5,3,3) set. It was felt to be unnecessary to carry out further calculations with the larger basis in view of the parallel results obtained for those conformations upon which computations were performed with both sets. A summary of the results is given in Table VI.

The effect of the position of one methyl group on the rotational barrier of the second is shown to better advantage in Table VII. As the first methyl group moves from a staggered to an eclipsed position with respect to the methylene, the barrier to internal rotation for

Table VI. Energy Results for Propane

φ_1 , deg	φ_2 , deg	(5,3,3) basis		(5,2,2) basis	
		E^a	ΔE^b	E^a	ΔE^b
0	0	-117.437865	0.000	-117.172057	0.000
0	30	...	(1.62) ^c	-117.169651	1.509
0	60	-117.432721	3.226	-117.167263	3.007
30	60	...	(5.59) ^c	-117.163709	5.236
60	60	-117.424960	8.094	-117.159939	7.600

^a Energy in atomic units. ^b Difference in energy in kcal/mole between the given conformation and that with $\varphi_1 = \varphi_2 = 0$. ^c Estimated.

Table VII. Rotational Barriers in Propane

φ_1 , deg	(5,3,3) basis ^a	(5,2,2) basis ^a
0	3.226	3.007
30	(3.97) ^b	3.727
60	4.868	4.593

^a Barrier to internal rotation in kcal/mole for the second methyl group with the first methyl group held fixed at an angle φ_1 . ^b Estimated.

the second methyl increases by a factor of about 1.5. Inspection of a model of the propane molecule shows that this is a reasonable result. When both methyls stagger the methylene they are eclipsed to each other so that rotation of one of them by 60° eclipses it with respect to the methylene but staggers it with respect to the other methyl. Now if this methyl group is held fixed and the other rotated so that both methyls are eclipsed with respect to the methylene, they also eclipse each other so that the barrier to rotation is much larger than in the previous case. A secondary effect is also operative in that the eclipsed position of the methyls in the latter case is energetically more unfavorable than in the conformation having $\varphi_1 = \varphi_2 = 0$. If the latter effect is ignored, then an approximate expression for ΔE (as defined in Table VI) is

$$\Delta E(\varphi_1, \varphi_2) = \frac{V_0}{2}(2 - \cos 3\varphi_1 - \cos 3\varphi_2) - \frac{V_1}{2}\{1 - \cos [3(\varphi_1 - \varphi_2)]\} \quad (7)$$

This assumes an average value of V_1 for the methyl-methyl barrier. If this were the case, then V_0 can be written in either of two ways

$$V_0 = \Delta E(60^\circ, 60^\circ)/2 \quad (8)$$

$$V_0 = \Delta E(30^\circ, 60^\circ) - \Delta E(0^\circ, 30^\circ)$$

(27) O. J. Sovers, M. Karplus, and C. W. Kern, *J. Chem. Phys.*, **45**, 3895 (1966).

(28) K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).

(29) J. R. Hoyland, *Chem. Phys. Letters*, **1**, 247 (1967).

(30) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960).

The results of these equations for V_0 agree to within a few per cent, and we assign a value of V_0 which is the average of these, namely 4.01 or 3.76 kcal/mole for the (5,3,3) and (5,2,2) basis sets, respectively. The value of V_1 is then found using the average result of the following three expressions.

$$\begin{aligned} V_1 &= V_0 - \Delta E(0^\circ, 60^\circ) \\ V_1 &= V_0 - 2\Delta E(0^\circ, 30^\circ) \\ V_1 &= 3V_0 - 2\Delta E(30^\circ, 60^\circ) \end{aligned} \quad (9)$$

The numerical results for V_1 are 0.80 kcal/mole for the (5,3,3) basis and 0.77 kcal/mole for the (5,2,2) set. These values for V_0 and V_1 give a good fit to the results of Table VI, the average deviation being about 0.03 kcal/mole.

The dipole moment of propane in the completely staggered conformation was computed to be 0.0019 D from the (5,3,3) basis and 0.0017 D from the (5,2,2) set. The experimental value³⁰ is 0.083 D. If the origin of the dipole moment vector is the methylene carbon, we find that this vector is directed toward the center of the triangle formed by the three carbons and away from the triangle formed by the central carbon and its two bonded hydrogens. It is not known experimentally if this is the correct orientation.

Calculations on Propylene

Internal rotation in propylene is interesting in that the lowest energy conformation in which a methyl C-H bond eclipses the C-C double bond³¹ has a much higher nuclear-nuclear repulsion energy than the conformation in which the methyl group is rotated 60° from this position. Therefore a theory of internal rotation such as the empirical model of Karplus and Parr³² in which nuclear-nuclear repulsions determine the lowest energy conformation is not applicable. It was therefore felt worthwhile to undertake calculations on this system in order to establish whether the present method is sensitive enough to yield quantitative predictions and, if so, to attempt an elucidation of the predominant factors giving rise to the barrier.

Propylene contains two carbon atoms which are, ideally, in a state of sp^2 hybridization. In order to establish a C-H bond function for a trigonal carbon and also to derive the best form of the $2p\pi$ orbital, preliminary calculations were carried out on the planar CH_3 radical. It was assumed that the representation of the $2p$ orbitals previously derived could be carried over without change for the $2p\sigma$ orbitals. A new linear combination of the $2p$ basis functions was computed for the $2p\pi$ orbital by minimization of the energy of CH_3 for both basis sets. As expected, the $2p\pi$ orbital was somewhat more diffuse than the $2p\sigma$ function. All calculations were carried out at a C-H bond distance of 2.02 au.

The propylene molecule was assumed to have the following bond lengths in atomic units: C-C single bond, 2.81; C-C double bond, 2.55; C-H (tetrahedral), 2.08; C-H (trigonal), 2.02. All angles were assumed to be either tetrahedral or trigonal as appropriate. This geometry is in fair agreement with that derived by Lide and Mann³¹ from the microwave spectra.

(31) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957).
(32) M. Karplus and R. G. Parr, *ibid.*, **38**, 1547 (1963).

The C-C single-bond function was taken to be

$$b_{cc} = N[t_1 + tr_2] \quad (10)$$

where t_1 is a tetrahedral hybrid on the first carbon and tr_2 is a trigonal hybrid on second carbon. The doubly occupied π orbital was written as

$$\Phi_\pi = N[\pi_1 + \pi_2] \quad (11)$$

so that the inductive effect of the methyl group was ignored. A more detailed calculation in which this effect was taken into account produced little change in the relative energies.

Calculations were carried out with both the (5,2,2) and (5,3,3) basis sets with energy results listed in Table VIII. The lowest energy conformation is correctly predicted to be that in which a methyl C-H bond eclipses the C-C double bond, but the computed magnitude of the rotational barrier is much less than the experimental result³¹ of 1.978 ± 0.017 kcal/mole. This poor result is due to the cancellation of the individual contributions to the barrier which are much larger than the barrier itself. This effect is much more evident here than in ethane in which the individual contributions are not nearly so large. Table IX presents a tabulation of these contributions for both basis sets and also for wave functions which are scaled³³ to satisfy the virial theorem. It would appear from these results that the nuclear-nuclear and electron-electron repulsion changes are both large and out of phase with the total energy change and that stabilization of the lowest energy conformation is due to an enhanced nuclear-electron attraction energy.

Table VIII. Energy Results for Propylene

φ_1 , deg	(5,3,3) basis		(5,2,2) basis	
	E^b	ΔE^c	E^b	ΔE^c
0	-116.237831	0.000	-115.938183	0.000
30	-116.237194	0.400
60	-116.236547	0.805	-115.937441	0.465

^a $\varphi = 0$ corresponds to a C-H bond eclipsing the C-C double bond. ^b Energy in atomic units. ^c Difference in energy, in kcal/mole, between the given conformation and that having $\varphi = 0$.

Table IX. Breakdown of Contributions to the Propylene Barrier

Quantity ^a	(5,3,3) basis		(5,2,2) basis	
	Unscaled	Scaled	Unscaled	Scaled
ΔT^b	-0.677	-0.805	-1.057	-0.456
ΔV_{ne}^c	26.365	26.606	26.814	25.709
ΔV_{ee}^d	-12.451	-12.517	-12.860	-12.562
ΔV_{nn}^e	-12.432	-12.478	-12.432	-12.235
ΔE^f	0.805	0.805	0.465	0.456

^a For any property, P , $\Delta P = P(\varphi = 60^\circ) - P(\varphi = 0^\circ)$. All values in kcal/mole. ^b Kinetic energy. ^c Nuclear-electron attraction. ^d Electron-electron repulsion. ^e Nuclear-nuclear repulsion. ^f Total energy.

If the inductive effect of the methyl group on the π electrons is taken into account, the π orbital is written as

$$\Phi_\pi = N[\pi_1 + \lambda\pi_2] \quad (12)$$

where π_1 is centered on the central carbon. Using the (5,3,3) basis set and minimizing the energy with respect

(33) P. O. Lowdin, *J. Mol. Spectry.*, **3**, 46 (1959).

to λ , it is found that the best λ for either $\varphi = 0$ or $\varphi = 60^\circ$ is 1.03. The minimized energies are -116.237952 and -116.236659 .

The dipole moment of the most stable conformation of propylene was calculated to be 0.089 D with the (5,3,3) basis and 0.058 D with the (5,2,2) set. The experimental value³¹ is 0.364 D. The dipole moment vector is computed (for either basis) to make an angle of 39° with the C-C single bond axis and points from the methyl carbon toward the hydrogen bonded to the central carbon. This is in agreement with experiment.

Discussion

The bond orbital approach proposed in this paper appears capable of giving a reasonable account of in-

ternal rotation in hydrocarbons and at least qualitatively correct results for many molecular properties. Calculations on larger systems such as butane and isobutane are now in progress. Future applications to other molecules containing nitrogen and oxygen are planned.

The method used here is also well suited to calculations on π -electron systems within the framework of π -electron theory. The σ electrons can be placed in orthogonalized bond orbitals and taken into account only through the potential which they exert on the π electrons. Such a method would be much more satisfactory than the older methods since all results for excitation energies, ionization potentials, and other π -electron properties would be computed, *ab initio*, but within a constant σ framework. Calculations along these lines are in progress.

How Efficient Is Diffusion-Controlled Triplet Energy Transfer?¹

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Abstract: The efficiency with which 2,5-dimethyl-2,4-hexadiene ($E_T < 58$ kcal) quenches the triplet-state photo-elimination of valerophenone ($E_T > 72$ kcal) has been measured in different solvents. In three tertiary alcohols, $k_{qT} = 160/\eta$ cP M^{-1} . In primary alcohols more viscous than 1-pentanol, $k_{qT} = 125/\eta$ cP M^{-1} . In the less viscous primary alcohols and in alkanes and cycloalkanes, k_{qT} rises as η decreases, but k_{qT} is not a linear function of $1/\eta$. These results suggest that, in solvents where $\eta > 3$ cP, the rate of exothermic triplet-energy transfer from ketones to conjugated dienes is truly limited by and is very nearly equal to the average rate of diffusion in the solution. In less viscous solvents rates of energy transfer are slower than rates of diffusion, indicating that there is enough inefficiency in the energy-transfer process that diffusion apart of triplet ketone and diene molecules can compete with energy transfer during the lifetime of a solution encounter. When the probability that energy transfer will occur during the lifetime of a solution encounter is close to unity, Stern-Volmer quenching plots should curve sharply upward at high quencher concentrations due to nearest neighbor "static" quenching. Quenching of γ -methylvalerophenone by 2,4-hexadien-1-ol in *t*-butyl alcohol displays just such behavior, whereas quenching of γ -phenylbutyrophenone by 1,3-pentadiene in pentane does not. These observations provide evidence that triplet energy transfer is not totally diffusion controlled in solvents of low viscosity.

It is well known that the rate of exothermic triplet energy transfer in solution is influenced by the viscosity of the solvent.² It is often assumed³ that such triplet energy transfer is so efficient that *every* encounter in solution between excited donor and acceptor molecules results in energy transfer, so that the rate of energy transfer is limited by *and equals* the rate of diffusion together of donor and acceptor. Recent reviews⁴ provide tables listing the viscosities of common solvents and the rates of diffusion in them as calculated from the Debye equation.⁵

(1) Triplet Energy Transfer. III. For a preliminary account, see part II: P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5715 (1967); and P. J. Wagner, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, R118.

(2) G. Porter and F. Wilkinson, *Proc. Roy. Soc. (London)*, **A264**, 1 (1961).

(3) For example, N. J. Turro, *Chem. Eng. News*, **45**, No. 20, 91 (1967).

(4) (a) F. Wilkinson, *Advan. Photochem.*, Vol. 3, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p 248; (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 627.

(5) P. J. W. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

The evidence that energy transfer is diffusion controlled comes from flash spectroscopic studies. In benzene at 25° there is an apparent maximum rate constant for energy transfer of $5 \pm 1 \times 10^9 M^{-1} \text{sec}^{-1}$ as long as the triplet excitation energy of the donor is 3-4 kcal higher than that of the acceptor (quencher).^{6,7} When account is taken of reverse energy transfer from excited quencher back to the original donor, it seems that the energy-transfer process need be no more than 1 kcal exothermic to proceed at the "maximum" rate.⁸ That *one* rate constant should describe exothermic energy transfer between literally dozens of donors and acceptors of different structures seems very good intuitive evidence that a common process is rate determining, namely the rate at which excited donor and acceptor molecules can diffuse together in solution.

(6) H. J. L. Bäckström and K. Sandros, *Acta Chem. Scand.*, **16**, 958 (1962).

(7) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

(8) K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964).