

pertain for other methods but that the dominance of the $1E_g-2E_u$ interaction may be reduced. Also, it seems likely that cancellation of effects due to A-type MO's may be less complete due to changes in coefficients and orbital energies.³¹

(31) C. Barbier and G. Berthier, *Theor. Chim. Acta*, **14**, 71 (1969); *Int. J. Quantum Chem.*, **1**, 657 (1967).

Acknowledgments. It is a pleasure to thank Professors L. M. Jackman and J. E. Baldwin for drawing my attention to this problem. I also thank Professor R. M. Pitzer for making available the virtual MO's from his *ab initio* ethane calculation and Professors O. H. Crawford, J. A. Pople, W. H. Saunders, and J. F. Bunnett for helpful criticisms of the manuscript.

A Floating Spherical Gaussian Orbital Model of Molecular Structure. X. C_3 and C_4 Saturated Hydrocarbons and Cyclobutane

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Abstract: The FSGO model is used to calculate geometries for three- and four-carbon hydrocarbons. By simply transferring, unchanged, most of the parameters from C_2H_6 , the C-C-C bond angles for C_3H_8 , $n-C_4H_{10}$, and $i-C_4H_{10}$ are determined to be 112.5, 112.5, and 111.0°, respectively, in agreement with experiment within 0.3°. More complete minimization accurately predicts the detailed geometry of propane and cyclobutane. The differences in the C-H bond lengths and H-C-H bond angles in propane are predicted correctly. A D_{2d} structure is predicted for cyclobutane, with a dihedral angle of 32° and a tilt of 7° for the methylene groups.

The floating spherical Gaussian orbital (FSGO) model is discussed in detail in paper I of this series.¹ As currently applied, the model predicts the electronic and geometric structure of singlet ground states of molecules with localized orbitals without the use of any arbitrary or semiempirical parameters. The localized orbitals are constructed by using single normalized spherical Gaussian functions

$$\Phi(\vec{r} - \vec{R}_i) = (2/\pi\rho_i^2)^{3/4} \exp[-(\vec{r} - \vec{R}_i)^2/\rho_i^2]$$

with orbital radius, ρ_i , and position, R_i . A single Slater determinant represents the total electronic wave function. If S is the overlap matrix of the set of non-orthogonal localized orbitals Φ_i and $T = S^{-1}$, then the energy expression for a molecule is

$$E = 2 \sum_{j,k} (j|k) T_{jk} + \sum_{k,l,p,q} (kl|pq) [2T_{kl} T_{pq} - T_{kq} T_{lp}]$$

where $(j|k) = \int \Phi_j h \Phi_k dv$ (h = one-electron operator) and $(kl|pq) = \int \Phi_k(1) \Phi_l(1) (1/r_{12}) \Phi_p(2) \Phi_q(2) dv_1 dv_2$. The energy is minimized by a direct search procedure with respect to all parameters: orbital radii, ρ_i , orbital positions, \vec{R}_i , and nuclear positions.

Previous work with the FSGO model¹ has indicated that the model works particularly well for molecules showing a high degree of covalency; in particular the hydrocarbons showed unusually good results.² With this in mind, work was extended to C_3 and C_4 saturated hydrocarbons and to cyclobutane. The emphasis in these studies is not toward calculation of accurate energies (simple FSGO typically gives about 85% of Hartree-Fock SCF values). Rather it is aimed at using the

model as a tool for obtaining geometries (bond angles and bond length within 1-2%) and trends in rotation barriers (FSGO typically gives rotational barriers nearly twice experimental).

Investigation into these various hydrocarbons was taken at two distinct levels. First, an attempt was made to obtain rough geometries by simply transferring many of the parameters from smaller molecules (*e.g.*, propane from ethane). Typically the C-C bond lengths and the C-C-C bond angles are varied for each new molecule and rotational barriers are then calculated by assuming rigid rotation, not minimizing at the top of the barrier. (Stevens³ has made a series of calculations on C_2H_6 and H_2O_2 and has concluded that rotational barriers can be calculated assuming rigid rotation if no lone pairs are present.) A second procedure involved determining details of the structure of propane and cyclobutane. These more extensive minimizations were carried out to test the simple FSGO's ability to conform with experimental results and to make predictions about geometries.

Transferability of Parameters

A method (hereafter termed SCF-FSGO) similar to the simple FSGO has been developed by Christoffersen and coworkers^{4,5} for calculations on hydrocarbons. Here the concept of transferring parameters from smaller molecules and fragments has been used to construct large hydrocarbons. It would be instructive

(3) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).

(1) S. Y. Chu and A. A. Frost, *J. Chem. Phys.*, **54**, 764 (1971); and references cited therein.

(2) A. A. Frost and R. A. Rouse, *J. Amer. Chem. Soc.*, **90**, 1965 (1968).

(4) (a) R. E. Christoffersen, *J. Amer. Chem. Soc.*, **93**, 4104 (1971); (b) R. E. Christoffersen, D. W. Genson, and G. M. Maggiora, *J. Chem. Phys.*, **54**, 239 (1971).

(5) G. M. Maggiora, D. W. Genson, R. E. Christoffersen, and B. V. Cheney, *Theor. Chim. Acta*, **22**, 337 (1971).

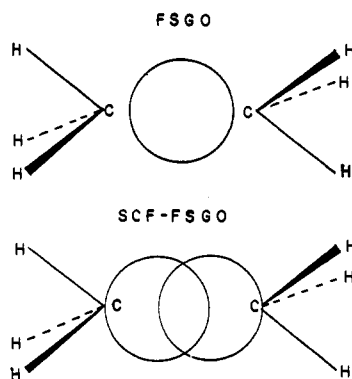


Figure 1. Comparison of FSGO and SCF-FSGO basis sets for ethane.

at this point to compare the two methods and their results.

Simple FSGO constructs molecules with an absolute minimum basis set (a Lewis set) of spherical Gaussians. For example, ethane would be constructed from methane by using two CH_3 groups (consisting of one inner shell and three C-H bonding orbitals) and adding a C-C bonding orbital (Figure 1). SCF-FSGO would construct ethane by taking two CH_3 groups (consisting of one inner shell and four bonding orbitals) and combining them (Figure 1). This basis set has one more orbital than the Lewis set and will give a better total wave function. However, the presence of this "extra" orbital necessitates an SCF procedure, requiring more computational time and making nonlinear variations more difficult.

A comparison of results is given in Table I. Surprisingly, the simple FSGO gives much better geometries than the more complex SCF-FSGO, and only

Table I. Comparison of FSGO and SCF-FSGO

	FSGO	SCF-FSGO ^a	Exptl
C_2H_4			
Bond length C=C (au)	2.55	2.47	2.56
Energy (au)	-65.835	-66.538	
C_2H_6			
Bond length C-C (au)	2.86	2.64	2.90
Energy (au)	-66.996	-67.348	
V_3 (kcal/mol)	6.1	5.38	2.98
C_3H_8			
Bond angle C-C-C (deg)	112.5	110.6	112.4
Energy (au)	-100.015	-100.647	
V_3 (kcal/mol)	5.6	5.63	3.3
V_3' (kcal/mol)	1.8	2.81	

^a See ref 4b.

slightly poorer energies. The rotational barriers, which one might expect to be more accurate with the SCF wave function, do not significantly differ from those given by the simpler model. However, the trend from C_2H_6 to C_3H_8 is not reproduced by the simple FSGO, while SCF-FSGO does show, correctly, that the barrier increases.

One should note that the simple FSGO is not capable of dealing with conjugated molecules easily, which SCF-FSGO can. Also, the Lewis basis set gives no virtual orbitals which limits its usefulness.

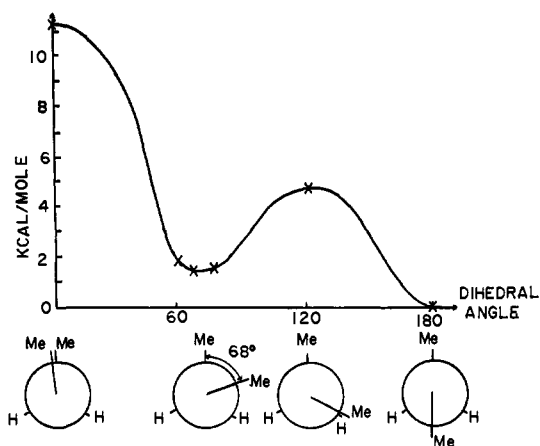


Figure 2. Predicted potential energy curve for internal rotation of the ethyl group in *n*-butane.

Transferability Results

The propane molecule was investigated using data from staggered ethane.² Methyl and methylene groups, and C-C bond distances and orbital radii, were taken from ethane without modification (Table II). The

Table II. Standard Parameters Taken from C_2H_6 for Calculations Utilizing Transferable Parameters

Bond distance C-C (au)	2.860
Bond distance C-H (au)	2.118
Bond angle H-C-H (deg)	108.61
C-H bond radius (au) ^a	1.698
C-C bond radius (au)	1.661
Inner shell radius (au)	0.328

^a Fixed 0.59 of the distance toward the hydrogen nucleus.

C-C-C bond angle was first set arbitrarily at 115° , and it was determined that the low-energy conformer had both methyl groups staggered with respect to the methylene group. A minimization with respect to the C-C-C bond angle gave a value of 113° . The C-C distance was then minimized, obtaining a value of 1.506 Å. A final minimization with respect to the C-C-C angle gave a result of 112.5° . Rotational barriers were calculated, assuming rigid rotation (Table III).

The butane molecule was constructed from the propane molecule parameters. The most stable form was assumed to have all C-H bonds on adjacent carbons staggered. A minimization with respect to the C-C-C bond angles and the C-C bond length showed them both to be unchanged from propane. Rigid rotation was used to calculate methyl and ethyl rotational barriers (Figure 2), and a minimization (with 5° increments and interpolation) gave the dihedral angle for the gauche conformer to be 68° .

The isobutane molecule was constructed from propane, assuming C_{3v} symmetry and assuming that the low-energy conformer had all methyl groups staggered with respect to the central carbon. A minimization with respect to the C-C-C angle was performed, obtaining a value of 111° . The rotational barrier due to eclipsing one, two, and three methyl groups was calculated (Table III).

Table III. Results from Calculations Using Transferred Parameters

	FSGO	Other calcn	Exptl
C₃H₈			
Bond length C-C (Å)	1.506		1.526 ± 0.002 ^a
Bond angle C-C-C (deg)	112.5	112.2 ^d	112.4 ± 0.2 ^a
V ₃ (kcal/mol)	5.6	3.42-3.69 ^d	3.32, ^b 3.68 ^c
V ₃ ' (kcal/mol)	1.8	0.571-1.207 ^d	
Energy (au)	-100.0149	-118.09211 ^e	
n-C₄H₁₀			
Bond length C-C (Å)	1.506		1.533 ± 0.003 ^f
Bond angle C-C-C (deg)	112.5	112.2 ^d	112.4 ± 0.3 ^f
Energy barriers (kcal/mol)			
V ₃ (CH ₃)	5.5	3.26-3.63 ^d	
V ₃ ' (CH ₃)	0.0	0.0 ^d	
Gauche-gauche	10.1	5.72-12.69 ^d	
Gauche-trans	5.2	3.50-4.00 ^d	3.4 ± 0.4 ^g
Gauche-trans energy difference	1.47	1.13-1.76 ^d	0.770 ± 0.09 ^h
Dihedral angle for gauche conformer	68	70.5-77.2 ^d	63 ± 8 ^f
Energy (au)	-133.0249	-155.46592 ^d	
i-C₄H₁₀			
Bond angle C-C-C (deg)	111	110.8 ^d	111.15 ⁱ
Energy (au)	-133.0231	-155.46572 ^d	
Barriers (kcal/mol)			
1 CH ₃ eclipsed	5.1	3.88-4.07 ^d	3.6, ^k 3.9 ^j
2 CH ₃ eclipsed	13.0		
3 CH ₃ eclipsed	23.0		

^a See ref 8. ^b E. Hirota, C. Matsumura, and Y. Morino, *Bull. Chem. Soc. Jap.*, **40**, 1124 (1967). ^c D. M. Grant, R. J. Puomire, R. C. Livingston, K. A. Strong, H. L. McCurry, and R. M. Brugger, *J. Chem. Phys.*, **52**, 4424 (1970). ^d Minimal STO basis, see ref 9. ^e Intermediate GTO basis. L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971). ^f See ref 6. ^g J. E. Piercy and M. G. S. Rao, *J. Chem. Phys.*, **46**, 3951 (1967). ^h G. J. Szasz, N. Sheppard, and D. H. Rank, *ibid.*, **16**, 704 (1948). ⁱ See ref 7. ^j See ref 10. ^k K. S. Pitzer and J. E. Kilpatrick, *Chem. Rev.*, **39**, 435 (1946).

Discussion of Transferability Results

In general the results coincide with expectations due to previous results. The energies of the three molecules were about 85% of the SCF values. The rotational barriers were found to be high by about a factor of two and geometries given within 1-2%.

A C-C-C bond angle of 112.5° for propane and the fact that it does not change from propane to butane are confirmed experimentally.⁶ The decrease in the C-C-C angle in going from normal butane to isobutane (112.5-111°) is also seen experimentally.⁷ The fact that the C-C bond length does not change from propane to butane also reflects experimental measurements.^{6,8}

It would appear then that the gross geometrical changes occurring in these alkanes (specifically the change in C-C-C bond angle in going from normal to isobutane) are not complicated phenomena, involving rearrangements in the methyl groups or gross changes in the electron distribution of the C-C bond (the orbital radii were held constant). These geometrical changes can be predicted semiquantitatively by relatively simple procedures, utilizing a relatively unsophisticated model.

The results on the propane rotational barriers show that the methyl rotations are coupled (as has been seen in other calculations⁹). While the barrier was much higher than the experimental and SCF values, the relative values of the interaction potential, V₃', and the barrier for a single methyl rotation, V₃, are found to parallel the SCF values. [V₃' is the energy (above V₃)

necessary to rotate the second methyl group; for independent rotations, V₃' = 0.0.]⁹

The rotation of the methyl groups in *n*-butane was found to give barriers very similar to the propane values (5.5 vs. 5.6 kcal/mol for propane, though the ordering is reversed from that found experimentally), indicating that the barrier is not due to any appreciable amount to interactions other than those with the adjacent methylene group. As has been seen in Pople's calculations with a minimal STO basis,⁹ the methyl rotations are not coupled. The rotational barriers for *n*-butane correspond qualitatively to the SCF and experimental results (see Table III and Figure 2). One should note that the dihedral angle for the gauche conformer is well reproduced (68° is predicted vs. 63 ± 8° seen experimentally⁶) within the context of FSGO.

The calculated rotational barriers for isobutane seem to conflict with the experimental evidence. Lide's^{7,10} microwave work could not give a value for the coupling between methyl groups; however, he stated that the spectra indicated only minor coupling. FSGO predicts that the coupling here is greater than propane (V₃ is given at 5.1 kcal/mol, while second rotation requires an additional 7.9 kcal/mol, and to eclipse the third methyl group requires 10 kcal/mol more). This result could be due to the assumption of rigid rotation. However, because all other systems considered gave qualitatively correct results within this approximation, this seems unlikely unless isobutane undergoes large geometrical changes in the eclipsing conformations.

Propane

The geometry of the propane molecule was investigated further to indicate if detailed features of the

(6) R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.*, **81**, 3491 (1959).

(7) D. R. Lide, *J. Chem. Phys.*, **33**, 1519 (1960).

(8) D. R. Lide, *ibid.*, **33**, 1514 (1960).

(9) L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

(10) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958).

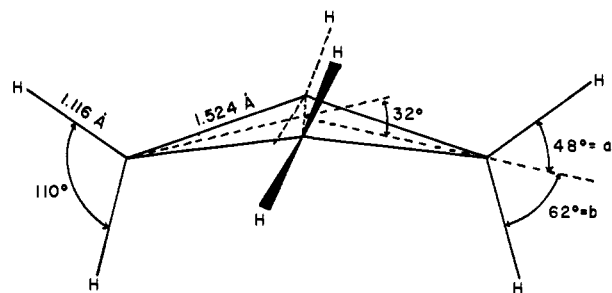


Figure 3. Predicted geometry of cyclobutane.

structure could be obtained within the context of the simple FSGO model. In these calculations all parameters were varied with the following limitations: (1) the inner shells were fixed on the carbon nuclei and their orbital radii held fixed to the value from C_2H_6 ; (2) the C-C bonding orbitals were fixed on the line between the carbons and held midway between the two; and (3) the C-H bond orbitals were kept on the line between C and H, 0.59 of the distance toward the H (as has been found in C_2H_6). All bond angles, bond distances, and orbital radii (excluding inner shells) were optimized. Results are given in Table IV.

Table IV. Propane. Results from Detailed Investigation

	FSGO	Other calcn	Exptl
Bond length			
C-C (Å)	1.506	1.541 ^b	1.526 ± 0.002 ^a
Bond angle			
C-C-C (deg)	112.5	112.4 ^b	112.4 ± 0.2 ^a
Bond length			
C-H (Å)			
CH ₃	1.122	1.086 ^b	1.091 ± 0.010 ^a
CH ₂	1.124	1.089 ^b	1.096 ± 0.002 ^a
Bond angle			
H-C-H (deg)			
CH ₃	108	108.2 ^b	107.7 ± 1 ^a
CH ₂	107	107.2 ^b	106.1 ± 0.2 ^a
C-H radius (au)			
CH ₃	1.705		
CH ₂	1.709		
C-C radius (au)	1.656		
Energy (au)	-100.0153	-118.09211 ^c	

^a See ref 8. ^b See ref 11. ^c L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971), minimal STO basis.

The C-C bond length and C-C-C bond angle remained unchanged. The details of the methyl and methylene groups were given very well: the C-H bond length for the methyl groups were found to be slightly shorter than for the methylene (0.002 Å), as is seen experimentally,⁸ and the H-C-H bond angles in the methyl group were found to be larger than in the methylene groups (by 1°), which has also been seen experimentally.⁸ All of these results are in excellent agreement (Table IV) with Pople and coworkers' recent results using a minimal STO-type basis set.¹¹

Cyclobutane

The second example of a detailed study involved the cyclobutane molecule. Again the inner shell orbitals were fixed on the carbons and their orbital radii fixed.

(11) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971).

The C-H orbitals were fixed as in propane, 0.59 of the distance between the C and H. The C-C bonding orbitals were not fixed on the line between the carbons, due to the possibility of a "bent bond" as had been found in cyclopropane.²

Minimizations on cyclobutane were first performed on the planar (D_{4h}) structure. The nonplanar (D_{2d}) form was then considered. The planar form was found to be the most stable when it was assumed that the methylene groups did not "rock" (in Figure 3, this corresponds to $a = b$). It was only when the methylene groups were allowed to rock that a minimum was found for nonplanar structure. Minimization with respect to all bond angles, bond lengths, and orbital parameters was performed for the nonplanar form. Results for both D_{2d} and D_{4h} forms are given in Tables V and VI.

Table V. Cyclobutane. Results from Detailed Investigation

	FSGO	Other calcn	Exptl
		D_{4h}	
Bond length C-C (Å)	1.535		
Bond length C-H (Å)	1.116		
Bond angle H-C-H (deg)	110		
Energy (au)	-131.9881	-131.989 ^a	
		D_{2d}	
Bond length C-C (Å)	1.524		1.548 ± 0.003 ^b
Bond length C-H (Å)	1.116		1.092 ± 0.010, ^b 1.113 ^c
Bond angle H-C-H	110		108, 110 ^d
Dihedral angle (deg)	32	20 ^f	27, ^e 35, ^d 34 ^e
Rocking angle (deg)	7	3 ^f	4 ^d
Energy (au)	-131.9937		
Inversion barrier (kcal/mol)	3.5	0.31 ^f	1.48 ^d

^a See ref 17, FSGO basis. ^b A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961). ^c See ref 12a. ^d See ref 12b. ^e See ref 13. ^f See ref 16, CNDO/2 calculation.

As has been seen experimentally,^{12,13} the nonplanar structure is found to be most stable; the predicted dihedral angle of 32° agrees very well with the experimental values of 27–35°. The C-C and C-H bond lengths are given within 2–3% of the experimental values, and the H-C-H bond angle of 110° corresponds well with the experimental values of 108^{12a}–110°.^{12b}

Experimentally, one finds that cyclobutane undergoes rapid inversion between two D_{2d} forms with an inversion barrier of 1.44^{12b}–1.48¹⁴ kcal/mol. FSGO gives the inversion barrier to be 3.5 kcal/mol, again the barrier being too high by about a factor of 2. The geometry of the D_{4h} conformer at the top of the barrier does not differ greatly from the D_{2d} species. However, there is a slight elongation of the C-C bond length (0.011 Å) in the D_{4h} conformation. Except for this, the geometrical parameters remain unchanged, except that the C-C bond is slightly more bent in the D_{4h} than in the D_{2d} form. (In D_{2d} , the orbital center is off the line between

(12) (a) S. Meiboom and L. C. Snyder, *J. Chem. Phys.*, **52**, 3857 (1970); (b) J. M. R. Stone and I. M. Mills, *Mol. Phys.*, **18**, 631 (1970).

(13) T. Ueda and T. Shimonouchi, *J. Chem. Phys.*, **49**, 470 (1968).

(14) G. A. Miller, 2nd International Conference on Raman Spectroscopy, Oxford, England, Sept 1970.

Table VI. Cyclobutane Nuclear and Orbital Data (au)

	Orbital radius	x	y	z
<i>D_{2d}</i>				
Nuclei				
C(1), C(2)		0.0	±1.996	0.286
H(11), H(21)		0.0	±2.435	2.350
H(12), H(22)		0.0	±3.785	-0.832
C(3), C(4)		±1.996	0.0	-0.286
H(31), H(41)		±3.785	0.0	0.832
H(32), H(42)		±2.435	0.0	-2.350
Orbitals				
S(1), S(2)	0.328	0.0	±1.996	0.286
B(11), B(21)	1.700	0.0	±2.262	1.540
B(12), B(22)	1.688	0.0	±3.083	-0.393
S(3), S(4)	0.328	±1.996	0.0	-0.286
B(31), B(41)	1.688	±3.083	0.0	0.393
B(32), B(42)	1.700	±2.262	0.0	-1.540
BCC	1.709	±1.021	±1.021	0.0
<i>D_{4h}</i>				
Nuclei				
C(1), C(2)		0.0	±2.051	0.0
C(3), C(4)		±2.051	0.0	0.0
H(11), H(12), H(21), H(22)		0.0	±3.265	±1.735
H(31), H(32), H(41), H(42)		±3.265	0.0	±1.735
Orbitals				
S(1), S(2)	0.328	0.0	±2.051	0.0
S(3), S(4)	0.328	±2.051	0.0	0.0
B(11), B(12), B(21), B(22)	1.698	0.0	±2.789	±1.054
B(31), B(32), B(41), B(42)	1.698	±2.789	0.0	±1.054
BCC	1.706	±1.052	±1.052	0.0

the carbons by an angle of 1.28°, while in the planar form, this increases to 1.5°.) The "amount of bending" in the C-C bonds is less for both of the cyclobutane forms than for the cyclopropane molecule (where the angle is 2.58°),² thus reaffirming the classical idea that the cyclobutane molecule is less strained.

Another point of comparison is the rocking motion of the methylene groups. Although their original studies indicated otherwise,¹⁵ Meiboom and Snyder's nematic nmr studies^{12a} have shown that the methylene groups are tilted by 4° so that axial hydrogens on the same side of the ring move toward each other. Our results (and recent CNDO calculations^{16,16a}) predict this same type of

(15) S. Meiboom and L. C. Snyder, *J. Amer. Chem. Soc.*, **89**, 1038 (1967).

(16) L. Salem and J. S. Wright, *Chem. Commun.*, 1370 (1969).

(16a) NOTE ADDED IN PROOF. J. S. Wright and L. Salem, *J. Amer.*

rocking motion showing a tilt of 7°. Thus it would appear that relieving the nonbonded interactions between neighboring methylene groups (staggering them) is more important than the interaction between the axial C-H bonds across the ring. (A tilt in the opposite direction would relieve this interaction.)

Conclusion

From these calculations, it can be concluded that the FSGO model can be used to obtain gross geometrical features and rotational barriers of hydrocarbons by transferring, without modification, data obtained from smaller systems. Furthermore, the model can be used to accurately give detailed geometries of intermediate-sized hydrocarbons. The simple FSGO method appears to be the most practical *ab initio* model, at this time, capable of doing extensive geometrical minimizations.

The one-electron energy levels given by FSGO for several hydrocarbon systems have been reported by Jungen.¹⁷ Work is in progress to analyze the one-electron levels for all of the hydrocarbons which have been studied by this group and will be reported in a subsequent paper. Such one-electron levels are readily obtained in the FSGO method since no SCF iterations are required.

Computational Details

Calculations were made using the CDC 6400 computer at the Vogelback Computing Center of Northwestern University. The program used in these calculations is equivalent to one reported earlier¹⁸ except that the routine to calculate the integral related to the error function has been replaced by a routine from Christoffersen and coworkers.¹⁹ Also, many of the routines were translated into symbolic machine language for more efficient running time and storage allocations.

Acknowledgments. This research was supported by a grant from the National Science Foundation. Carlee Cobb assisted with the computer programming. Robert Rouse made preliminary calculations.

Chem. Soc., **94**, 322 (1972). These authors report a minimal STO calculation resulting in a dihedral angle of 15° and a rocking angle of 2.4°.

(17) M. Jungen, *Theor. Chim. Acta*, **22**, 255 (1971).

(18) A. A. Frost, R. A. Rouse, and L. Vescelius, *Int. J. Quantum Chem.*, **2**, 43 (1968).

(19) L. L. Shipman and R. E. Christoffersen, *Comput. Phys. Commun.*, **2**, 201 (1971).