REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE 1992 March	3. REPORT TYPE AND DATES COVERED Final, 91 May - 91 Aug

4. TITLE AND SUBTITLE Rotational Barriers in Model Compounds
of Poly (Vinyl Chloride): 2-Chlorobutane
and 1,3,5,7,9,11-Hexachlorododecane

5. FUNDING NUMBERS ✓
PR-1C162622A553L
C-DAAL03-86-D-0001
(Delivery Order
No. 2453)

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8. PERFORMING ORGANIZATION REPORT NUMBER
CRDEC-CR-144
(TCN 91123)

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
ARO, P.O. Box 12211, Research Triangle Park, NC 27709

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
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Task was performed under a Scientific Services Agreement issued by Battelle,
(Continued on page 2)

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Rotational barriers and conformational energy differences have been calculated for 2-chlorobutane and 1,3,5,7,9,11-hexachlorododecane. These are considered as model compounds for syndiotactic poly vinyl chloride. The theoretical methods include high level ab initio SCF and configuration interaction methods. Accessability to gauche and gauche states in the polymer are in light of these model compounds.

14. SUBJECT TERMS

ab initio	Chloride	Interaction
Vinyl	Configuration	polymer
SCF method	Rotational barriers	

15. NUMBER OF PAGES 18

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

11. SUPPLEMENTARY NOTES (Continued)

Research Triangle Park Office, 200 Park Drive, P.O. Box 12297, Research
Triangle Park, NC 27709

PREFACE

The work described in this report was authorized under Project No. 1C162622A553L, CB Defense Assessment Technology, and Contract No. DAAL03-86-D-0001, Delivery Order No. 2453. This work was started in May 1991 and completed in August 1991.

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Rotational Barriers in Model Compounds of Poly (Vinyl Chloride): 2–Chlorobutane and 1,3,5,7,9,11 – hexachlorododecane

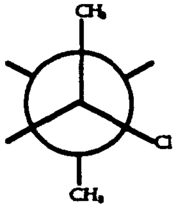
Introduction

Theoretical computational techniques are now being used in the study of the physical properties of polymers such as deformation, flexibility and internal rotational barriers.[1–4] There are two tendencies in handling the computations. Non quantum mechanical force field methods such as molecular mechanics[5] are used in handling computations for oligomers and even polymers of short length. Despite their success, these remain to be empirical techniques which must be modeled after potentials which are derived either experimentally or theoretically form small molecules. The next approach involves quantum mechanical techniques which range form the semi–empirical[6,7,8] to the *ab initio* molecular orbital techniques[9,10] of single or even multi determinant quality. These latter techniques require considerable amount of computer time to accurately calculate the rotation barriers of even small molecules such as butane.[11,12,13] Semi–empirical techniques require much less time, but the calculated barriers for model compounds are about one half to that of the experiment and this fraction varies according to the parameter set used.[14,15,16]

The object of this study is to calculate the barriers toward carbon internal rotation in poly (vinyl chloride) using two model compounds. In the first compound, 2–chlorobutane, basis sets and electron correlation effects are studied to the fullest extent of the theoretical methods available. The second model compound, 1,3,5,7,9,11–hexachlorododecane, is studied with a single determinant, SCF method, using two intermediate basis sets. The rotational barriers using these basis sets can be compared with those results obtained for the smaller model compound and extrapolations can be made to the more extensive techniques. Other authors11,13 have used n–butane to study the effects of basis set, electron correlation and calculated thermodynamic properties on the rotational barriers. The results using these advanced techniques gave calculated anti–syn barrier to be 1 to 2 kcal/mol higher than the experimental value of 4.54 kcal/mol.[17] It was found that the effects of basis sets on the barriers was asymptotic in the single determinant SCF case, and the effect of correlation lowered the barrier by about one half kcal/mol no matter which correlation method or basis set was used. The combination of a very large basis set, namely triple zeta plus polarization functions and low level electron correlation method namely MP2[18,19] brought the calculated barrier to 5.37 kcal/mol form the SCF value of 6.03 kcal/mol.[13] Further calculated thermodynamic properties lowered the barrier by another half kcal/mol.

There are three conformational minima proposed for 2–chlorobutane. In comparison with n–butane, there is an anti conformation where the terminal methyl groups are 180° dihedral angle and two gauche conformations, one being the g conformation where the chloro group is anti to the 4–CH_3 group and the other g' where it is gauche. Between these minima are three transition states which we have designated as the syn, where the CH_3 groups are eclipsed, the ag where each CH_3 and

Cl group is eclipsed by a H atom; and the ag' where the 4–CH_3 group eclipses the chlorine.



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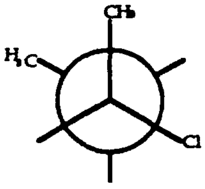

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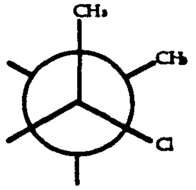

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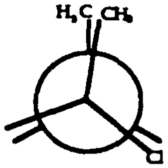

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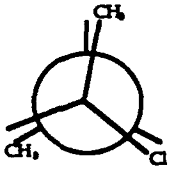

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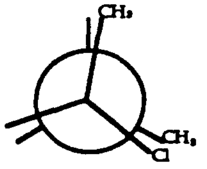
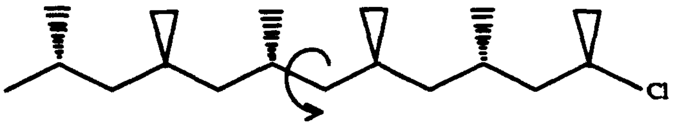
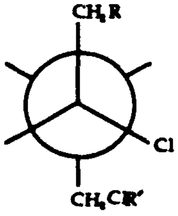


ag'

Similar designation can be derived for the 1,3,5,7,9,11–hexachlorododecane, which is itself a hexamer of vinyl chloride. The bond rotation studied here is about the C_6–C_7 bond.





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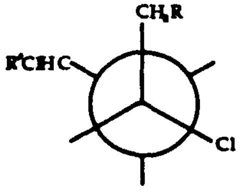

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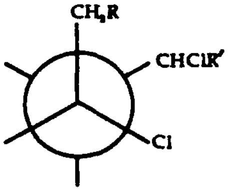

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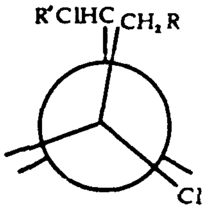

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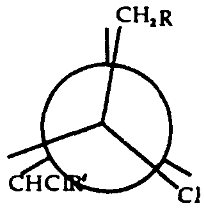

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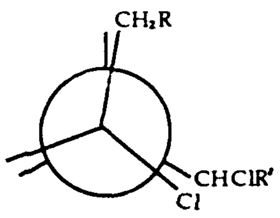

ag′

$R = CHCl\text{–}CH_2\text{–}CHCl\text{–}CH_3$

$R' = CH_2\text{–}CHCl\text{–}CH_2\text{–}CH_2Cl$

Theoretical Methods

All calculations were carried out using the Gaussian 90 series of computer programs.[20] The basis sets used are the 3–21 G*[21] where a d polarization function is included only on the Cl atoms of these molecules. The next basis set used on both molecules is the 6–31G*.[21] A still extensive basis set was used on 2–chlorobutane. The effect of correlation on 2–chlorobutane was studied with a configuration interaction method including all single and double excitations over the 6–31G* SCF molecular orbitals. The optimization procedure assumed no parametric constraints. The proper number of negative eigien values were found for the 2–chlorobutane conformers using second derivative methods on the SCF results. Computations including electron correlations included optimization methods using analytical first derivatives. In the case of the hexamer, analytical first derivatives were also used in geometry optimization and no geometric constraints were applied. The 1–chloro group was started in the trans position; there are, of course, two other conformers, these being the gauche and gauche′. However, all calculations for the hexamer assumed the starting trans 1–chloro position.

Results and Discussion

The effect of basis sets and electron correlation on the geometrical parameters of 2–chlorobutane can be gathered from Table 1. The greatest change in geometry for any conformation arises, going from the small 3–21G* basis set to the moderate size 6–31G*. Only minor differences are encountered in going from 6–31G* to either the triple zeta plus polarization basis set or to an optimized geometry using configuration interactions.

Within any given basis set, or electron correlation method, certain trends can be found for variation of geometrical parameters with rotation about the central carbon bond giving the three equilibrium and the three transition state conformers. For example, the angle θ (C_1, C_2, C_3) is found to be greatest when rotations of the middle dihedral angle brings the CH_3 group into close contact in or near the syn conformer. For studying the differences in effect, of a chloro substituent when compared to a methyl substituent, one parameter which may be observed from table 1 is the θ (C_2, C_3, C_4). As the methyl groups are rotated about the central C_2–C_3 bond, this bond angle would be expected to increase as the terminal CH_3 group rotates past either the beginning methyl group or the chloro group. In the case of 2–chlorobutane, this bond angle is found to be a minimum when it is in the ag transition state; then slightly higher in the anti or gauche conformers (the latter being where the CH_3 and chloro groups are anti). Two maxima are found, one in the syn position and a slightly higher in the ag' transition state. In all cases, it was found that the $C_2C_3C_4$ bond angle was higher when the terminal CH_3 group was eclipsed with the chloro group than with the starting CH_3 group (i.e. methyl group on C_1). In the hexamer case, the same results are seen except that instead of a CH_3 group, one is dealing with alkyl groups. Another indication of the eclipsing of a methyl group with another methyl or a chloro group may be seen from the central C_2–C_3 bond distance. Here again, there are two maxima corresponding to the syn and ag' transition states. In this case, however, there is very little difference in bond lengths between these two conformers when the larger basis set results are considered.

In differing from the previous studies on butane where symmetry constrained the anti and syn conformers to be 180° and 0° exactly, the presence of a Cl group in the 2–chlorobutane breaks the symmetry. Furthermore, interaction between the terminal methyl group and the chloro substituent are to be considered. In the anti position, no matter which basis set, the dihedral angle is found to be at least 6° towards the chloro group. In the syn position, this effect is smaller, on the order of 1°.

Table 2 summarizes the calculated energy differences relative to the anti position for the five other conformations for 2–chlorobutane, hexamer and n–butane. Figure #1 illustrates the same relative energy differences as found in Table 2.

Summary

In the model compound 2–chlorobutane, the equilibrium points a and g are found to be very close energetically (within 0.5 kcal/mol). The barrier between a→g is ≈ 4 kcal/mol. The g′ state is only slightly higher, the barrier between a→g′ is ≈ 6 kcal/mol. The result in the hexamer differed in that the g position is about 3 kcal/mol different from anti, but the barrier between a and g is still ≈ 4 kcal/mol. However, the g′ energy difference is about 5 kcal/mol and the barrier between a and g′ is about 9 kcal/mol. These results have implications in the polymer conformations. The g conformation is thermodynamically little populated and the g′ is certainly populated much less than 1% and most likely inaccessible, kinetically.

Figure #1: Relative Energy differences for all conformers in 2–chlorobutane and hexamer. (Energy in kcal/mol.)

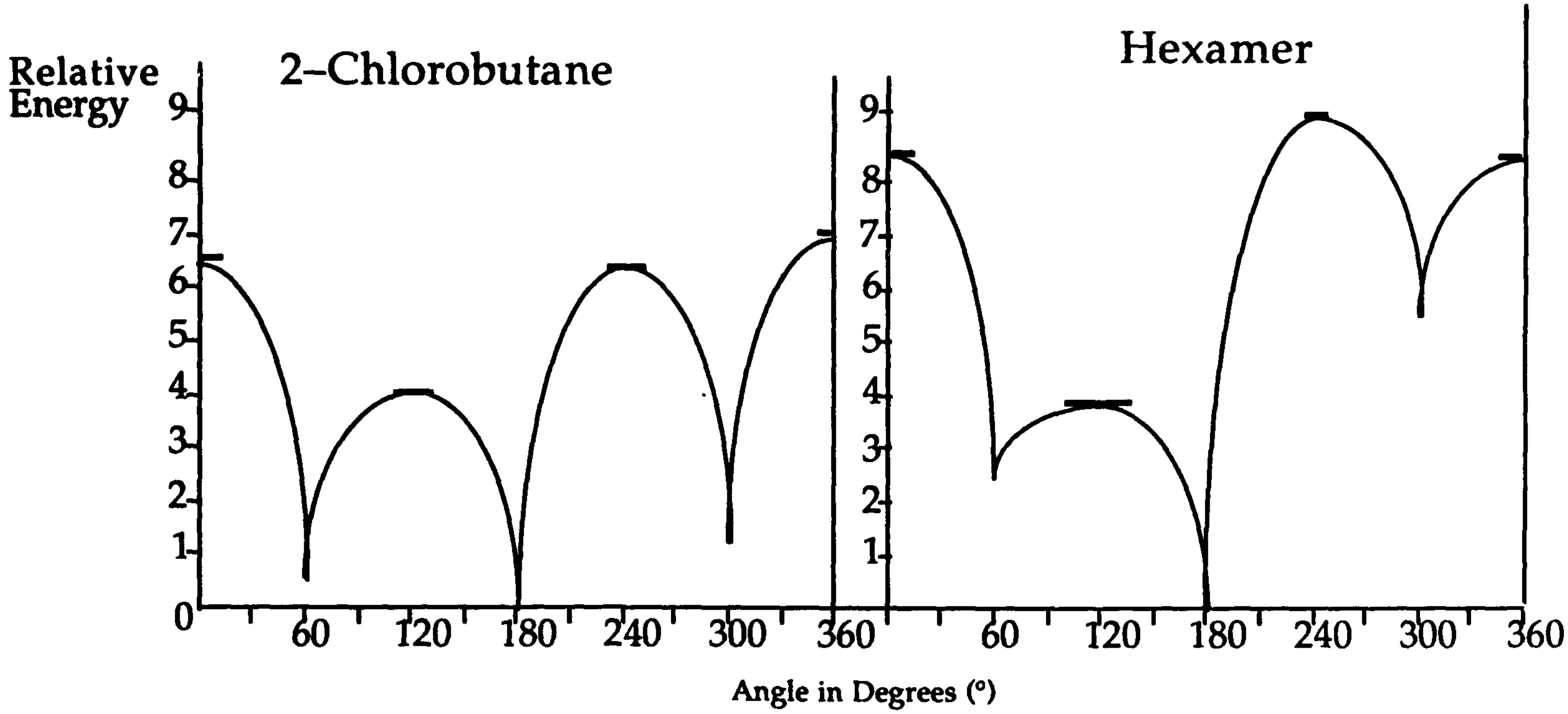

Table 1. Optimized geometrical parameters for the three minima and the three maxima conformations of 2–chlorobutane

Method	Conformation	$r(C_1C_2)$	$r(C_2C_3)$	$r(C_3C_4)$	$r(C_2Cl)$	$\theta(C_1C_2C_3)$	$\theta(C_2\ C3C_4)$	$d(C_1C_2C_3C_4)$
SCF/3–21G*	S(Transition state)	1.523	1.552	1.532	1.822	116.6	116.5	–5.0
SCF/6–31G*		1.523	1.552	1.531	1.822	116.9	116.6	1.3
CISD/6–31G*		1.518	1.546	1.525	1.808	116.4	116.5	0.9
SCF/3–21G*	G(Equilibrium)	1.529	1.533	1.542	1.834	113.8	112.0	67.4
SCF/6–31G*		1.521	1.527	1.531	1.818	114.7	113.1	65.2
CISD/6–31G*		1.516	1.521	1.525	1.803	114.3	113.0	64.2
SCF/3–21G*	A(Equilibrium)	1.530	1.532	1.538	1.833	112.4	113.6	185.9
SCF/6–31G*		1.521	1.526	1.527	1.818	112.9	114.8	186.6
CISD/6–31G*		1.516	1.529	1.521	1.803	112.8	114.6	186.0
SCF/3–21G*	ag(Transition state)	1.530	1.550	1.591	1.834	113.1	111.8	120.4
SCF/6–31G*		1.521	1.543	1.529	1.819	113.5	112.5	119.0
CISD/6–31G*		1.516	1.536	1.523	1.805	113.2	112.3	119.0
SCF/3–21G*	agg(Transition state)	1.531	1.560	1.540	1.833	112.1	117.1	240.1
SCF/6–31G*		1.522	1.551	1.529	1.818	112.7	118.4	239.9
CISD/6–31G*		1.517	1.546	1.523	1.805	112.3	117.9	240.0
SCF/3–21G*	g1(Equilibrium)	1.529	1.536	1.539	1.834	114.3	114.71	–57.5
SCF/6–31G*		1.521	1.529	1.528	1.819	115.0	116.2	–57.2
CISD/6–31G*		1.516	1.523	1.522	1.804	114.5	115.7	–57.4

Table 2. Calculated energy difference relative to the anti (a) position for the conformations in n–Butane, 2–Chlorobutane and hexamer.

Method	$\Delta E_{g,a}$	$\Delta E_{g',a}$	$E^{\#}_{syn}$	$E^{\#}_{ag}$	$E^{\#}_{ag'}$
Butane					
SCF/6–31G*11	0.95	0.95	6.19	3.63	3.63
SCF/DZ (dp)13	–	–	6.19	–	–
CISD/DZ (dp)13	–	–	5.89	–	–
2–Chlorobutane					
SCF/3–21G*	0.56	1.39	6.52	4.01	6.35
SCF/6–31G*	0.46	0.87	6.50	3.85	6.28
CISD/6–31G*	0.47	0.78	6.58	4.08	6.24
Hexamer					
SCF/3–21	2.77	5.21	8.16	3.80	9.05

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