Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XXVI. Geometries, Energies, and Polarities of C$_4$ Hydrocarbons

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Abstract: Single determinant ab initio molecular orbital theory has been applied to the description of equilibrium structures, energetics and electric dipole moments, and distribution of charge in the C$_4$ hydrocarbons. Where comparison has been possible, agreement between calculated and experimentally determined geometric structures, rotational potentials, relative isomer stabilities, and direction and magnitude of electric dipole moments has been found to be favorable, so much so as to lend credence to the predictions of the theory in those instances where physical data are lacking. The theory finds singlet cyclobutadiene to be a rectangular molecule, in contrast to the square geometry assumed by the triplet species. Neither state of cyclobutadiene is, however, as stable as another cyclic form on the C$_4$H$_4$ potential surface, namely methylenecyclopropene, but both are lower in energy than yet another alternative, tetrahedrane. Two other cyclic isomers of C$_4$H$_4$ are found to be reasonably stable. The energy of methylcyclopropenylidene lies between those of triplet and singlet 1,3-cyclobutadiene, while that of 1,2-cyclobutadiene, more descriptively termed homocyclopropenylidene, falls just above the value for tetrahedrane. Methyl groups in methylcyclopropane and 3-methylcyclopropene are found to prefer arrangements in which one C–H bond bisects the small ring, analogous to their tendency to eclipse unsaturated linkages. The presence of a second methyl group in isobutene leads to an increase in the rotational barrier, while that in *cis*-2-butene results in a decrease. Explanation in terms of simple perturbation theoretical arguments is presented. Examination of dipole moment in 1-methylcyclopropene provides further evidence for our previous theoretical assignment of +▷– as the direction of the moment in the unsubstituted hydrocarbon.

In previous papers in this series we have applied simple levels of single determinant molecular orbital theory to problems of equilibrium and transition state geometries,[2] relative energies,[3] charge distributions and electric dipole moments,[4] and conformations[5] of small organic molecules. Preferential attention has been given to the series of C$_1$, C$_2$, and C$_3$ neutral hydrocarbons and to their positive ions. Here the theory has met with considerable success in direct comparison with experiment, so much so as to lend considerable force to the predictive aspects of the work. Extension of our studies to the C$_4$ neutral hydrocarbons is motivated somewhat beyond the obvious desires to broaden the reach of our theoretical treatment. We meet here for the first time a number of interesting chemical phenomena, situations which may be treated as prototypes to more complex environments. Thus, for example, we might ask: How does 1,3-cyclobutadiene, the simplest neutral 4-π electron system, display its antiaromatic destabilization? Is the cyclic conjugation of 3-π electrons in methylenecyclopropene of benefit energetically or does it lead to instability? We meet in the realm of C$_4$ hydrocarbons the simplest examples of puckered and fused rings, of twisted and bent multiple bonds, situations all which are of interest to pursue theoretically. We have one further motive. With one or two notable exceptions, the first fascinating hydrocarbon rearrangements occur within the C$_4$ manifold. Here, not only is the knowledge of the structure and energetics of the starting reactants and end products a necessary prerequisite to the elucidation of entire reaction surfaces, but also the establishment of a level of confidence in the theory is essential. We and others have already dwelt at length on the methylenecyclopropane degenerate rearrangement[6]

on the decomposition of cyclobutane to two ethylenes[7]
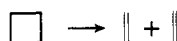
and on the symmetry-allowed and -forbidden pathways to the electrocyclic ring closure of 1,3-butadiene to cyclobutene.[8]
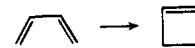
In addition, the related cation rearrangement surfaces C$_4$H$_7^+$ (cyclopropylcarbinyl–cyclobutyl–allylcarbinyl)[9] and C$_4$H$_5^+$ (cyclopropenylcarbinyl–cyclobutenyl)[10] and the C$_4$H$_7$ radical surface (cyclopropylcarbinyl–allylcarbinyl)[11] have come under considerable scrutiny. Other examples are currently under study.

We shall restrict our discussion of the C$_4$ hydrocarbons to neutral species where simple valence structures may be drawn, and, with one important exception (triplet cyclobutadiene), only to ground singlet states. Within this framework most isomers of the series C$_4$H$_{10}$, C$_4$H$_8$, C$_4$H$_6$, C$_4$H$_4$, and C$_4$H$_2$ will be dealt with.

Quantum Mechanical Methods

Standard single determinant ab initio molecular orbital theory has been used throughout.[12] Following our past practice, we have employed the minimal STO-3G basis[13a]

Table I. Corrections to 6-31G Energies Due to Introduction of Polarization Type Functions on Carbon (kcal/mol)

^{a} Correction for three-membered rings only; in four-membered rings 10.2 kcal/mol, based on weighted average of acyclic and three-membered ring values; see text. ^{b} Correction for three-membered rings only; in four-membered rings 10.6 kcal/mol, based on weighted average of acyclic and three-membered ring values; see text. ^{c} Value for ═C═ (better represented as —C̈—) in three-membered ring; in four-membered ring, 6.9 kcal/mol, based on weighted average of acyclic and three-membered ring values; see text.

Table II. Molecular Equilibrium Geometries

Molecule	Symmetry constraint	Parameter[a]	STO-3G	Exptl	Ref
Cyclobutane (I)	D_{2d}	$r(C-C)$	1.554	1.548	32b,e,f
		$r(C-H_1)$	1.087	1.092	
		$r(C-H_2)$	1.087	1.092	
		$\angle(H_1CH_2)$	108.7	110.	
		$\angle(C_1C_{24}C_3)$	173.1	b	
		$\angle(\alpha)$	-1.2	-4.0	
trans-1,3-Butadiene (II)	D_{2h}	$r(C_1=C_2)$	1.313	1.337	39b
		$r(C_2-C_3)$	1.488	1.483	
		$r(C_1-H_1)$	1.081	1.083	
		$r(C_1-H_2)$	1.080	1.083	
		$r(C_2-H_3)$	1.085	1.083	
		$\angle(C_1C_2C_3)$	124.2	122.4	
		$\angle(H_1C_1C_2)$	121.9	119.8	
		$\angle(H_2C_1C_2)$	122.1	119.8	
		$\angle(H_3C_2C_1)$	120.2	119.8	
Cyclobutene (III)	C_{2v}	$r(C_1=C_2)$	1.314	1.342	45
		$r(C_2-C_3)$	1.526	1.517	
		$r(C_3-C_4)$	1.565	1.566	
		$r(C_1-H_1)$	1.082	1.083	
		$r(C_3-H_3)$	1.089	1.094	
		$\angle(HC_1C_2)$	134.2	133.5	
		$\angle(H_3C_3H_4)$	109.0	109.5	
		$\angle(H_{34}C_3C_4)$	136.3	135.8	
Methylenecyclopropane (IV)	C_{2v}	$r(C_1=C_2)$	1.298	1.332	49
		$r(C_2-C_3)$	1.474	1.457	
		$r(C_3-C_4)$	1.522	1.542	
		$r(C_1-H_1)$	1.083	1.088	
		$r(C_3-H_3)$	1.083	1.09	
		$\angle(H_1C_1H_2)$	116.0	114.3	
		$\angle(H_3C_3H_4)$	113.6	113.5	
		$\angle(H_{34}C_3C_4)$	149.4	150.8	
Bicyclo[1.1.0]butane (V)	C_{2v}	$r(C_1-C_2)$	1.501	1.498	50
		$r(C_1-C_3)$	1.469	1.497	
		$r(C_1-H)$	1.077	1.071	
		$r(C_2-H_2)$	1.086	1.093	
		$r(C_2-H_3)$	1.084	1.093	
		$\angle(C_4C_{13}C_2)$	117.4	121.7	
		$\angle(HC_1C_3)$	135.2	128.3	
		$\angle(H_2C_2H_3)$	113.8	115.5	
		$\angle(\alpha)$	2.2	-0.7	
But-1-yn-3-ene (VI)	C_s	$r(C_1\equiv C_2)$	1.171	1.208	58
		$r(C_2-C_3)$	1.459	1.431	
		$r(C_3=C_4)$	1.320	1.341	
		$r(C_1-H_1)$	1.064	1.062	
		$r(C_3-H_2)$	1.086	$\left\{ \begin{array}{c} c \\ 1.087 \end{array} \right.$	
		$r(C_4-H_3)$	1.082		
		$r(C_4-H_4)$	1.082		
		$\angle(C_1C_2C_3)$	179.7	177.9	
		$\angle(C_2C_3C_4)$	124.0	123.1	
		$\angle(H_1C_1C_2)$	180.0	182.3	
		$\angle(H_2C_3C_4)$	120.3	$\left\{ \begin{array}{c} c \\ 120.6 \end{array} \right.$	
		$\angle(H_3C_4C_3)$	122.3		
		$\angle(H_4C_4C_3)$	121.4		
		$\angle(C_1C_2C_3C_4)$	180.0	180.0	
		$\angle(H_1C_1C_2C_3)$		180.0	
Butatriene (VII)[d]	D_{2h}	$r(C_1=C_2)$	1.296	1.318	56b
		$r(C_2=C_3)$	1.257	1.283	
		$r(C-H)$	1.085	1.083	
		$\angle(HCH)$	115.9		
Methylenecyclopropene (VIII)	C_{2v}	$r(C_1=C_2)$	1.303		
		$r(C_2-C_3)$	1.444		
		$r(C_3-C_4)$	1.305		
		$r(C_1-H_1)$	1.077		
		$r(C_3-H_3)$	1.077		
		$\angle(H_1C_1H_2)$	117.0		
		$\angle(H_3C_3C_4)$	148.4		
1,3-Cyclobutadiene $^3A_{2g}$	$D_{2h} \rightarrow D_{4h}$	$rC-C)$	1.431		
		$r(C-H)$	1.080		
1,2-Cyclobutadiene (IX)	C_s	$r(C_1-C_2)$	1.472		
		$r(C_2-C_3)$	1.498		
		$r(C_2-C_4)$	1.547		
		$r(C_2-H_1)$	1.079		
		$r(C_3-H_2)$	1.085		
		$r(C_3-H_3)$	1.085		
		$\angle(C_1C_{24}C_3)$	129.0		
		$\angle(H_1C_2C_1)$	130.4		

Table II (Continued)

Molecule	Symmetry constraint	Parameter[a]	STO-3G	Exptl	Ref
		$\angle(H_1C_2C_4)$	137.4		
		$\angle(H_2C_3C_{24})$	124.8		
		$\angle(H_3C_3C_{24})$	121.9		
1,3-Cyclobutadiene $^1A_{1g}$	D_{2h}	$r(C=C)$	1.313		
		$r(C-C)$	1.569		
		$r(C-H)$	1.081		
		$\angle(HC=C)$	136.2		
Tetrahedrane[e]	$C_2 \rightarrow T_d$	$r(C-C)$	1.473		
		$r(C-H)$	1.069		
Cyclobutyne (X)	C_{2v}	$r(C_1\equiv C_2)$	1.227		
		$r(C_2-C_3)$	1.596		
		$r(C_3-C_4)$	1.528		
		$\angle(H_1C_3H_2)$	111.8		
		$\angle(H_{12}C_3C_4)$	142.5		
Bicyclo[1.1.0]butene $\Delta^{1,3}$ (XI)	C_{2v}	$r(C_1-C_2)$	1.535		
		$r(C_1=C_3)$	1.343		
		$r(C_2-H_1)$	1.092		
		$r(C_2-H_2)$	1.086		
		$\angle(C_2C_{13}C_4)$	128.3		
		$\angle(H_1C_2H_2)$	113.7		
		$\angle(\alpha)$	-5.5		
Butadiyne	$D_{\infty h}$	$r(C\equiv C)$	1.175	(1.205)	84
		$r(C-C)$	1.408	1.376	
		$r(C-H)$	1.066	1.046	

[a] The symbol X_{ij} (e.g., C_{24} or H_{34}) denotes the midpoint of the line X_iX_j. [b] See text for discussion. [c] Parameters assumed to be identical. [d] Theoretical (STO-3G) structure from ref 56a. [e] Theoretical (STO-3G) structure identical with that given in ref 81a.

for the optimization of molecular equilibrium geometry, followed by a single calculation at the extended 4-31G level[13b] in order to assess relative molecular energetics more accurately. Recent studies have indicated, however, that even this level of theory may not be entirely satisfactory for accurate energetic comparisons between wholly acyclic molecules and those containing small rings, and have suggested that inclusion of polarization-type functions in the basis can lead to improved results.[14] Unfortunately, polarization basis calculations (even at the simplest 6-31G* level)[14,15] are only just within the capability of our present computer programs for the C_4H_6 and C_4H_4 systems. 6-31G* computations have been done on several such isomers. For the larger C_4H_{10} and C_4H_8 molecules and for many of the remaining C_4H_6 and C_4H_4 systems we have estimated the effects of polarization functions on the 6-31G basis by analogy with previously published results on the smaller cyclic and acyclic hydrocarbons. The group corrections, presented in Table I, are taken directly from the work of Hariharan and Pople[14b,c] for carbons with acyclic environments and from that of Lathan, Radom, Hariharan, Hehre, and Pople[2g] for centers incorporated into three-membered rings. We have approximated corrections for centers associated with four-membered rings by using weighted averages of the acyclic and three-carbon ring data, the weighting scheme based on relative bond angles. Thus the correction for an acyclic methylene group is 9.8 kcal/mol vs. 10.7 kcal/mol for CH_2 in say cyclopropane. If we consider the "normal" bond angle in the former to be 110° as opposed to 60° in cyclopropane and 90° in cyclobutane then a (rounded) average for polarization basis correction in the last would be 10.2 kcal/mol. Similiar reasoning leads to the tabulated values for the other carbon environments within four-membered rings. All computations have been carried out using the Gaussian 70 series of computer programs.[16]

Results and Discussion

For the acyclic C_4H_{10}, C_4H_8, and C_4H_6 isomers (except 1,3-butadiene) we have employed the geometries calculated by Radom and Pople using a flexible rotor approximation.[5a] Within such a framework standard model bond lengths and

angles[17] are used throughout with the exception of all CCC angles which are optimized for each conformation of interest. A detailed description has been presented elsewhere.[5a] The geometrical structures of 1,3-butadiene, the acyclic C_4H_4 isomers, and butadiyne have been fully optimized at the STO-3G level. The geometries of molecules formed by replacement of hydrogen by a methyl on the three-membered rings cyclopropane, cyclopropene, cyclopropyne, and cyclopropenylidene have been specified by retaining the original (STO-3G) ring geometry[1b,g] and affixing a standard CH_3 (tetrahedral, $r(C-H) = 1.09$ Å) at the same bond angles as the hydrogen it replaced. Connecting CC bond lengths of either 1.52 Å or 1.48 Å have been chosen depending on whether a tetra or trigonally coordinated ring carbon is involved, values which are in accord with available experimental information.[18] Finally the geometries (Chart I) of all remaining molecules have been fully optimized using the STO-3G basis, subject only to an overall symmetry constraint, and are presented in detail in Table II along with experimental structural information where available.

Total (STO-3G, 4-31G, and 6-31G*[19]) energies for all C_4 hydrocarbons dealt with in this paper are presented in Table III. We shall not discuss these data as such but shall use them to construct relative energy comparisons for each of the C_4H_{10}, C_4H_8, C_4H_6, C_4H_4, and C_4H_2 systems in turn.

C_4H_{10}. Energies (relative to that of isobutane) and electric dipole moments for the three stable C_4H_{10} hydrocarbons are presented in Table IV. The theory (at the 4-31G level) is successful in assigning the relative stabilities of the three, although the calculated energy of branched isobutane is somewhat too high in comparison with the other two, no doubt due in part to incomplete geometrical optimization. Internal rotation in n-butane has been discussed at length in earlier publications[5a,c] (and has also been considered in detail by Hoyland[20a] and by Nelson and Frost[20b]) but for the sake of completeness we summarize the results here (Figure 1). Gauche n-butane is, by 4-31G, 1.09 kcal/mol less stable than the trans conformer (vs. 0.77 kcal/mol experimentally[21a]), the two being separated by interconversion barriers: gauche → trans of 2.49 kcal/mol (2.8 to 3.4 kcal/mol ex-
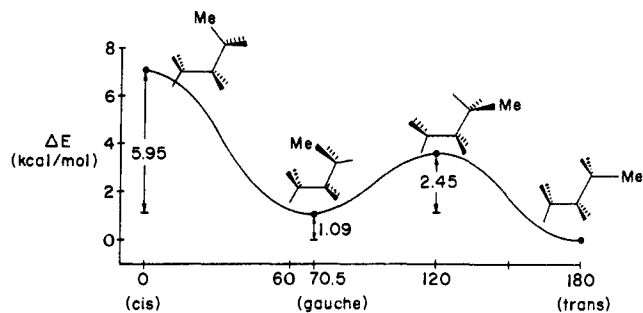
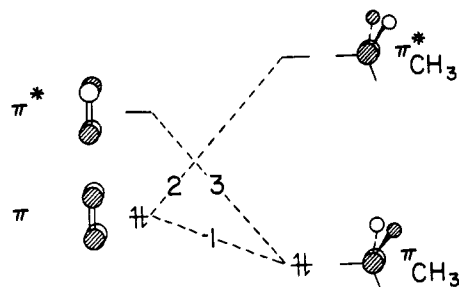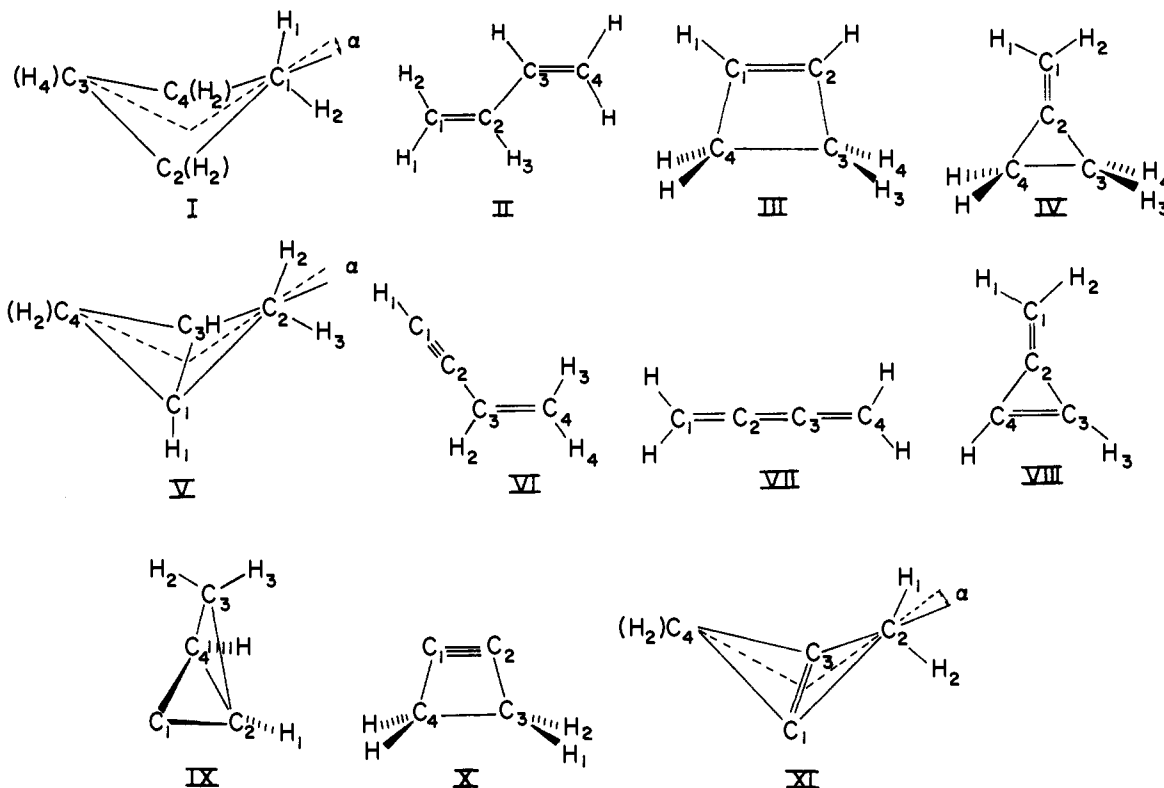**Figure 1.** Internal rotation in n-butane (4-31G).

Figure 2. Interaction of the π orbitals of a double bond with those of appropriate symmetry on a methyl group.

Chart I

perimentally[21b,c,d]) and gauche → gauche of 5.95 kcal/mol (5.3 to 6.7 kcal/mol experimentally[21c,d]).

The sign of the theoretical electric dipole moment in isobutane is consistent with out earlier studies on propane,[4] and in agreement with experimental notions on the subject based on microwave analysis of deuterium-substituted species.[22] The dipole sign for gauche n-butane also implies that the methyl groups are more negative than the methylenes.
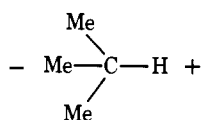
C₄H₈. Energies (relative to isobutene) and electric dipole moment data for the C_4H_8 isomers are presented in Table V. With the exception of the cyclobutane-methylcyclopropane pair, both 4-31G and (estimated) 6-31G* data are in agreement with experiment regarding the proper ordering of stabilities. The only other comparison we can find in the theoretical literature between the stabilities of C_4H_8 isomers is due to Preuss and Janoschek,[23] who find the trans

isomer of 2-butene to be 1.1 kcal/mol lower in energy than the cis, in excellent agreement with experiment. Also noteworthy in the tabulated data is the high level of agreement between calculated (4-31G) and experimental electric dipole moments.

The large variation in barriers hindering methyl rotation about the carbon–carbon double bond in the series isobutene and trans- and cis-2-butene has attracted attention before, but in the view of these authors, remains unexplained. Table VI gives results at the STO-3G level. In order to fully understand the possible causes we need first to consider the rationale behind the methyl group's preference to eclipse rather than to stagger unsaturated linkages.[24] Three interactions are of consequence between the π orbitals of a double bond and the valence function of appropriate symmetry on a methyl group (Figure 2). Interaction 1 between π and π_{CH_3} involves four electrons and hence is destabilizing;[25] that is to say the conformer (eclipsed or staggered) in which overlap between the two fragments is greater will be the disfavored. Inspection clearly shows that because of secondary (methyl hydrogen, double bond) overlap present in the staggered conformer an eclipsed arrangement is preferred.

Table III. Energy Data

| | E, hartrees | | | ΔH$f°_{298}$, |
	STO-3G	4-31G	6-31G*^{a}	kcal/mol^b
		C$_4$H$_{10}$		
Isobutane	-155.46572	-157.07118	(-157.29729)	-32.15
trans-n-Butane	-155.46591	-157.07044	(-157.29655)	-30.15
n-Butane (gauche)	-155.46411	-157.06870	(-157.29481)	-29.38^c
		C$_4$H$_8$		
Isobutene	-154.24341	-155.88548	(-156.10745)	-4.04
trans-2-Butene	-154.24375	-155.88498	(-156.10695)	-2.67
cis-2-Butene	-154.24109	-155.88230	(-156.10427)	-1.67
1-Butene (skew)	-154.23771	-155.88080	(-156.10277)	-0.03
cis-1-Butene	-154.23585	-155.87936	(-156.10133)	
Methylcyclopropane	-154.24850	-155.86313	(-156.09357)	5.7^d
Cyclobutane	-154.27390	-155.86606	(-156.09472)	6.37
		C$_4$H$_6$		
trans-1,3-Butadiene	-153.02036	-154.69906	-154.91905	26.33
cis-1,3-Butadiene	-153.01335	-154.69218	(-154.91000)	
2-Butyne	-153.03667	-154.68866	(-154.90840)	34.97
Cyclobutene	-153.04028	-154.66729	-154.89926	37.5
1,2-Butadiene	-153.00442	-154.67844	(-154.89754)	38.77
1-Butyne	-153.02533	-154.67829	(-154.89803)	39.48
Methylenecyclopropane	-153.01118	-154.65870	-154.88685	48.0
Bicyclo[1.1.0]butane	-153.00193	-154.62374	-154.87054	51.9
1-Methylcyclopropene	-152.99207	-154.62995	(-154.86674)	58.2
3-Methylcyclopropene	-152.98386	-154.62219	(-154.85898)	
		C$_4$H$_4$		
But-1-yn-3-ene	-151.80626	-153.48995	-153.70661	72.80^e
Butatriene	-151.77399	-153.47496	-153.68963	
Methylenecyclopropene	-151.76162	-153.43225	-153.66899	
1,3-Cyclobutadiene (^{3}A$_{2g}$)	-151.75406	-153.41718	-153.65012	
Methylcyclopropenylidene	-151.77018	-153.41559	(-153.64568)	
1,3-Cyclobutadiene (^{1}B$_g$)	-151.74812	-153.40819	-153.64080	
Tetrahedrane	-151.70782	-153.34046	-153.59741	
1,2-Cyclobutadiene	-151.72769	-153.36539	(-153.59007)	
Bicyclo[1.1.0] butene Δ^{1,3}	-151.65018	-153.30346		
Cyclobutyne	-151.63531	-153.30268		
Methylcyclopropyne	-151.59324^f	-153.27830^{f,g}		
		C$_4$H$_2$		
Butadiyne	-150.59577	-152.28374	-152.49677	113.00^e

^{a}Values in parentheses estimated as described in the text. ^{b}Unless otherwise noted all experimental heats of formation are taken from S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 69, 279 (1969). ^{c}Reference 21a. ^{d}S. W. Benson and H. E. O'Neal, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 21, 225 (1970). ^{e}D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969. ^{f}Energy from complex SCF procedure. ^{g}Upper bound. Calculation failed to converge.

Table IV. Relative Energies (kcal/mol) and Electric Dipole Moments (D) for C$_4$H$_{10}$ Hydrocarbons

| | Relative energy | | | μ | |
Molecule	4-31G	6-31G*^{a}	Exptl	4-31G	Exptl^b
Isobutane	0	0	0	0.11	0.132
trans-n-Butane	0.5	(0.5)	2.0	0	0
n-Butane (gauche)	1.6	(1.6)	2.8	0.09	

^{a}Values in parentheses estimated as described in text. ^{b}Unless otherwise specified experimental electric dipole moments from R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 10 (1967).


Repulsion
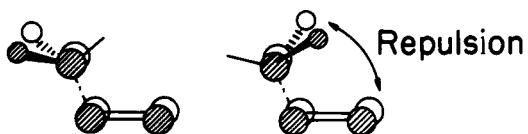
The eclipsed structure is seen also to benefit the more from the two-electron stabilizing interactions 2 and 3. In the staggered conformation the primary overlap between the carbon component of π_{CH_3}* and π (or π_{CH_3} and π*) is reduced by overlap of opposite sign between the H$_2$ component of π_{CH_3}* and π (or of π_{CH_3} and π*).

Table V. Relative Energies (kcal/mol) and Electric Dipole Moments (D) for C$_4$H$_8$ Hydrocarbons

| | Relative energy | | | μ | |
Molecule	4-31G	6-31G*^{a}	Exptl	4-31G^b	Exptl^c
Isobutene	0	0	0	0.53	0.50
trans-2-Butene	0.3	(0.3)	1.4	0	0
cis-2-Butene	2.0	(2.0)	2.4	0.13	0.257^d
1-Butene (skew)	2.9	(2.9)	4.0	0.32	0.359^e
cis-1-Butene	3.8	(3.8)	4.2	0.41	0.438^e
Methylcyclopropane	14.0	(8.7)	9.7	0.11	0.139^f
Cyclobutane	12.1	(8.0)	10.4	0	0

^{a}Values in parentheses estimated as described in text. ^{b}All the dipolar molecules have the positive end of the electric dipole at the methyl group(s). ^{c}Unless otherwise specified experimental electric dipole moments from footnote b, Table IV. ^{d}Reference 25g. ^{e}Reference 30c. ^{f}Reference 18a.


Negative Overlap
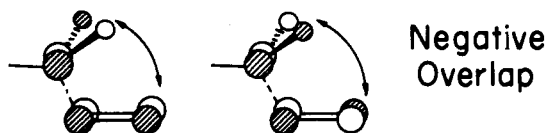
We now apply the same arguments to the preferred conformation of a second methyl group attached to a double

Table VI. Barriers Hindering Methyl Rotation about Carbon–Carbon Double Bonds (kcal/mol)[a]

Molecule	I → II		II → III
	STO-3G	Exptl	STO-3G
Propene	1.55	1.950,[26a] 1.978,[26d] 1.995,[26d] 2.031,[26c] 2.039[26h]	
Isobutene	1.70	2.12,[26f] 2.21,[26c] 2.35[26a]	1.94
trans-2-Butene	1.54	1.95[26a]	1.56
cis-2-Butene	0.42	0.73[26a,g]	0.47

[a] Rotation in a molecule with two methyl rotors is considered as a stepwise process (e.g., in isobutene)
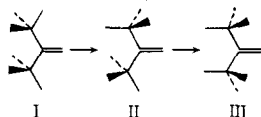
I II III

Theoretical values for both processes (I → II, II → III) are given.

bond (interaction of propene and methyl as a prelude to formation of either isobutene or cis- or trans-2-butene). The two methyls in trans-2-butene are sufficiently far removed from one another that any such interaction scheme would undoubtably show them to be relatively independent. Experimentally (and theoretically at the STO-3G level) methyl rotational barriers in propene[26a-d] and in trans-2-butene[26a] are indistinguishable. The situation in isobutene[26a,e,f] and in cis-2-butene,[26e,g] where the attached methyls are in close proximity, is more interesting. In the ground-state conformer of isobutene there exists an attraction between the two pairs of out-of-plane methyl hydrogens which might be thought of as being primarily due to the stabilizing two-electron interaction involving the highest occupied molecular orbital in propene (in its ground-state eclipsed conformation) and the lowest unfilled pseudo π function on methyl[27]
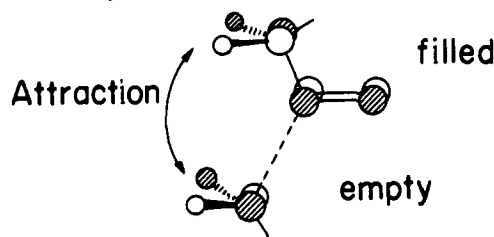

Thus rotation of the first methyl, away from its ground-state eclipsed arrangement, results not only in repulsive interaction between the out-of-plane methyl hydrogens and the double bond π orbitals, as in propene, but also in the loss of the secondary (hydrogen–hydrogen) attraction. Repulsion between the pair of in-plane methyl hydrogens in the totally staggered conformation is the obvious reason for the unusually large barrier to rotation away from equilibrium of the second methyl.
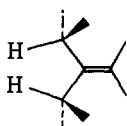
Repulsion present between the pair of in-plane methyl hydrogens in cis-2-butene causes it to be less stable than consideration based on the single rotor system propene would have us believe.[29] Since this repulsion would seem to be largely relieved with the rotation of one methyl group away from its equilibrium H-eclipsed conformation, anoth-

er explanation needs be sought for the low barrier to rotation of the second methyl. It is, as was the case with isobutene, attraction between the two pairs of out-of-plane methyl hydrogens in the totally staggered form of the molecule, and, as before, may be envisioned as due to the presence of a stabilizing two-electron interaction between interacting (propene and methyl) fragments.
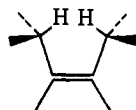
Attraction
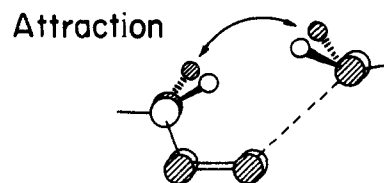
Experimentally 1-butene is known to exist as a mixture of two conformers, skew ($\angle CCCC \sim 120°$) and cis, of nearly equal stability.[30] The 4-31G calculations are in qualitative agreement but indicate a skew-cis energy difference (skew ground state) of 0.9 kcal/mol, some 0.7 kcal/mol greater than is believed to be the case. The theoretical rotational potential (Figure 3) suggests barriers of 1.97 kcal/mol (skew → skew) and 2.17 kcal/mol (skew → cis), the first in reasonable agreement with the experimental value of 1.74 kcal/mol.

Complete optimization of the geometrical structure of cyclobutane at the STO-3G level indicates that the overall carbon skeleton deviates from planarity (angle between the two 3-carbon planes of 173.1° instead of 180° for a planar ring) but by considerably less than experiment would seem to indicate[31] (electron diffraction, 160° (+10, −20),[32a] 145° [32b]; infared and Raman spectroscopy, 143° (±6),[32c] 146° (±0.5),[32d] 145° [32e]; and NMR spectroscopy, 153° [32f]). As a consequence our theoretical value for the barrier to ring inversion is an order of magnitude smaller than that determined experimentally (0.1 kcal/mol at 4-31G vs. 1.28[32d] and 1.44 kcal/mol[32e] from ir and Raman measurements, respectively). An independent optimization of the cyclobutane structure at the extended basis 4-31G level has been carried out by Ditchfield, Hariharan, and Snyder.[33] Here, theoretical values for both the ring puckering angle and the inversion barrier through a planar ring are in somewhat better agreement with experiment.

Wright and Salem have already dwelt at length on the "rocking" of the methylene groups which accompanies, and seems to largely parallel, the degree of ring puckering. The direction in which the motion occurs leads to a partial staggering of methylene hydrogens from their totally eclipsed arrangement in the planar molecule. As was the case with the ring puckering angle itself, the theoretical STO-3G calculations badly underestimate the magnitude of rocking, suggesting a distortion of only 1.2° compared with experimental, NMR[32f] and ir,[32e] determinations both of 4°.

That methylcyclopropane adopts an equilibrium conformation in which one methyl hydrogen bisects the ring rather than straddling it may be seen from consideration of the orbital interaction diagram given in Figure 4. Paralleling our treatment of propene and the isomeric butenes we consider interaction of the pseudo-π orbitals on a methyl group, this time with the valence Walsh orbitals of cyclopropane.[34] As before three component terms need to be analyzed. The destabilizing four-electron interaction (1) favors the conformer, bisected or straddled, with the lesser overall overlap. As was the case with propene, secondary overlap involving the symmetry related pair of methyl hydrogens needs to be minimized, dictating the preferred arrangement be bisected. The pair of two-electron stabilizing interactions (2 and 3) are, on the contrary, most effective where positive
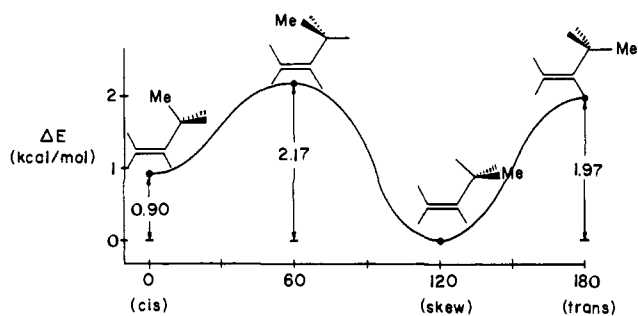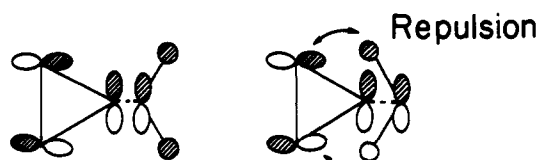
Figure 3. Internal rotation in 1-butene (4-31G).

Repulsion

overlap between partner orbitals is at a maximum. It can be seen that in both of these, secondary overlap of the symmetrically disposed methyl hydrogens with the cyclopropane skeleton, which is nearly zero in the bisected conformation, is actually negative in the straddled, thus subtracting from the overall stabilizing effect of the interactions. Of course,

Negative Overlap
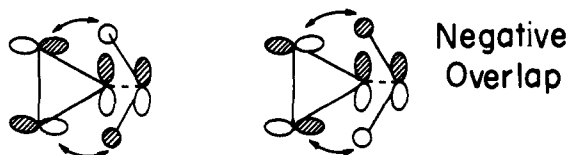
one might justify the preference for a methyl group to bisect the cyclopropyl ring simply in terms of a staggering of single bonds. Indeed, Hoffmann has already provided an orbital model similar to ours to account for the conformation of ethane.[24e,g]

The quantitative (STO-3G level) molecular orbital calculations do indeed favor a bisected ground state geometry, and suggest an energy difference between it and the methyl straddled conformer (methyl rotational barrier) of 2.53 kcal/mol. Experimentally the ground-state conformation of methylcyclopropane remains undetermined but the torsional barrier hindering methyl rotation has been reported as 2.86 kcal/mol.[18a] Leroy and coworkers have also carried out ab initio calculations on methylcyclopropane, but did not consider the problem of its conformation.[35]

Realizing the overall similarity of the valence orbitals of cyclopropane to those of a double bond it is interesting to compare their relative abilities to conjugate with, and hence to stabilize, a substituent methyl. The calculated (4-31G) energies of the *isodesmic* processes 1 and 2 provide such an indicator, suggesting that in neutral hydrocarbons, cyclo-

	4-31G	Exptl	
▷—Me + ⟩ → △ + ⟩—Me	1.3	0.3	(1)
⟩⟩—Me + ⟩ → ⟩⟩ + ⟩—Me	2.1	1.6	(2)
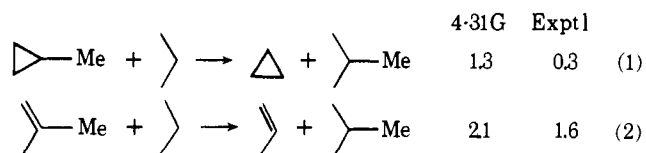
propyl-alkyl interactions are weaker than those involving double bonds and alkyl groups.

For all the C_4H_8 alkenes listed in Table V, the polarity of the electric dipole moment has terminal methyl groups at the positive end. This is consistent with normal ideas about hyperconjugation. Also noteworthy is the dipole moment sign and direction for methylcyclopropane, clearly related to that for isobutane. The inclination of the theoretical dipole direction to the ring plane is 25°. This is in reasonable
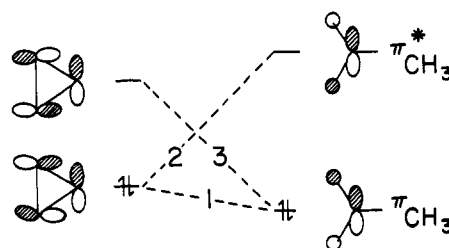

Figure 4. Interaction of the asymmetric (filled and empty) Walsh orbitals on cyclopropane with those of appropriate (π) symmetry on a methyl group.

Table VII, Relative Energies (kcal/mol) and Electric Dipole Moments (D) for C_4H_6 Hydrocarbons

Molecule	Relative energy			μ	
	4-31G	6-31G*[a]	Exptl	4-31G	Exptl[b]
trans-1,3-Butadiene	0	0	0	0	0
cis-1,3-Butadiene	4.3	(5.7)		0.10	
2-Butyne	6.5	(6.7)	8.6	0	0
Cyclobutene	19.9	12.4	11.2	0.07	0.132
1,2-Butadiene	12.9	(12.1)	12.4	0.39	0.403
1-Butyne	13.0	(11.8)	13.2	0.67	0.80
Methylenecyclopropane	25.3	20.2	21.7	0.35	0.402[c]
Bicyclo[1.1.0]butane	47.2	30.4	25.6	0.75	0.68[d]
1-Methylcyclopropene	43.3	(31.4)	31.9	0.90	0.84[e]
3-Methylcyclopropene	48.2	(36.3)		0.51	

[a] Values in parentheses estimated as described in text. [b] Unless otherwise specified experimental electric dipole moments from footnote b, Table IV. [c] Reference 48. [d] Reference 50. [e] Reference 18b.
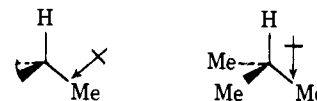
agreement with the direction found by Ford and Beaudet.[18a]

C_4H_6. Data for the isomeric C_4H_6 hydrocarbons are presented in Table VII. As before energies are relative to the most stable, in this instance *trans*-1,3-butadiene. As before the experimental ordering of isomer energies is reproduced by the theory although, even at the 6-31G* level, the stability of bicyclo[1.1.0]butane is somewhat underestimated. Minimal basis set calculations on three of the C_4H_6 isomers, *cis*-1,3-butadiene, cyclobutene, and bicyclo[1.1.0]butane, have already been reported by Wipff.[36] It is not surprising, in view of our own STO-3G results, that they badly overestimate the stability of the two small ring molecules relative to the acyclic diene.

A reasonable model for the conformation of 1,3-butadiene[37] closely parallels that which we have already proposed for propene.[23] Consider the interaction of π systems on two isolated double bonds constrained to lie in a single plane (Figure 5). If both are in their normal (π^2) ground states we need consider the conformational preferences of only the four-electron interaction (1) and the pair of two-electron terms (2 and 3). Interaction between π^* orbitals is not of consequence energetically as neither level is occupied.[38] *All three effects favor a trans over cis arrangement of double bonds.*

As was the case in the propene system, the lone four-electron interaction (1) is net destabilizing. The cis conformer, in which the proximity of the terminal π lobes permits their interaction, exhibits the greater total overlap and hence is the more destabilized.
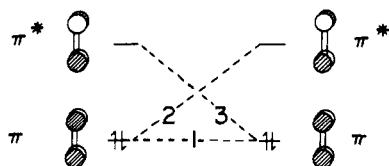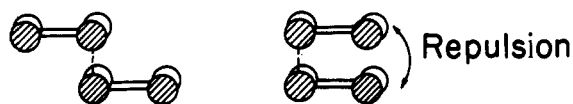
Figure 5. Interaction of the π orbitals on 1,3-disposed double bonds.

Repulsion

The single node introduced into the molecular orbitals resulting from the equivalent pair of two-electron interaction (2 and 3) is the reason that they also dictate a trans as opposed to cis orientation of the double bonds. It should, of course, be mentioned that H–H repulsions, not accounted for in our simple orbital picture, would tend to disfavor a planar cis skeletal arrangement.

Negative Overlap

Experiment[39] and ab initio molecular orbital calculations,[5a,40-42] including the one described here, do assign 1,3-butadiene to possess a trans planar ground state conformation as the simple perturbational treatment would have. Also the energy difference between this ground-state structure and the second minimum on the potential is reasonably well pinned down experimentally (2.5 ± 0.5 kcal/mol from calorimetric measurements,[43a] 1.7 ± 0.5 kcal/mol from the temperature dependence of the ir spectra,[43b] and >2 kcal/mol from molecular beam investigations[43c]). The theoretical 4-31G difference (4.3 kcal/mol) given in Table VII is somewhat large since the trans geometry has been fully optimized, but the cis form has not. If the trans is treated at the same level as the cis, the energy difference is lowered to 3.7 kcal/mol. What is not at all certain at this time is the detailed conformation of this secondary form, be it planar cis or gauche.[40] The STO-3G level calculations on rotation in 1,3-butadiene reported by Radom and Pople,[5a] in which partial geometry optimization was performed, concluded that the second minimum energy form was indeed cis planar. Actually, optimization at the 4-31G level yields a slightly non planar geometry for the second minimum energy form. Full details as well as a rationalization of this behavior are presented elsewhere.[37]

The theoretical dipole moment of cis-1,3-butadiene is very small (0.10 D) and in the direction making the single bond positive and the CH$_2$ groups negative. The origin of this polarity appears to be in the π system for the total π populations on C$_1$ and C$_4$ are 1.008 and those on C$_2$ and C$_3$ are 0.992.

Theoretical[44] (STO-3G) and experimental[45] structures for cyclobutene are in excellent accord with one another. It is interesting to note that the double bond incorporated into the small ring is actually somewhat longer than that observed for a "normal" acyclic alkene (the experimentally determined double bond length in cyclobutene is 1.342 Å vs. 1.336 Å in, for example, propene), unexpected in light of the extreme shortness of the double bond in cyclopropene (experimentally 1.300 Å[46]). Again we call on simple perturbation arguments. Charge transfer resulting from interactions between the valence molecular orbitals on single and double bond fragments (coming together to form cyclobu-
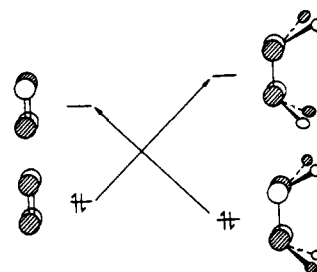

Figure 6. Interaction of the π orbitals of a double bond with those of appropriate symmetry on a single linkage.

tene) is depicted in Figure 6. Not only is the double bond π orbital of appropriate symmetry to interact with and transfer electrons to the lowest empty function on the facing single bond (hence leading to a weakening and presumably a lengthening of the former) but charge transfer in the opposite direction (between the highest filled orbital on the saturated linkage and the double bond π^*) takes place as well, compounding the geometric effect. It must be noted, however, that the model we have presented here, consideration of the consequences of interaction of the (pseudo) π orbitals alone, leads to the incorrect prediction of shortening of the single linkage across from the double bond.

The same orbital interaction diagram (Figure 6) may also be used to rationalize the small dipole moment observed for cyclobutene. Thus, electron transfer to and from the double bond π orbital severely limits the development of significant charge polarity at either end.

The rotational barrier in methylallene (1,2-butadiene) is somewhat smaller than that found in propene (experimentally, 1.589 kcal/mol for 1,2-butadiene[47] vs. from 1.95 to 2.039 for propene;[26] 1.40 kcal/mol vs. 1.55 at STO-3G for the same pair). The reason for this reduction is unclear to us at the present time. The dipole moment of 1,2-butadiene is comparable to that of propene, both having the methyl group at the positive end. The theoretical direction makes an angle of 19.6° with the C=C=C line,
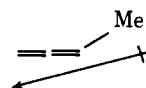


which may be compared with the experimental value of 29°.

The theoretical dipole moment of 1-butyne is quite large (0.67 D) in good agreement with the experimental result (0.80 D). The direction is close to that of the triple bond (deviating by 6° toward the methyl group). As with propyne, the alkyl part of the molecule is the positive end of the dipole.

Methylenecyclopropane is the central member of an interesting series of hydrocarbons, allene, methylenecyclopropane, and spiropentane, in which two (pseudo) π systems are arranged in an orthogonal manner, so as not to interact. As was the case with allene, methylenecyclopropane is less stable than the products of the isodesmic reaction 3 (−4.9 kcal/mol using experimental thermochemical data, −4.3

$$\text{A} + CH_4 \longrightarrow \triangle + \text{||} \qquad (3)$$

kcal/mol at the 4-31G level) indicating increased strain over that noted for cyclopropane itself. While the energy of the corresponding isodesmic process for allene (eq 4) was

$$\text{||} + CH_4 \longrightarrow \text{||} + \text{||} \qquad (4)$$
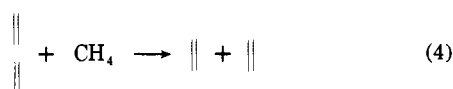
found experimentally to be -4.1 kcal/mol (-3.5 kcal/mol at 4-31G), the available thermochemical data indicate spiropentane to be only 0.9 kcal/mol less stable than a pair of cyclopropane rings.

$$\text{[structure]} + CH_4 \longrightarrow \triangle + \triangle \qquad (5)$$

The equilibrium structure of methylenecyclopropane[48] is interesting in that it indicates extreme shortening of two of the cyclopropane bonds (experimentally 1.457 Å in methylenecyclopropane vs. 1.510 Å in cyclopropane, 1.474 Å vs. 1.501 Å at STO-3G) and lengthening of the third (experimentally up to 1.542 Å, 1.522 Å at STO-3G). This latter geometrical distortion anticipates the ease with which the 2-3 bond of methylenecyclopropane undergoes cleavage.[49] The polarity of methylenecyclopropane is

$$- \; =\!\!\triangleleft \; +$$
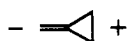
This is the same as isobutene, although the magnitude of the moment is somewhat less.

The calculated geometrical structure of bicyclo[1.1.0]butane, the simplest of the saturated bicyclic hydrocarbons, is in reasonable agreement with the experimental microwave structure of Cox, Harmony, Nelson, and Wiberg[50] and with an earlier ab initio 4-31G investigation by Newton and Schulman.[51] We find the central (ring-fused) bond to be very short (1.469 Å vs. 1.502 Å using the same level of theory for cyclopropane) in qualitative agreement with, but overestimating, the experimental trend (1.497 Å in bicyclo[1.1.0]butane vs. 1.510 Å in cyclopropane[52]). Such a shortening may be rationalized by considering the molecular orbitals of bicyclo[1.1.0]butane to be formed as a result of interaction of the valence (Walsh) functions of cyclopropane with the empty p orbital on an encroaching methylene group. The resulting charge transfer (from cyclopropane to methylene) would lessen the antibonding character of the (to be) ring-fused linkage, leading presumably to its shortening.

This molecule has a large dipole moment (0.75 D theoretically and 0.68 D experimentally) for a system with only carbon–carbon single bonds. The theoretical value is in close agreement with that of Newton and Schulman.[51] The polarity is such that the bridging bond is at the positive end and the methylene groups at the negative end. This is, perhaps, further evidence for the transfer of electrons from the cyclopropane fragments to the methylenes. It is interesting to note that this molecule is one in which electrons are transferred *away from* the unsaturated part (the bridging bond) to the more saturated part. It is analogous to cyclopropene which shows a similar polarity.

filled [orbital structure] empty
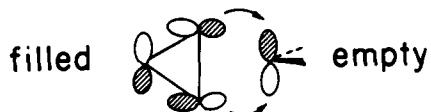
1-Methylcyclopropene is found to adopt an equilibrium conformation in which one of the methyl hydrogens eclipses the ring double bond, not at all surprising in view of experience with acyclic counterparts. What is a bit unexpected is the small magnitude of the methyl rotation barrier (experimentally 1.38[18b] and 0.83 kcal/mol at the STO-3G level) with respect to that of, say propene (experimentally between 1.95 and 2.039 kcal/mol,[26a-d,h] 1.55 kcal/mol at STO-3G). Recall that secondary interaction between the out-of-plane methyl hydrogens and the double bond π system was, according to the simple orbital model, responsible for the instability of staggered arrangements of vinylic

methyl groups.[24] In the staggered form of 1-methylcyclopropene this pair of hydrogens is much further removed from the unsaturated linkage than is the case in acyclic propene and hence destabilization is less.[53]

[structures labeled 3.1 Å and 2.8 Å]
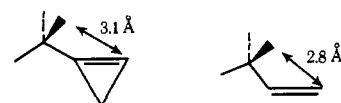
The dipole moment of 1-methylcyclopropene is of some interest. The large theoretical magnitude (0.90 D) is in good agreement with the experimental value of Kemp and Flygare.[18b] The theoretical direction is

Me [structure]   [structure with 58°]
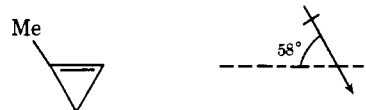
with the methyl group at the positive end. This appears to be consistent with the microwave study of Kemp and Flygare although they do not determine the polarity. The dipole direction in 1-methylcyclopropene is relevant to the discussion of the direction for cyclopropene itself where we have earlier[2b] challenged the experimental assignment of Benson and Flygare.[54] These authors have suggested a polarity

$$\underset{+}{\overset{-}{\triangledown}}$$

based on a study of high-field rotational Zeeman effects, opposite to that suggested by theory. Our results on 1-methylcyclopropane throw further light on the subject. Realizing that the dipole moment of propene *places the methyl group at the positive end*, we can reasonably expect that the total moment of 1-methylcyclopropene is approximately a vector sum of moments of propene and cyclopropene. Using the theoretical directions of both we obtain, consistently

[structure] + [structure] = giving [structure]
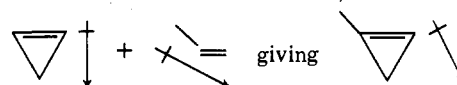
However, if the cyclopropene polarity were reversed, corresponding vector addition gives

[structure] + [structure] = giving [structure]
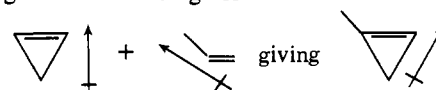
This is inconsistent both with the theoretical results and with the experimental observation that the direction of the resultant dipole is close to the a inertial axis (which is approximately along the C–C methyl bond). The methylcyclopropene results are obviously in better agreement with the notion that the double bond is at the positive pole of cyclopropene rather than the other way around.

The reduction in methyl rotation barrier in 3-methylcyclopropene over that found in its saturated analogue methylcyclopropane (2.07 kcal/mol vs. 2.53 kcal/mol at STO-3G, experimental data for comparison not available) may also be rationalized by consideration of the simple perturba-

Attraction [orbital structure] filled
empty
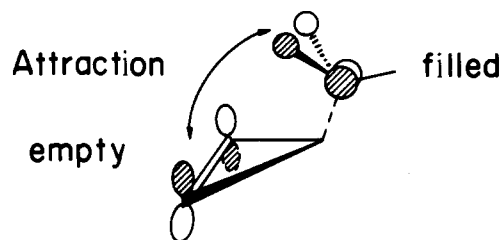
tion model. Here, long-range attraction between the highest occupied molecular orbital on the methyl and the empty π^* on the small ring stabilizes the normally unfavorable eclipsed form, while having no effect on the ground state bisected structure. A net reduction in barrier results. Such stabilization is akin to that resulting from an allowed suprafacial migration of a filled p symmetry orbital between the oppositely signed termini of a polyene lowest unoccupied molecular orbital.[55] It might be commented that a similar
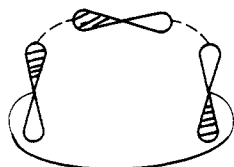
parallel can be drawn with a symmetry disallowed sigmatropic migration process. Thus, the methyl straddled conformer of 5-methylcyclopentadiene
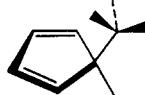
may be likened to p orbital migration in which stabilization through two-electron interaction (this time between the filled migrating center and the lowest unoccupied butadiene
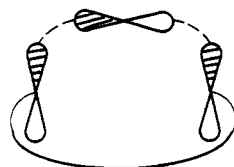
orbital) is zero by symmetry. Indeed, STO-3G calculations show a rather larger methyl rotation barrier (4.6 kcal/mol) than one would have otherwise anticipated.

C_4H_4. Energy (relative to but-1-yn-3-ene) and electric dipole moment data for a limited set of isomeric C_4H_4 hydrocarbons are presented in Table VIII. We have performed full geometry optimization (at the STO-3G level) on the two acyclic molecules included in the set. This is because physical data on the individual C_4H_4 members is very limited indeed, and we shall have to rely almost totally on the theoretical calculations. The experience gained in earlier sections, where comparisons between theory and experiment were both numerous and diverse, should serve a useful basis for assessment of our findings here. With the advent of low-temperature techniques, in particular, infrared and Raman spectroscopy, many of the theory's conclusions regarding structure and stability will probably be brought to test in the coming years.

Experimental and theoretical (STO-3G) structures for but-1-yn-3-ene show lengthening of both double and triple bonds from parent ethylene and acetylene, respectively (ethylene, $r(C=C) = 1.330$ Å, 1.306 Å at STO-3G; acetylene, $r(C\equiv C) = 1.208$ Å, 1.168 Å at STO-3G). The interconnecting single bond undergoes shrinkage. Both experiment and theory reveal a nonlinear acetylenic moiety (indicative of repulsion between the two unsaturated linkages) but the calculations appear to underestimate the magnitude of the distortion. The dipole moment of the but-1-yn-3-ene is a reasonable agreement with the microwave value (component along the a axis only). The theoretical direction of the angle with the triple bond being 20°. This is quite close
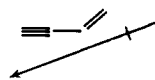

Table VIII. Theoretical Relative Energies (kcal/mol) and Electric Dipole Moments (D) for C_4H_4 Hydrocarbons

| Molecule | Relative energy | | μ |
	4-31G	6-31G*[a]	4-31G
But-1-yn-3-ene	0	0	0.45[b]
Butatriene	11.6	10.7	0
Methylenecyclopropene	36.2	23.6	2.08
1,3-Cyclobutadiene ($^3A_{2g}$)	45.7	35.4	0
Methylcyclopropenylidene	46.6	(38.2)	3.60
1,3-Cyclobutadiene ($^1A_{1g}$)	51.3	41.3	0
Tetrahedrane	93.8	68.5	0
1,2-Cyclobutadiene	78.2	(73.1)	3.20
Bicyclo[1.1.0]butene $\Delta^{1,3}$	117.0		1.19
Cyclobutyne	117.5		3.46
Methylcyclopropyne	132.8		

[a] Numbers in parentheses estimated as described in text. [b] Experimental moment 0.4 D, footnote b, Table IV.

to the a axis. The π-electron populations on the carbon atom show some alternation which contributes to this dipole moment.
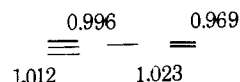

The optimized (STO-3G) geometrical structure for butatriene has already been reported,[56] and shows extreme shortening of the central carbon–carbon double bond (1.257 Å compared to an STO-3G value of 1.306 Å for ethylene). This is consistent with our notions concerning the consequences of conjugation of 1,3-disposed double bonds, and with experimental evidence on related systems (e.g., 1,3-butadiene,[57] but-1-yn-3-ene,[58] 1,3-butadiyne[59]). No overall interaction between the consenting pair of double bonds (as given by the energy of the *isodesmic* process (eq 6)) is ob-

$$E(\text{4-31G}) = 0.0 \text{ kcal/mol}$$
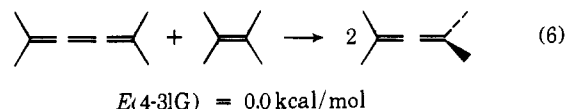
served in contrast to the appreciable stabilization which results from interaction of multiple bonds connected via a single linkage. One is tempted to suggest that repulsive interactions arising due to the shortening of the interconnecting double bond in butatriene are of more serious consequence than those resulting from similar shrinkage of single linkages.

We noted previously that methylenecyclopropane exhibited more strain than did its incorporated three-membered ring, cyclopropane; that is to say the energy of the *isodesmic* process 7 was negative. This, we rationalized, was not
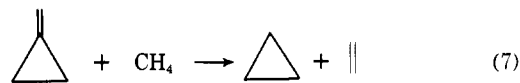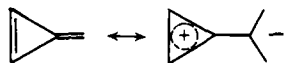

at all surprising in view of the necessity of incorporating an sp^2 hybridized carbon, instead of an sp^3 center, into the small ring. Consider now the energy of the analogous *isodesmic* process 8, providing a measure of the strain present in methylenecyclopropene, relative to that in cyclopropene.
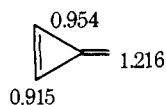

It is positive (by 5.3 kcal/mol at the 4-31G level and 6.1 kcal/mol using the 6-31G* polarization basis functions) indicating and additional factor at work, more than compensating for the increased ring strain. Examination of the cal-

culated (STO-3G) geometrical structure provides further insight. Here the small ring double bond is somewhat longer than that in cyclopropene (1.305 Å, up from 1.277 Å) while the other pair of cyclic linkages are far shorter (1.444 Å in methylenecyclopropene compared to 1.520 Å in cyclopropene). The large dipole moment (2.08 D at 4-31G, the small ring at the positive end) provides a further clue, and suggests that one way of regarding methylenecyclopropene is in terms of a zwitterionic species;[60] that is to say a carbanion center attached to the 2π electron aromatic cyclopro-

penyl cation. Our calculated π electron populations fully support such a contention as does the available experimen-

tal data by indicating strong stabilization of the ion by electron-withdrawing groups attached to the external methylene.[60] Furthermore, the geometry of the three-membered ring in methylenecyclopropene is quite close to the STO-3G structure of cyclopropenyl cation,[61] and to the recently reported microwave determination of cyclopropenone.[62]

It should be mentioned, of course, that simple Hückel theory has long regarded molecules such as methylenecyclopropene, where it is possible to write a valence structure incorporating an aromatic moiety, as species of exceptional stability.[63]

Methylcyclopropenylidene,[64] like the unsubstituted ring, is best represented in terms of incorporation of an aromatic (2π electron) cycle. The extra pair of electrons lies in the ring plane.
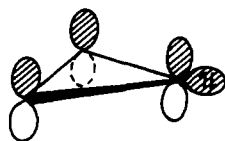
The enhanced stability which results is very clearly evident from the energy of the bond separation process 9[2g] for the parent compound, to be compared with the corresponding

$$\triangle + 2CH_4 + :CH_2 \longrightarrow 2CH_3—\ddot{C}H + CH_2=\!\!=CH_2 \quad (9)$$

$$E(6\text{-}31G^*) = 5.5 \text{ kcal/mol}$$
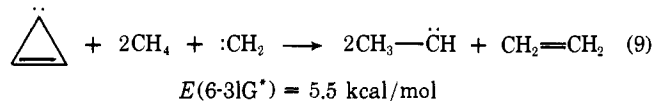
bond separation reaction for cyclopropene (eq 10).[2g] Stabilization afforded to parent cyclopropenylidene by attachment of a single methyl group (8.0 kcal/mol at the STO-3G

$$\triangle + 3CH_4 \longrightarrow 2CH_3—CH_3 + CH_2=\!\!=CH_2 \quad (10)$$

$$E(6\text{-}31G^*) = -50.4 \text{ kcal/mol}$$
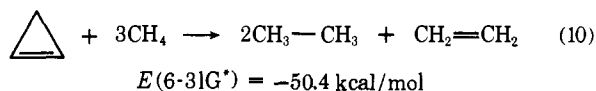
level, as given by the energy of the isodesmic reaction 11) is significantly greater than that given to a neutral aromatic (e.g., toluene which exhibits a methyl stabilization energy relative to benzene of 3.1 kcal/mol at STO-3G).[3c] Yet it is smaller than that found for the charged 2π electron cycle
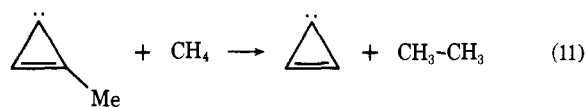
methylcyclopropenyl cation (19.6 kcal/mol relative to the cyclopropenyl cation at STO-3G[61]). This leads us to suggest that cyclopropenylidene is in fact a dipolar species. Methyl substitution should then further separate the ends of the dipole, hence leading to an increased moment. The calculations bear out this contention.

As was the case with methylenecyclopropene, the ring geometry here strongly resembles that of the aromatic cyclopropenyl cation.[61]

Although cyclobutadiene has been actively sought for the past 100 years,[65] only recently has convincing evidence for its stable existence emerged. Lin and Krantz[66] and Chapman and his collaborators[67] simultaneously reported the infrared spectrum of the species, formed upon continued irradiation of 2-pyrone.
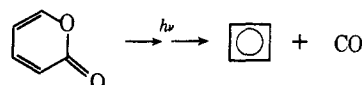
Both groups interpreted their experimental data as consistent with a square-planar geometry; a later report by Krantz, Lin, and Newton[68a] suggested but then discounted[68a,b] the possibility of rapid equilibration between two rectangular forms as a viable alternative. Chapman's fur-

ther studies[69] with deuterated 2-pyrones provided additional support for the square (static or dynamic) geometry of the transient cyclobutadiene. Thus, photochemical decomposition of 1,2-dideuteriocyclobutadiene (formed initially from 2-pyrone-5,6-d_2) led to all three possible acetylenes while fragmentation of 1,3-dideuteriocyclobutadiene (this time from 2-pyrene-3,6-d_2) led to only one product (ruling out the possibility of hydrogen scrambling). The calculations we report, as those of other authors,[68,70] suggest two
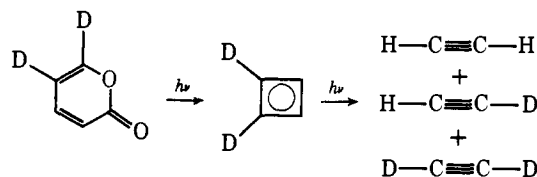
electronic states of similar energy; a square-planar (D_{4h}) triplet, and a rectangular (D_{2h}) singlet. Although the best level of theory available to us assigns a triplet ground state
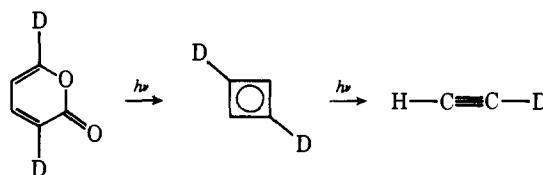
(by 5.9 kcal/mol at the 6-31G* level) this is almost certainly incorrect in view of the known preference of single determinant methods to favor states of high-spin multiplicity. For example, calculations at the 6-31G* level conclude that

the energy of triplet ($^3B_1$) methylene is some 31 kcal/mol beneath that of the singlet ($^1A_1$) state.[71] Experimentally, methylene is known to possess a triplet ground state although the excited singlet is now believed to be no more than 10 kcal/mol higher in energy.[72] The small singlet-triplet splitting, obtained by the single determinant theory in the case of cyclobutadiene, presents a reasonable case for a singlet ground state of the molecule. The calculations of Buenker and Peyerimhoff,[70a] which employ a limited level of configuration interaction on top of the single determinant framework, also assign the ground state of cyclobutadiene to be a rectangular singlet, but differ from our work, and from that of Krantz, Lin, and Newton, by suggesting that the structure of the triplet species is not a perfect square. If, as the quantitative calculations seem to suggest, cyclobutadiene indeed possesses a singlet ground state, then according to the Jahn-Teller theorem its geometrical structure may not be that of a square.[73] Thus, the assignment of a singlet ground state to cyclobutadiene perhaps contradicts the available experimental evidence regarding the geometry of the molecule (unless, of course, we are willing to interpret it in terms of equilibrating rectangular forms).

In an earlier paper we suggested that the energy of the *isodesmic* reaction 12 provided an indicator of the "aromatic" stabilization afforded to benzene.[3a] The calculated (4-

$$\text{benzene} + 6CH_4 \longrightarrow 3CH_3-CH_3 + 3CH_2=CH_2 \quad (12)$$
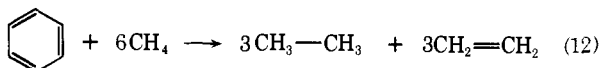
31G level) heat of 64 kcal/mol was noted to be in excellent agreement with the experimental value of 61 kcal/mol. We might expect then that any "antiaromatic" destabilization accompanying the formation of the 4π electron cyclic, 1,3-butadiene, would be revealed by the energy of the corresponding process 13. Indeed, destabilization inherent to sin-

$$\text{cyclobutadiene} + 4CH_4 \longrightarrow 2CH_3-CH_3 + 2CH_2=CH_2 \quad (13)$$
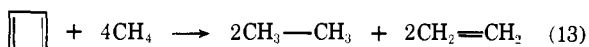
glet cyclobutadiene is large, the estimate of the 4-31G basis set calculations being −68 kcal/mol. However, part of this can be attributed to bond strain in the σ system.

We find the cyclopropenylidene moiety again in the theoretical structure for 1,2-cyclobutadiene, perhaps more appropriately termed homocyclopropylidene at this point. Thus, we may envision the molecule as being constructed by replacement of the π and π^* orbitals of the ethylenic double bond in parent cyclopropenylidene by the highest occupied Walsh pair in cyclopropane. As we did in our treatment of homoaromatic cations,[10,74] we can anticipate the gross features of the resulting molecule's geometrical structure by consideration of the interaction between the empty p symmetry orbital on the carbene center, with the filled symmetric Walsh component.[34]
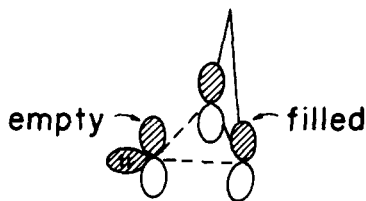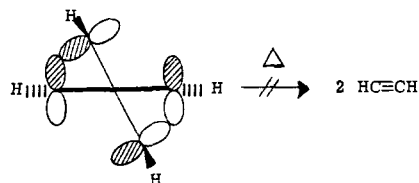
Charge transfer from the symmetric Walsh component on cyclopropane to the vacant p orbital at the carbene center should result in a draining of bonding electron density from the ring-fused linkage, leading to its lengthening, as indeed is suggested by the quantitative calculations (1.547 Å compared to an STO-3G value of 1.501 Å for cyclopropane[2b]). Homocyclopropenylidene is seen to prefer the bent carbon

skeleton of a bicyclic molecule, rather than the nearly planar four-membered ring arrangement as has been found for the isoelectronic $C_4H_5^+$ cation.[10,75] Such structures have been investigated here but found to be significantly higher in energy. To our knowledge parent or substituted homocyclopropenylidene species have as yet to be observed experimentally. In view of their seemingly high stability, and with the advent of low-temperature matrix isolation techniques, they should present a tempting target within the next decade.

That tetrahedrane should be a stable minimum on the C_4H_4 potential surface may be seen by consideration of interaction of the molecular orbitals of cyclopropenyl (cation or anion) and CH (anion or cation) fragments (Figure 7). The stabilization afforded to six electrons here is analogous to that originally proposed by Stohrer and Hoffmann[76] who suggested the possibility of a minimum-energy square-based pyramid form of the cyclopentadienyl cation
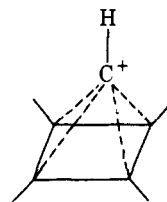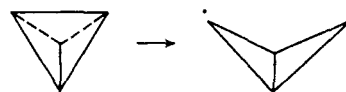
It should also be noted that the thermal (antarafacial-antarafacial) decomposition of tetrahedrane into two acetylenes, though predicted (4-31G) to be 50 kcal/mol exothermic, is a symmetry-forbidden process (photochemical de-

composition should be allowed and has already been postulated in the literature as evidence for the tetrahedrane molecule).[65,80]

Schulman and Venanzi[81] have already reported the structure of tetrahedrane at both the STO-3G and 4-31G levels, and by systematic investigation of the energy surface around the potential minima have concluded that it is indeed stable with respect to arbitrary geometrical distortions. Despite numerous attempts though, the tetrahedrane molecule remains to be observed and characterized experimentally. The question naturally arises then as to the depth of the potential well in which it rests, particularly with regard to bond cleavage to form the bicyclobutyl diradical. Schulman and Venanzi report a difference of 47 kcal/mol between tetrahedrane and the bicyclobutyl diradical (using the STO-3G basis and a 2 × 2 CI procedure) but this esti-

mate is certainly too high due both to the known tendency of the minimal basis to overestimate the stability of tight ring structures and to the limited configuration mixing allowed for the diradical state. Buenker and Peyerimhoff have also reported ab initio calculations on the tetrahedrane molecule.[82] Within a single determinant framework the species is found to be 35 kcal/mol higher in energy than singlet cyclobutadiene. When partial account is taken for the effects of electron correlation, however, this difference
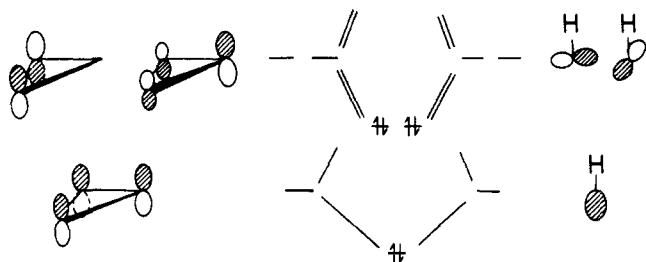
Figure 7. Interaction of the π orbitals of cyclopropenyl (cation or anion) with those of CH (anion or cation). See text for discussion.

Figure 8. CCC vs. HCH bond angles for internal methylene positions.

increases to 70 kcal/mol. In addition, these authors report the carbon–carbon distance in tetrahedrane to be 1.560 Å, similar, but slightly longer than both the STO-3G and 4-31G values.

The remaining species which we have considered within the C_4H_4 manifold are far less stable, and the possibility of their detection, much less characterization, seems remote. Indeed, the smallest ring cycloalkyne yet suggested as a viable reactive intermediate is cyclopentyne, while cyclooctyne is the lowest member of the series which has actually been isolated.[83]

C_4H_2. Although a number of possible cyclic structures can be drawn for C_4H_2, they are all likely to be highly strained, and therefore have not been investigated in this study. In order to complete the set of lowest energy structures for the entire series of C_4 hydrocarbons, we have carried out a geometry optimization on a single acyclic form, butadiyne. The resulting structure is particularly noteworthy for the exceptionally short carbon–carbon single bond incorporated into it. Indeed, this is the shortest such linkage we have encountered in a neutral hydrocarbon.

Conclusion

We have employed single determinant ab initio molecular orbital theory to the study of equilibrium geometries, relative energies, and electric dipole moments and charge distributions of the series of hydrocarbons of formulas C_4H_{10}, C_4H_8, C_4H_6, C_4H_4, and C_4H_2. The following points deserve special note.

STO-3G calculated equilibrium geometries are generally in excellent quantitative agreement with available experimental data, including those of bicyclic and four-membered ring molecules encountered for the first time in this paper. It is only the ring puckering angle in cyclobutane which stands out as poorly reproduced by the theory. Relative isomer stabilities calculated using the 4-31G extended basis set reasonably parallel the known thermochemical data, although some serious discrepancies occur at this level in attempted comparisons between acyclic and small ring molecules. These differences are largely rectified by introduction of polarization-type functions to the basis. Finally the magnitudes of electric dipole moments calculated at the 4-31G level are impressively close to the known values. Indeed mean absolute deviation of theory from experiment for 13 known (and nonzero) moments is only 0.04 D, with but two systems being in error by more than 0.1 D.

In agreement with available experimental data and with previous theoretical calculations, methyl C–H bonds were found to eclipse rather than to stagger unsaturated linkages. Rationalization in terms of simple perturbation theory was presented. Conformations and barriers of the two rotor systems isobutene and cis- and trans-2-butene were discussed, both in terms of the quantitative calculations and with reference to the basic perturbation arguments. Whereas the individual methyl groups in isobutene are each more difficult to torque than the single rotor of, say, propene, those in
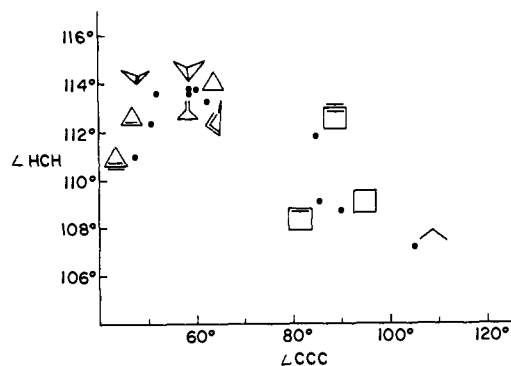
cis-2-butene twist somewhat more easily. Both methylcyclopropane and methylcyclopropene are shown by the calculations to be most stable in a conformation in which one of the rotors C–H bonds bisects the small ring. This preference, as well as the ordering of the rotational barriers in the two molecules

methylcyclopropane > methylcyclopropene

is simply rationalized by the perturbation theory.

Further evidence is presented in support of our earlier assignment of the direction of the electric dipole moment in cyclopropene, opposite to that indicated by Flygares micro-

wave spectral measurements. Thus we find the dipole in 1-methylcyclopropene to be greater, not less, than that of the parent, corresponding to vector addition rather than subtraction of the moments in propene ($Me^+-CH=CH_2^-$) and of the small ring.

Methylenecyclopropane is the most stable ring system within the C_4H_4 manifold, no doubt suggestive of the possibility of its incorporation of an aromatic 2π electron cycle. Although our calculations show a triplet ground state for 1,3-cyclobutadiene, the energy of the corresponding singlet is so near that we strongly suspect that correction for the effects of differential correlation will indeed show it to be the lower energy species. The energy of methylcyclopropenylidene, another system which incorporates an aromatic π cycle, falls midway in between those of the triplet and singlet states of 1,3-cyclobutadiene. Tetrehedrane, though apparently a stable potential minima on the C_4H_4 surface, is significantly less stable than cyclobutadiene making it the far more difficult target for experimental scrutiny. Among the remaining C_4H_4 isomers, homocyclopropenylidene stands out as a likely candidate for eventual experimental detection and characterization. The calculations suggest a bicyclic ring structure, much as one would obtain by formal replacement of the double bond in cyclopropenylidene by a cyclopropane moiety.

Finally, we have collected enough data on a variety of small hydrocarbons that we are now in a position to test Mislow's hypothesis relating the CCC and HCH bond angles of internal methylene groups.[85] The data in Figure 8 clearly indicate a number of exceptions to the general notion that a decrease in the methylene CCC angle necessarily leads to an increase in the corresponding HCH angle. Most noteworthy are the bond angle about the methylene carbon in the series of compounds cyclopropane, cyclopropene, and cyclopropyne, where HCH monotonically decreases as the CCC becomes smaller.

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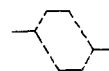
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This leads to the suggestion that methyl rotational barriers in molecules such as acetone, in which zwitterionic structures of the form

contribute heavily, should be smaller than those in the analogous monorotor systems (e.g., acetaldehyde). That is to say, here the cycle contains fewer than 6 π electrons, and in the limit of total description in terms of a zwitterion is 4-π electron antiaromatic. Indeed, whereas we have seen that methyl rotation in isobutene is more difficult than that in propene, the corresponding experimental barrier in acetone (0.78 kcal/mol[26a]) is actually smaller than that in acetaldehyde (1.17 kcal/mol[26b,c]). Even larger effects are to be expected if the π orbital on the central atom connecting the two methyl rotors is vacant, as, for example, in dimethylborane and in the isopropyl cation. For a discussion, see D. Cremer, J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 6900 (1974).

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