with most radicals which is intermediate between that of $(MeO)_3P$ and $(MeO)_3PO$. The large couplings with DTBN and TANO suggest asymmetrical hydrogen bonding, P–H$\cdots$O–N, between radical and receptor.[13] Such a view was earlier suggested from a much weaker scalar effect with tri-*t*-butylphenoxyl radical.[2] The strongest effects here are with TANO and DTBN, in which the free electron is highly localized to the NO group, rather than being delocalized into a π ring orbital. Not only is the available spin density high, but the molecule is probably more highly polar,[14] with negative charge on the NO group to favor H bonding. In this view, the moderate scalar coupling shown with DANO reflects an electron distribution which reduces the hydrogen-bonding tendency, and also offers a smaller unpaired spin density at the active NO site.

The nmr signal of the bonding proton (presuming that transient H bonding does indeed exist here) is a 700-Hz doublet because of nuclear spin–spin coupling with P. It is observable at 74 G and shows essentially the full dipolar coupling with the radical electron. In consideration of the proton's centralized position in an H bond, it may seem surprising that it feels no scalar coupling, particularly since scalar coupling is transmitted over the proton from radical to phosphorus. The absence of scalar coupling at H is, however, consistent with either an electrostatic H bond or with a bond involving only π orbitals. These four samples would be of special interest in a multifield dnp study, where the effects of coupling strength and complexation time could be separately delineated.

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Molecular Orbital Theory of the Electronic Structure of Organic Compounds. IV. Internal Rotation in Hydrocarbons Using a Minimal Slater-Type Basis

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Abstract: Self-consistent molecular orbital theory with a minimal basis of atomic orbitals is used to study internal rotation in hydrocarbons with two, three, or four carbon atoms. For the range of conformations in which steric interactions are not strong, calculated energy differences are found to be insensitive to the choice of bond lengths and bond angles. However, if steric interactions are large, the rigid rotor model is found to be inadequate. Good results are then obtained with a flexible rotor model in which each CCC angle is separately optimized for each conformation considered.

A number of workers have successfully used *ab initio* LCAO SCF MO calculations to calculate barriers to rotation of methyl groups[1–15] and to investigate the conformations of some important hydrocarbons.[15–17] In general, the results obtained are in good agreement with experiment. It has been found[18] that values of the rotational barriers are not particularly sensitive to the basis set employed.

In the work reported so far, only small numbers of molecules have been treated. It was of interest to apply a uniform model to a larger set of molecules, and in this paper we report the results of such a study on 19 hydrocarbons through C_4. We use a level of calculation (STO-3G) which has been described previously[19] and develop a procedure which may be generally applied to a large set of molecules. In addition, we examine the form of the potential function required to describe the rotation in the various molecules.

Potential Energy Functions

The potential energy function $V(\alpha)$ describing the internal rotation of one part of a molecule (rotor) relative to the remainder (framework) may be expanded as a Fourier series

$$V(\alpha) = \sum_i {}^1\!/_2 V_{Ni}(1 - \cos iN\alpha) \qquad (1)$$

where α is the angle of rotation and N represents the degree of symmetry of the molecule. In general, α is taken as zero for the minimum energy conformation. Thus, for example, for ethane, in which the rotating methyl group has threefold symmetry, $N = 3$ and the potential function may be written

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$$V(\alpha) = {}^1/_2V_3(1 - \cos 3\alpha) + {}^1/_2V_6(1 - \cos 6\alpha) + \ldots \quad (2)$$

It is commonly assumed that the second and succeeding terms of (2) are much smaller than the first and it is of interest to test this assumption. In the two-term expansion of $V(\alpha)$, V_3 is the value of the potential barrier while V_6, though not contributing to the barrier itself, modifies the shape of the potential function.[20] Thus, for example, a positive V_6 leads to broadened maxima and narrowed minima. Put a different way, a positive V_6 implies that more energy is required for rotation from $\alpha = 0°$ to $\alpha = 30°$ than from $\alpha = 30°$ to $\alpha = 60°$. A potential energy function of the type (2) applies to rotors of C_3 symmetry attached to any framework. It may be noted that if the framework has C_2 symmetry (*e.g.*, nitromethane), the V_3 term vanishes and the leading term is the V_6 term.

A complicating factor arises if there is more than one rotating group. Thus, in a molecule with two equivalent methyl rotors (*e.g.*, propane), the energy required to rotate one methyl group depends on the orientation of the second methyl group. This coupling or gearing of the two rotors modifies the potential energy function which may be expressed this time in the form

$$V(\alpha_1, \alpha_2) = {}^1/_2V_3(1 - \cos 3\alpha_1) + {}^1/_2V_3(1 - \cos 3\alpha_2) + {}^1/_2V_6(1 - \cos 6\alpha_1) + {}^1/_2V_6(1 - \cos 6\alpha_2) + {}^1/_4V_3'(1 - \cos 3\alpha_1)(1 - \cos 3\alpha_2) - {}^1/_4V_3'' \sin 3\alpha_1 \sin 3\alpha_2 + \ldots \quad (3)$$

where α_1 and α_2 are the angles of rotation of the two rotors and the terms in V_3' and V_3'' represent the interaction of the two rotors. More specifically, with the potential written in the form (3), V_3 is the energy required to rotate one methyl group by 60° with the second methyl group in its minimum energy conformation ($\alpha = 0$), while V_3' is the additional energy (*i.e.*, compared with V_3) required for the subsequent 60° rotation of the second group. For independent rotation of the groups, V_3' is zero.

Although the presence of coupling terms has been known for some time,[21-24] most treatments (experimental or theoretical) reported so far have either made the approximation of independent rotation or have made assumptions concerning the relative values of V_3' and V_3'' (see, *e.g.*, ref 14, 25, and 26). We shall test the validity of these approximations.

A similar situation exists for molecules in which there are three equivalent methyl rotors (*e.g.*, isobutane). Here we can write[27] the potential function in terms of the three internal rotation angles α_1, α_2, and α_3 and obtain an expression analogous to (3), but this time with four interaction terms.

For molecules in which the rotating group has C_2 symmetry (*e.g.*, ethylene, allene, butatriene), the potential function has the form

$$V(\alpha) = {}^1/_2V_2(1 - \cos 2\alpha) + {}^1/_2V_4(1 - \cos 4\alpha) + \ldots \quad (4)$$

In the molecules of this class considered here, rotation about a double bond is involved and the magnitudes of the potential parameters are expected to be much greater than those involved in rotation about a single bond.

Finally, if both the rotor and the framework are asymmetric, a full potential energy function of the type (1) with $N = 1$ must be used

$$V(\alpha) = {}^1/_2V_1(1 - \cos \alpha) + {}^1/_2V_2(1 - \cos 2\alpha) + {}^1/_2V_3(1 - \cos 3\alpha) + \ldots \quad (5)$$

Since expressions of this type are commonly terminated after three terms in the analysis of spectroscopic data,[28] it is of interest to evaluate the higher order terms and hence to determine what sized expansions adequately describe the potential functions.

Geometric Model

In studying the internal rotation in the hydrocarbons considered here, one has a choice as to which geometric model to use. Most commonly, the experimentally determined geometry for the most stable form is taken and other conformations are generated by rigid rotation[29] of the molecule. In many cases, however (especially for nonpolar species which cannot be studied by microwave methods), high quality structural data are not available. In addition, for comparative studies, the use of experimental data from a variety of sources and of varying precision means that important contrasts may be buried in the varying experimental errors. Finally, even in favorable cases, the experimental geometry is generally known only for one, or at most two, forms of a molecule, and so assumptions must be made (generally that of rigid rotation) to generate other conformations.

An alternative method is to use standard values of bond lengths and angles.[30] The advantages of this method are its wide applicability, *i.e.*, it is not limited to molecules whose geometry has been determined experimentally, and its usefulness in comparative studies. However, when there are large deviations from the standard bond lengths and angles (as caused by steric interactions, for example), one desires yet another method.

Ideally, complete energy minimization with respect to all bond lengths and angles should give the most accurate results. However, this is at present too expensive. As a compromise, the geometry may be partially optimized and a limited number of geometric parameters allowed to vary. If the molecule is given this small number of (well-chosen) degrees of freedom in each conformation, any strong steric interaction may be relieved and, although the energy values calculated in this way will not be as accurate as those obtained from a fully optimized geometry, the energy differences between conformations will have reasonable

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values. Rotation of this type is referred to as partially flexible rotation.

Most theoretical studies of internal rotation so far reported assume rigid rotation. Since only small molecules have been considered, there has been little occasion for steric forces to be prominent and the rigid rotor approximation is unlikely to have led to large errors in these calculations. However, even for ethane, Veillard[10] has recently shown that optimization of the geometries of the staggered and eclipsed forms leads to improved values of the potential barrier.

Hoyland[12–16] has considered larger hydrocarbon molecules than other workers, and his results for propane[14] and *n*-butane[15] are in excellent agreement with experiment. However, Hoyland assumes rigid rotation from the experimental geometry. We show here that in certain cases, the rigid rotor model is inadequate, but that by partial optimization and flexible rotation, realistic results may be obtained.

We have chosen the CCC angle(s) as the geometric parameter(s) to be optimized in the molecules treated in this paper. This was considered to be a more efficient method of relieving steric strain than by varying any other single bond length or angle. The flexible rotor model we use is thus one with standard values of bond lengths and angles except for the CCC angles which are optimized for each conformation. In the procedure for optimization of CCC angles, the following assumptions were made concerning the remaining angles at the central carbon. When the CCC angle is at a trigonal carbon, the other two angles are taken to be equal. When the CCC angle is at a secondary tetrahedral carbon atom, the remaining angles are determined by assuming that the CCH angles have the tetrahedral value (which is close to the experimental result for propane[31]). Finally, for isobutane, which is the only molecule which we have considered which has CCC angles at a tertiary tetrahedral carbon, all angles are determined once a value is assigned to the CCC angle. For several molecules in which there are either no CCC angles (*e.g.*, ethane), or in which the CCC angle is required to be 180° (*e.g.*, allene), only the barriers computed from standard geometry calculations are reported. The question of complete geometry optimization in barrier calculations for small molecules will be discussed elsewhere.[11] For 1-butene, in which there are two different types of CCC angles, both were optimized.

In discussing the internal rotation in individual molecules, we have compared calculations based on several geometric models. These are (A) standard geometry[30] with rigid rotation; (B) optimized CCC angle(s) for the minimum energy conformation and rigid rotation; (C) optimized CCC angles for all conformations (*i.e.*, flexible rotation); and (D) experimental geometry for the most stable conformation and rigid rotation. The abbreviations A, B, C, and D are used in the remainder of this paper.

SCF Calculations

The LCAO SCF calculations were performed using a least-squares fit of *N* Gaussian functions to a minimal basis set of Slater-type atomic orbitals (STO's). Details of this STO-NG method have been given previously[19] and we have used the standard exponents reported in that paper. The results approach those of a full STO basis when *N* is large. Except where stated, we have employed a three-Gaussian fit (STO-3G). The convergence of the derived energy differences was confirmed by doing additional calculations at the STO-4G level for several molecules. All calculations have been carried out at single precision on a CDC 1604A computer, the limit of significance of the calculated energies being approximately 10^{-5} au.

Ethane, 1-Butyne, 2-Butyne

The internal rotation in ethane has been extensively studied using *ab initio* calculations. Values of the potential barrier, taken as the difference in energy of the eclipsed and staggered forms, ranging from 2.52 to 3.62 kcal mol^{-1}, have been reported.[1–3,6,7,10,13,17] Experimental values of the barrier are 2.875 kcal mol^{-1} from calorimetric measurements[32] and 3.030 and 2.928 kcal mol^{-1} from infrared studies,[33,34] the most accurate value being that from ref 34, which was derived from a direct observation of the torsional spectrum. Our calculations based on the standard model[30] for ethane (Table I) give barriers of 3.32 and 3.33 kcal mol^{-1} at the STO-4G and STO-3G levels, respectively. In this paper, we are concerned with the application of a uniform model (standard geometry with optimized CCC angles) to the complete series of molecules, so we have not used the fully optimized geometry[17] of ethane. Nevertheless, our result is in reasonable agreement with the experimental values.

Table I. Potential Energies[a] and Derived Parameters for Conformations of Ethane and 2-Butyne (Model A)

Molecule	ϕ,[b] deg	STO-3G	STO-4G
Ethane	0	−78.305487	−78.862315
	30	−78.302855	−78.859687
	60	−78.300179	−78.857021
V_3[c]		3.331	3.322
V_6[c]		−0.014	−0.012
2-Butyne	0	−153.036672	−154.140064
	60	−153.036663	−154.140056
V_3[c]		0.006	0.005

[a] Unless otherwise stated, energies in this paper are given in atomic units (au). [b] ϕ is the change in HCCH dihedral angle measured from the staggered conformation ($\phi = 0°$). [c] V in kcal mol^{-1}.

For the closely related molecule 1-butyne (in which one hydrogen of ethane is replaced by the linear -C≡C—H group), the results (Table II) are similar to those for ethane. The conformation in which the methyl group is staggered with respect to the rest of the molecule has the minimum energy and the potential barrier is 3.76 kcal mol^{-1} on standard model calculations. Using optimized CCC angles of 112.4 and 113.1° for the staggered and eclipsed forms, respectively, the barrier is calculated as 3.46 kcal mol^{-1}, which is close to the ethane value.

Very few experimental estimates of V_6 have appeared in the literature, but they all suggest that V_6 is much smaller than V_3. Our results (Tables I and II) confirm that V_6 is very small for ethane and 1-butyne, and the

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Table II. Potential Energies and Derived Parameters for Conformations of 1-Butyne

ϕ,[a] deg	A	C	
		θ,[b] deg	
0	−153.024667	112.4	−153.025330
30	−153.021701	112.7	−153.022573
60	−153.018682	113.1	−153.019824
V_3[c]	3.756		3.455
V_6[c]	−0.017		−0.003

[a] ϕ is the change in HCCH dihedral angle measured from the staggered conformation (ϕ = 0°). [b] θ is the value of the optimized CCC angle. [c] V in kcal mol^{-1}.

Table III. Potential Energies and Derived Parameters for Conformations of Propene and 1,2-Butadiene

Molecule	ϕ, deg	A	C		
			θ, deg	STO-3G	STO-4G
Propene	0	−115.656681	124.7	−115.657787	−116.488399
	30	−115.655552	124.5	−115.656550	−116.487205
	60	−115.654422	124.3	−115.655322	−116.486023
V_3[a]		1.418		1.547	1.491
V_6[a]		0		0.003	0.004
1,2-Butadiene	0	−153.003628	124.4	−153.004422	−154.108285
	30	−153.002512	124.3	−153.003301	−154.107204
	60	−153.001408	124.3	−153.002187	−154.106136
V_3[a]		1.393		1.402	1.348
V_6[a]		0.004		0.003	0.004

[a] V in kcal mol^{-1}.

values we have obtained are on the threshold of significance as determined by the computorial accuracy. The fact that V_6 is negative is in agreement with results (for ethane) from other theoretical calculations.[8,13]

2-Butyne (dimethylacetylene) is an interesting molecule in that the two methyl groups in this molecule are separated by an acetylenic linkage and the interaction between them is expected to be small. Thermodynamic[35,36] and infrared[37,38] results have indicated that the barrier is very small, but no precise estimate has been given. An upper limit of approximately 30 cal mol^{-1} has been set.[37] A microwave determination[39] gives a barrier of less than 3 cal mol^{-1} for the closely related molecule methylsilylacetylene. We find that the barrier in 2-butyne is indeed small and obtain values of 5 and 6 cal mol^{-1} from our STO-4G and STO-3G calculations, respectively (Table I).

Another point of interest in 2-butyne is that the consideration[40] of the triple bond as three bent single bonds predicts that the two methyl groups will be eclipsed. This situation arises because both terminal methyl groups would tend to stagger the bent bonds of the central carbon–carbon linkage. Our calculations indicate, however, that the conformation with methyl groups staggered has minimum energy.

Propene, 1,2-Butadiene

The potential energies for conformations of propene and 1,2-butadiene defined by the dihedral CCCH angle (ϕ) are shown in Table III. For both molecules, the minimum energy form is that in which a C—H bond eclipses the C═C double bond (ϕ = 0°), and this result agrees with experiment.[41,42] The optimized CCC angle (θ) of 124.7° for the most stable form of propene may be compared with the microwave-determined[43] angle of 124.3°. No accurate value has been reported for the corresponding angle in 1,2-butadiene.

Experimental (calorimetric, microwave, and infrared) values[20,44–47] of the barrier to rotation of the methyl group in propene range from 1.950 to 2.039 kcal mol^{-1}. *Ab initio* calculations by Hoyland[13] and Unland[9] give barriers of 0.805 and 1.480 kcal mol^{-1}, respectively. We obtain values of 1.418 kcal mol^{-1} from standard model calculations and 1.547 and 1.491 kcal mol^{-1} from STO-3G and STO-4G calculations, respectively, using optimized CCC angles.

A barrier of 1.589 kcal mol^{-1} has been obtained[42] for 1,2-butadiene by microwave spectroscopy. Our values are 1.393 kcal mol^{-1} from standard model calculations and 1.402 and 1.348 kcal mol^{-1} from STO-3G and STO-4G calculations, respectively, using optimized CCC angles. Although our computed barriers for propene and 1,2-butadiene are both lower than the experimental results, they do reproduce the relative values well.

The small positive values of V_6 may be contrasted with the negative values obtained in ethane-type systems. However, estimates of V_6 for propene from infrared and microwave studies[20,46,47] are in the range −37 to −63 cal mol^{-1}.

Propane, 2-Methylpropene (Isobutylene), *cis*-2-Butene, *trans*-2-Butene

Each of these four molecules has two equivalent methyl groups which may interact. Potential energies were calculated for each molecule for a series of conformations defined by the angles of rotation α_1, α_2 of each methyl group from its minimum energy orientation. A least-squares fit to expression 3 for the potential energy was then obtained where possible.

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Table IV. Optimized and Experimental CCC Angles for Conformations (α_1,α_2, deg) of Propane, 2-Methylpropene, *cis*-2-Butene, and *trans*-2-Butene

Conformation	Exptl CCC angle, deg 0,0	Optimized CCC angles, deg 0,0	0,30	0,60	30,30	30,60	60,60
Propane	112.4^b	112.2	112.5	112.8	112.8	113.5	114.2
2-Methylpropene^a	115.3^c	115.7	116.1	116.6	116.5	117.5	118.4
cis-2-Butene	125.0, 127.8^d	128.0	127.2	126.2	126.2	125.5	124.6
trans-2-Butene		124.5	124.4	124.3	124.3	124.2	124.1

^{a} Values quoted for the C–C–C angle. ^{b} From ref 31. ^{c} L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, 39, 1732 (1963). ^{d} From ref 52.

Table V. Potential Energies and Derived Parameters for Conformations of Propane

α_1, deg	α_2, deg	A	B	C	D^a
0	0	−116.885121	−116.885743	−116.885743	−116.885803
0	30	−116.882195	−116.882991	−116.883002	−116.883094
0	60	−116.879240	−116.880207	−116.880244	−116.880351
30	30	−116.879272	−116.880234	−116.880271	−116.880376
30	60	−116.875413	−116.876860	−116.877043	−116.877109
60	60	−116.871421	−116.873399	−116.873836	−116.873765
$V_3{}^b$		3.690	3.474	3.451	3.421
$V_3{}'{}^b$		1.207	0.792	0.571	0.707
$V_3{}''{}^b$		1.062	0.688	0.609	0.608
$V_6{}^b$		−0.028	−0.021	−0.004	−0.020

^{a} Experimental geometry from ref 31. ^{b} V in kcal mol^{-1}.

For propane, the most stable form is found to be that in which both CH_3 groups are staggered with respect to the CH_2 group and the molecule has C_{2v} symmetry. This is in agreement with the microwave result.[31] For each of the three butene molecules, the minimum energy form has two methyl C—H bonds eclipsing the C=C double bond. This is in accordance with the microwave result for 2-methylpropene,[48] but the other two molecules have not as yet had their structures fully determined experimentally.

Optimized CCC angles (θ) are shown in Table IV. The values for the lowest energy conformation are very close to those obtained from microwave spectroscopy. The large change in θ in going from the (0,0) conformation to the (60,60) conformation in some of the molecules should be noted. In particular, the large value (128.0°) of θ for the (0,0) form of *cis*-2-butene is indicative of the strong steric repulsion between the two methyl groups in this molecule that would exist with (the more usual) smaller values of θ.

The potential energy parameters for propane are shown in Table V. The results for this molecule are not particularly sensitive to the model used, although the interaction terms appear to be overestimated when rigid rotation is assumed (A, B, and D). Our V_3 value compares favorably with calorimetric[49,50] (3.40 and 3.30 kcal mol^{-1}) and microwave[26] (3.555 kcal mol^{-1}) results in which independent rotation is assumed. Recently, Hirota has considered interaction terms in the analysis of the microwave spectrum of propane and has obtained[51] $V_3 = 3.325$ and $V_3'' = 0.680$ kcal mol^{-1}. Hoyland[14] has reanalyzed Hirota's experimental results and also performed *ab initio* calculations using a potential of the form of eq 3, but with $V_3' = V_3''$ and $V_6 = 0$. He obtains $V_3 = 3.265$, $V_3' = 0.620$ kcal mol^{-1} from the experimental results and $V_3 = 3.123$, $V_3' = 0.714$ kcal mol^{-1} from his theoretical calculations. Our results are in good agreement with both Hirota's and Hoyland's interpretations of the microwave spectrum. Our V_3', V_3'', and V_6 values indicate that Hoyland's assumptions regarding these parameters are reasonable for propane. Hoyland's theoretical estimate of V_3' could be slightly high because of his assumption of rigid rotation.

Experimental (thermodynamic,[44] infrared,[25] and microwave[48]) values of the potential barrier in 2-methylpropene range from 2.12 to 2.35 kcal mol^{-1} and have all been calculated assuming the interaction between the methyl groups is small. Our value of V_3 (Table VI) is slightly low, but the increase in barrier with methyl substitution in going from propene to 2-methylpropene is reproduced. The V_3' and V_3'' terms are again not widely different, while the small positive value of V_6 is in agreement with our result for propene.

Table VI. Potential Energies and Derived Parameters for Conformations of 2-Methylpropene

α_1, deg	α_2, deg	A	B	C
0	0	−154.242404	−154.243410	−154.243410
0	30			−154.242039
0	60	−154.240042	−154.240663	−154.240698
30	30			−154.240685
30	60			−154.238968
60	60	−154.237142	−154.236823	−154.237298
$V_3{}^a$		1.482	1.724	1.702
$V_3{}'{}^a$		0.338	0.686	0.434
$V_3{}''{}^a$				0.510
$V_6{}^a$				0.014

^{a} V in kcal mol^{-1}.

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Table VII. Potential Energies and Derived Parameters for Conformations of *cis*-2-Butene

α_1, deg	α_2, deg	A	B	C
0	0	−154.225571	−154.241094	−154.241094
0	30			−154.240719
0	60	−154.234736	−154.240061	−154.240424
30	30			−154.240346
30	60			−154.240025
60	60	−154.237235	−154.238664	−154.239669
V_3[a]		−5.751	0.648	0.420
V_3'[a]		4.183	0.228	0.051
V_3''[a]				0.015
V_6[a]				0.020

[a] V in kcal mol^{-1}.

Table VIII. Potential Energies and Derived Parameters for Conformations of *trans*-2-Butene

α_1, deg	α_2, deg	A	C
0	0	−154.241567	−154.243752
0	30		−154.242524
0	60	−154.239333	−154.241299
30	30		−154.241281
30	60		−154.240052
60	60	−154.237047	−154.238812
V_3[a]		1.402	1.539
V_3'[a]		0.033	0.022
V_3''[a]			−0.012
V_6[a]			0.002

[a] V in kcal mol^{-1}.

The parameters for *cis*-2-butene and *trans*-2-butene are shown in Tables VII and VIII. Early calorimetric results[44] for these molecules showed that while the barrier (1.95 kcal mol^{-1}) to methyl group rotation for *trans*-2-butene was close to the propene value, the barrier (0.45 kcal mol^{-1}) in *cis*-2-butene was strikingly lower. The low barrier in *cis*-2-butene has since been confirmed by microwave measurements[52] which yielded 0.73 kcal mol^{-1}. This result can be rationalized[53] by noting that substitution *cis* to a methyl group attached to a double bond raises the energy of the potential minimum, with relatively little effect on the potential maximum.

We find V_3 = 0.42 kcal mol^{-1} for *cis*-2-butene and V_3 = 1.54 kcal mol^{-1} for *trans*-2-butene, the latter value being close to our result for propene. The fact that V_3' and V_3'' are small for *trans*-2-butene is expected since the methyl groups are far apart. In *cis*-2-butene, one might predict a negative value of V_3' since the (0,0) form is sterically crowded, and so rotation from (0,0) to (0,60) could involve more energy than that from (0,60) to (60,60). However, widening of the CCC angles opposes this effect and, in fact, small positive values of V_3' and V_3'' are obtained. The energy parameters for *cis*-2-butene are sensitively dependent on the model used (see Table VII), and flexible rotation is essential in this case because of the large changes in the CCC angle. Thus, for example, model A predicts that the most stable form is that in which both methyl groups are staggered with respect to the double bond. Small positive V_6 values are again obtained for *cis*- and *trans*-2-butene. The calculated energy difference between the *cis* and *trans* isomers of 2-butene, $E(cis) - E(trans)$ = 1.67 kcal mol^{-1}, compares favorably with the experimental value[54] of 1.24 kcal mol^{-1}.

Isobutane (2-Methylpropane)

2-Methylpropane has three equivalent methyl groups. Our results for conformations defined by the internal rotation angles α_1, α_2, and α_3 of the three methyl groups from staggered configurations are shown in Table IX.

Table IX. Potential Energies and Derived Parameters for Conformations of 2-Methylpropane

α_1, deg	α_2, deg	α_3, deg	A	B
0	0	0	−155.46511	−155.46572
0	0	60	−155.45862	−155.45953
V_3[a]			4.072	3.884

[a] V in kcal mol^{-1}.

We find the most stable form has C_{3v} symmetry with staggered configurations around each C–C bond ($\alpha_1 = \alpha_2 = \alpha_3 = 0$), in agreement with the microwave result.[55] In order to determine the potential function fully, we would have to do optimization studies on at least six conformations. In this work, we have not attempted to do this and have only obtained the energy (V_3) required to rotate one methyl group with the other groups in their minimum energy configuration. Our result, V_3 = 3.88 kcal mol^{-1}, obtained using the optimized CCC angle for the (0,0,0) conformation of 110.8°, is in good agreement with the thermodynamic[56,57] (3.62 and 3.87 kcal mol^{-1}) and microwave[58] (3.90 kcal mol^{-1}) values.

Ethylene, Allene, Butatriene, Vinylacetylene

Ethylene, allene, and butatriene are the first three members of the series of molecules called the cumulenes, of general formula $CH_2{=}(C{=})_nCH_2$. It is well established[59,60] that the early members of the series are alternately planar and orthogonal. This result is confirmed by our calculated (closed shell, single configuration) energies which are shown in Table X for conformations defined by the angle between the planes of the two CH_2 groups.

The potential energy function cannot be fitted to a short- (*e.g.*, six-) term expansion of the form (4). A probable cause is the inadequacy of a single configuration treatment. This is particularly so for the perpendicular forms of ethylene and butatriene, in which the highest occupied levels are doubly degenerate, and there is marked improvement in the calculated energies

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Table X. Potential Energies and Derived Parameters for Conformations of Ethylene, Allene, and Butatriene

α, deg	Ethylene	Allene	Butatriene
0	−77.07121	−114.27299	−151.77131
10	−77.06841	−114.30323	−151.76984
20	−77.06005	−114.32909	−151.76543
30	−77.04614	−114.35240	−151.75808
40	−77.02676	−114.37256	−151.74781
45	−77.01504	−114.38136	−151.74159
50	−77.00199	−114.38928	−151.73464
60	−76.97199	−114.40241	−151.71859
70	−76.93694	−114.41184	−151.69969
80	−76.89712	−114.41752	−151.67798
90	−76.85291	−114.41941	−151.65350
Barrier, kcal mol^{-1}	138.6	91.9	73.9
Force constant, eV rad^{-2}	4.96	3.39	2.63
Twisting frequency, cm^{-1}	1237	1022	901

with the inclusion of configuration interaction terms.[61,62] Our calculated barriers (Table X) decrease along the series ethylene, allene, and butatriene and are similar to those obtained from other single configuration calculations. Values of 126.1 and 128.9 kcal mol^{-1} for ethylene[62,61] and 82.2 and 74.6 kcal mol^{-1} for allene[62,63] have been reported. Two-term configuration interaction treatments by Kaldor and Shavitt[61] and Buenker[62] have yielded ethylene barriers of 83.2 and 83.5 kcal mol^{-1}. Experimentally, the best estimate of the barrier in ethylene is given[64] by the activation energy for the thermal isomerization of *trans*-dideuterioethylene, the result being 65 kcal mol^{-1}. Although it is believed[64] that the rotation process proceeds *via* a singlet mechanism, there is a possibility that it goes *via* a triplet state.[65–67] We obtain a singlet–triplet barrier of 48.3 kcal mol^{-1}.

From the energies of conformations around the potential minima, force constants and thence twisting frequencies were calculated for the three molecules. The values obtained are included in Table X. Experimental values[68,69] of the twisting frequencies of ethylene and allene are 1027 and 812 cm^{-1}, respectively, so our values are both somewhat high, but in the correct order. Our results indicate that rotation about the double bond becomes easier as one proceeds along the cumulene series. Other calculated values of the ethylene force constant between 4.35 and 5.64 eV rad^{-2} have been reported[61,62,70] compared with the experimental 3.36 eV rad^{-2} and our value of 4.96 eV rad^{-2}. Buenker[62] has calculated a force constant of 5.49 eV rad^{-2} for allene.

Vinylacetylene is the analog of ethylene in which a C–H bond is replaced by the linear $-C{\equiv}C{-}H$ group and the results for this molecule are given in Table XI. We find the rotational barrier is 137.7 kcal mol^{-1} when optimized CCC angles (θ) are used, and this is close to the ethylene value. A striking feature of the calculation is that θ changes from 123.6° for the planar conformation to 74.4° for the orthogonal form, a result which may be interpreted by the presence of a cyclic species.

Table XI. Potential Energies and Derived Parameters for Conformations of Vinylacetylene

α, deg	A	C
0	−151.80209	−151.80266
90.0	−151.54762	−151.58315
Barrier, kcal mol^{-1}	−159.680	−137.743

1,3-Butadiene, *n*-Butane, 1-Butene

Rotation about the central C–C bond in these three molecules in which neither the rotor nor the frame have C_2 symmetry must be described by eq 5.

1,3-Butadiene. Although 1,3-butadiene has received a great deal of attention from chemists, the form of the potential energy function for this molecule is currently uncertain. It has been well established[71,72] that the most stable form is *trans*[73] planar, but no pseudostable form has been detected. Resonance arguments would favor a pseudostable planar *cis* form, while the consideration[40] of a double bond as two bent single bonds leads to the prediction of a *gauche* (or skew) form. There is no conclusive experimental evidence in favor of either theory.

Extensive microwave studies on related molecules[74–82] such as isoprene and acrolein have shown the stable form in these molecules to be *trans* planar, but have given no indication of a second isomer. Recently,

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Table XII. Potential Energy Parameters (kcal mol^{-1}) for 1,3-Butadiene and *n*-Butane

Molecule	Model	V_1	V_2	V_3	V_4	V_5	V_6	V^*
1,3-Butadiene	A	2.645	4.124	2.332	−1.176	0.635	−0.235	28.750
	D	1.197	5.223	1.424	−0.542	0.289	−0.097	29.964
	C	0.728	5.695	1.175	−0.331	0.144	−0.027	31.433
n-Butane	A	8.340	−4.676	5.628	−0.362	0.456	−0.398	31.587
	D	4.397	−2.348	4.261	−0.184	0.233	−0.202	28.976
	C	3.001	−1.341	3.764	0.099	0.061	−0.130	29.945

nuclear magnetic resonance,[83] infrared,[84,85] and microwave[86,87] results have shown the pseudostable form to be *cis* planar in a number of halogen- and oxygen-substituted butadiene-type molecules in which stabilization of the *cis* form through hydrogen bonding is possible. On the other hand, studies[88–92] of heavily substituted butadienes (in which there is steric hindrance to the planar forms) indicate the presence of nonplanar conformations for these molecules. The situation in 1,3-butadiene itself is still uncertain and it was therefore of interest to investigate the potential function for this molecule.

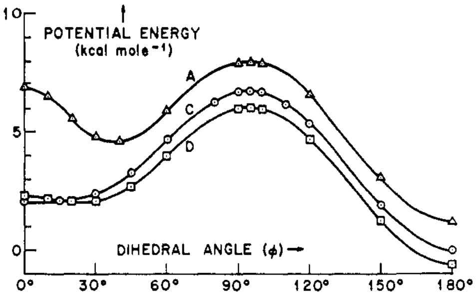

Figure 1. Potential energy functions (with energies calculated relative to the energy, −153.01661 au, of the *trans*-optimized conformation) describing internal rotation in 1,3-butadiene: curve A, standard geometry, rigid rotation; C, optimized CCC angles, flexible rotation; D, experimental geometry, rigid rotation.

We have calculated the potential energy of this molecule as a function of the CCCC dihedral angle (ϕ), and the results obtained are shown in Figure 1. Curve A gives the energies for conformations generated using the standard model. D gives the corresponding energies of those conformations generated by rigid rotation of the experimentally determined[93] geometry for *trans*-1,3-butadiene. Both these curves have potential maxima at the *cis* position ($\phi = 0$) and potential minima for nonplanar conformations, supporting the bent bond predictions. However, if the approximation of rigid rotation has forced the *cis* conformation into a sterically unfavorable geometry, its energy may have been overestimated using the above models.

Intuitively, we would expect some widening of the CCC angle in the *cis* form compared with the *trans*. To test this theory, optimized CCC angles (θ) were calculated for a number of dihedral angles, and the results are shown in Figure 2. It can be seen that there is indeed a widening in θ in going from *trans*-1,3-butadiene (θ = 124.2°) to *cis*-1,3-butadiene (θ = 126.6°).

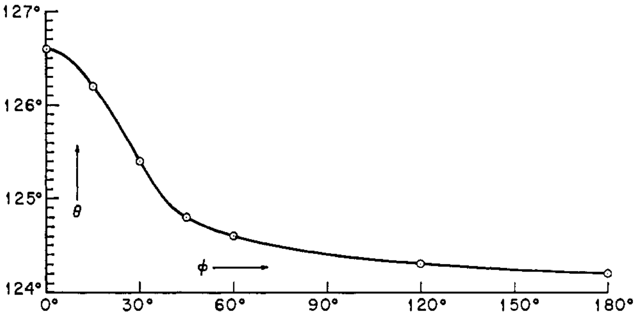

Figure 2. Variation in optimized CCC angles (θ) of 1,3-butadiene with CCCC dihedral angle (ϕ).

Curve C in Figure 1 gives the energies obtained using the optimized CCC angles (from Figure 2) for all conformations. For large values of ϕ ($\phi > 90°$, say) in which region the steric interaction is small, the curves A, D, and C are very similar. However, for small ϕ, there are striking deviations in the three curves. C predicts a potential minimum at $\phi = 0$, while A and D both predict potential maxima. We believe the steric interaction due to the smaller θ in A (120°) and D (124.2°) as compared to the optimized value (126.4°) is probably responsible for this difference.

Our results thus support a pseudostable planar *cis* form, but it should be noted that the potential energy function is very flat in the region of this conformation so that skew forms with $\phi <$ *ca.* 30° will have comparable populations.

It is of interest to obtain a theoretical estimate of the quantity V^* which is available from infrared spectroscopy. This is related to the curvature at the *trans* position, $\phi = 0°$, and is given by

$$V^* = V_1 + 4V_2 + 9V_3 + 16V_4 + 25V_5 + 36V_6 \quad (6)$$

We have fitted our potential energy functions to a six-term cosine series of the form (5) (with $\alpha = 180° - \phi$) by a least-squares procedure to obtain the parameters $V_1, \ldots, V_6$ and hence V^*, for comparison with the experimental value. These results are shown in Table XII. The values of V^* are in good agreement with the experimental result[28] (V^* = 28.1 kcal mol^{-1}) and,

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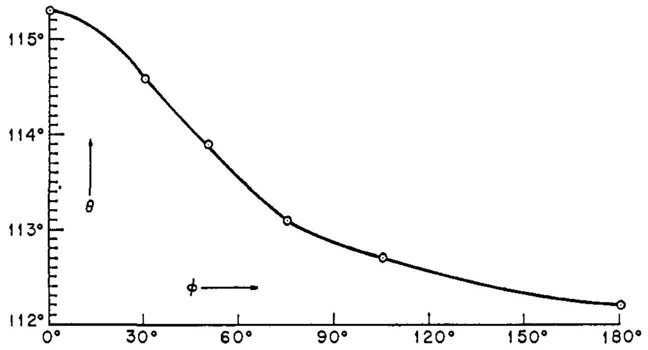

Figure 3. Variation in optimized CCC angles (θ) of *n*-butane with CCCC dihedral angle (φ).

unlike the individual parameters V_i, do not differ significantly for models A, D, and C. This indicates that the curvature at the *trans* position is similar for all three potential curves, although other regions of the potential function are very different for A, D, and C.

Table XIII gives the values of the energy parameters calculated using A, D, and C, and compares them to those estimated from calorimetric measurements.[94] This table illustrates the fact that, in the absence of strong steric effects, computed energy differences are not sensitively dependent on the model chosen. Thus the *trans-cis* barrier, which is obtained from that part of the potential energy curve in which steric interactions are small, does not differ greatly for models A, D, and C. However, the computed *cis-trans* energy differences do depend on the model chosen. The values obtained from A and D (5.66 and 2.92 kcal mol^{-1}, respectively) are most likely too high because the *cis* energy has been overestimated. The value (2.05 kcal mol^{-1}) obtained from the flexible rotor model (C) is more realistic and closer to the calorimetric result of 2.3 kcal mol^{-1}. Buenker[95] calculates a *cis-trans* energy difference of 5.0 kcal mol^{-1} on a rigid rotor model.

Table XIII. Calculated and Experimental Energy Parameters (kcal mol^{-1}) for 1,3-Butadiene

	cis-trans energy difference	*trans-cis* barrier
A	5.66	6.71
D	2.92	6.61
C	2.05	6.73
Calorimetric	2.3	5.0

***n*-Butane.** The treatment for *n*-butane is similar to that given for 1,3-butadiene. Figure 3 gives the optimized CCC angles (θ) as a function of the CCCC dihedral angle (φ), while curves A, D, and C of Figure 4 give the potential functions for conformations generated using standard geometry with rigid rotation, experimental geometry[96] with rigid rotation, and standard geometry with optimized CCC angles, respectively. The high energy for the *cis* forms in A and D may be attributed to interactions between the methyl hydrogen atoms. We have again fitted the potential function to a six-term series of the type (5) (with $\alpha = 180° - \phi$), and the results are included in Table XII. The small variation in the V^*'s calculated from A, D, and C should be noted.

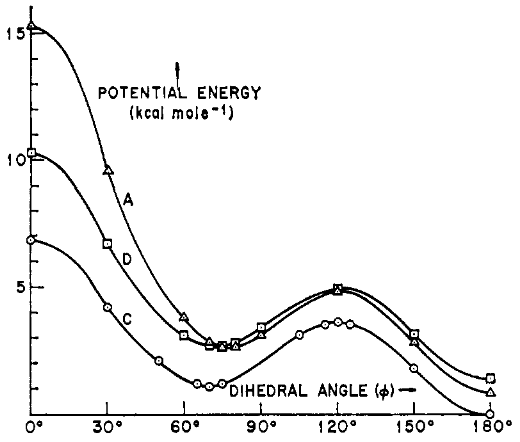

Figure 4. Potential energy functions (with energies calculated relative to the energy, −155.46592 au, of the *trans*-optimized conformation) describing internal rotation in *n*-butane: curve A, standard geometry, rigid rotation; C, optimized CCC angles, flexible rotation; D, experimental geometry, rigid rotation.

The potential energy parameters calculated from A, D, and C are compared with experimental values in Table XIV. Values of the *trans-gauche* barrier and of the methyl group rotational barrier are similar for A, D, and C and agree well with the experimental results. These parameters are both calculated using the part of the curve ($\phi > 90°$) in which steric interactions are weak. However, the remaining parameters use the region of the potential curve in which steric forces are significant, and values obtained using A, D, and C differ quite markedly. Closest agreement with experiment is obtained from curve C, in which the rotation is flexible.

Hoyland[15] has also reported *ab initio* calculations on *n*-butane. He takes the experimental geometry of Kuchitsu[96] and assumes rigid rotation. Although most of the parameters he calculates are in excellent agreement with the experimental values, we believe the *cis* energy value is too high for the reasons outlined above. Hoyland's results are included in Table XIV.

The *cis-trans* energy difference for 1,3-butadiene and the *gauche-trans* energy difference for *n*-butane were also computed at the STO-4G level. The results agree with the STO-3G values to 10^{-5} au.

1-Butene. 1-Butene is an example of a molecule containing a single bond between a tetrahedral and trigonal carbon atom. Unlike propene, the simplest member of this set, the tetrahedral carbon in this case is asymmetrically substituted and hence there is the possibility of rotational isomerism. It has been found[97-101] that in molecules of this type (*i.e.*, substituted propenes), the C=C double bond is eclipsed with one of the bonds on the tetrahedral carbon. In particular, for 1-butene, where we may define the conformations by the CCCC

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Table XIV. Comparison of Calculated and Experimental Quantities for *n*-Butane

	A	D	C	T[a]	E[b]	Ref
gauche–trans energy difference, kcal mol^{-1}	1.76	1.22	1.13	0.761	0.77	*c*
gauche dihedral angle, deg	77.2	72.3	70.5	68.7	67.5	*d*
trans–gauche barrier, kcal mol^{-1}	4.00	3.50	3.58	3.619	3.6–4.2	*e–g*
gauche–gauche barrier, kcal mol^{-1}	12.69	7.68	5.72	6.834	5.3–6.7	*f, g*
Methyl group rotational barrier, kcal mol^{-1}	3.63	3.26	3.40	2.94		

[a] T gives the theoretical results of Hoyland. [b] E gives the experimental result together with reference. [c] G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, **16**, 704 (1948). [d] Reference 96. [e] K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940). [f] K. Ito, *J. Amer. Chem. Soc.*, **75**, 2430 (1953). [g] J. E. Piercy and M. G. S. Rao, *J. Chem. Phys.*, **46**, 3951 (1967).

dihedral angle (ϕ), nmr spectral data[97,98] suggest that two forms, *cis* (ϕ = 0°) and skew (ϕ = 120°), are present and approximately equally populated. Hirota, *et al.*,[102] have recorded the microwave spectra of these two forms.

Because there are two different types of CCC angle in 1-butene, both angles were optimized. Calculations were performed for various ϕ and results are shown in Table XV, with derived energy parameters in Table XVI.

Table XV. Potential Energies for Conformations of 1-Butene

ϕ, deg	A	C			D
		θ_1, deg	θ_2, deg		
0	−154.22858	127.0	114.0	−154.23585	−154.23647
0[a]	−154.20558	129.5	115.7	−154.22795	−154.22773
60	−154.23245	124.9	112.7	−154.23472	
120	−154.23603	124.7	112.0	−154.23771	−154.23689
120[a]	−154.23011	124.8	112.6	−154.23219	−154.23145
180	−154.23329	124.5	112.6	−154.23513	

[a] These values are for conformations with the methyl and methylene groups eclipsed.

Table XVI. Calculated and Experimental Energy Parameters (kcal mol^{-1}) for 1-Butene

	A	C	D	Exptl
Skew–skew barrier	1.72	1.62		1.74
cis–skew energy difference	4.67	1.17	0.26	0.15
Barrier to rotation of methyl group				
(a) skew	3.72	3.46	3.41	3.16
(b) *cis*	14.43	4.96	5.48	3.99

We find the *cis* and skew forms at potential minima. Hirota has found strong steric interaction in the *cis* form, as indicated by the increase in the C=C—C angle (θ_1) from 125.4° in the skew form to 126.7° in the *cis* form and the corresponding change in the C–C–C angle (θ_2) from 112.1° to 114.8°. We reproduce this widening in the CCC angles. Thus we find θ_1 = 124.7°, θ_2 = 112.0° in the skew form and θ_1 = 127.0°, θ_2 = 114.0° in the *cis* form. As further evidence of steric interaction in the *cis* form, Hirota has found a high barrier to rotation for the methyl group (V_3 = 3.99 kcal mol^{-1}) compared to the barrier in the skew form (V_3 = 3.16 kcal mol^{-1}). Our flexible model (C) gives V_3 = 3.46 and 4.96 kcal mol^{-1} for the skew and *cis* forms, respectively, confirming this result. The rigid rotor models A and D overestimate the methyl rotational barrier in the *cis* form while giving reasonable results for the skew form. Our skew–skew barriers are in good agreement with the experimental values. However, the *cis*–skew energy difference is too large, and this may be due to some residual steric interaction in our partially optimized *cis* structure.

Propyne, 1,3-Butadiyne

The remaining two molecules examined, propyne and butadiyne, presented no conformational problem. We give their computed energies without further comment. For propyne, E = −114.44558 au, while for 1,3-butadiyne, E = −150.59159 au.

Conclusion

On the basis of this systematic series of calculations, we may conclude that a single-determinant molecular orbital theory using a simple Slater-type minimal basis set gives a reasonably satisfactory account of internal rotation in hydrocarbons. Steric-type interactions and associated distortions are clearly of importance, but these are apparently well handled at this level of approximation. The STO-3G basis is simple enough to permit some applications to larger systems, where the theory may have useful predictive value.

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