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SHORT COMMUNICATIONS

COMPARISON OF MNDO, AM1 AND PM3 ROTATIONAL BARRIERS IN BRANCHED ALKANES

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The MNDO, AM1 and PM3 semi-empirical methods were used to calculate the equilibrium points and transition-state structures of the rotational barriers of ethane and all methyl-substituted propanes and butanes. Force constant methods were used to ensure proper geometries. In general, AM1 barriers tend to be lower than MNDO calculated ones, which are themselves generally lower than experiment. The PM3 values are closest to experiment, ranging from slightly above to slightly below the experimental values. The complexity of various possible rotational minima makes the development of empirical rules to predict barrier heights difficult.

The physical properties of polymers such as deformation, flexibility and internal rotational barriers are becoming subjects of theoretical computational techniques. Empirical force field methods such as molecular mechanics can handle computations of oligomers and even polymers of considerable length. These remain empirical techniques modeled after the potentials in smaller molecules. Quantum mechanical techniques range from the semi-empirical to the so called *ab initio* molecular orbital techniques. The latter can require enormous amounts of computer time to calculate accurately the rotational barriers of even small molecules such as butane.[1,2] Other physical properties such as adsorption or diffusion of atoms or molecules through polymers will need to be treated on a quantum mechanical level, or at the least a combination of quantum mechanical level at the site of interaction and a less rigorous level for the bulk. At present, semi-empirical quantum mechanical methods seem to be most tractable for the studies of rotation barriers in oligomers. The original papers of Dewar and co-workers[3–5] introducing the MNDO and AM1 methods describe a limited number of rotational barriers. Of the compounds considered in this study, only butane (for AM1 only)[4] has been previously reported. Although the limitations of both the AM1 and MNDO methods for determining rotational barriers are outlined in these papers, there has been no systematic reporting of rotational barriers for simple alkanes for either method. Because of the controversy surrounding PM3 and AM1, we have also included a consideration of PM3. Stewart[6] reported several literature rotational barrier values, and these are reported here for completeness.

A series of seven alkanes were studied in order to locate the equilibrium and transition-state structures as calculated by MNDO and AM1 methods found in the MOPAC version 5·0 series of programs.[4–7] The procedure used here for computing conformational barriers followed two steps. First, torsional angles to be studied were kept at constant values between 0 and 360° in 10° and all other lengths and angles were optimized. Subsequently, transitions states and equilibrium structures indicated by maxima and minima in the first step were obtained by a full, precise optimization involving

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all geometric parameters. The proper number of negative eigenvalues were verified in each case from the force constant matrices.

The molecules considered here are ethane (ET), 2-methylpropane (MP), dimethylpropane (DMP), butane (BU), methylbutane (MB) 2,2-dimethylbutane (22DMB), 2,3-dimethylbutane (23DMB), trimethylbutane (TRB) and tetramethylbutane (TTB). These were chosen for their representative *gauche* and eclipsing interactions between hydrogen–hydrogen, hydrogen–methyl and methyl–methyl groups.

There are two unique equilibria positions in BU, the *anti* and the *gauche* staggered positions, in addition to two transition states, that between the *anti* and *gauche* confirmers, which is designated by its C_2 symmetry, and the so-called *syn* structure, where the carbon atoms are eclipsed.

In 23DMB there are also two unique equilibrium structures designated by C_{2h} and C_2. The MNDO method calculates the C_{2h} structure to be 1·30 kcal mol^{-1} (1 kcal = 4·184 kJ) higher in energy than the C_2 structure, which is in conflict with the experimental value of 0·05 kcal mol^{-1} favouring the C_{2h} structure.[10] The AM1 calculations give the C_{2h} structure to be lower by 0·06 kcal mol^{-1}, which is close to the 6–31G* *ab initio* results of Wiberg and Murko.[2] Similarly, the PM3 method gives a value of 0·53 kcal mol^{-1}. This is the only case where MNDO did not give the expected global minimum for branched alkanes. This is consistent with the notion that AM1 parameterization gives a better accounting of the equilibrium structure heats of formation. Figure 1 shows the relative positions of the methyl groups in the C_{2h} and C_2 minima.

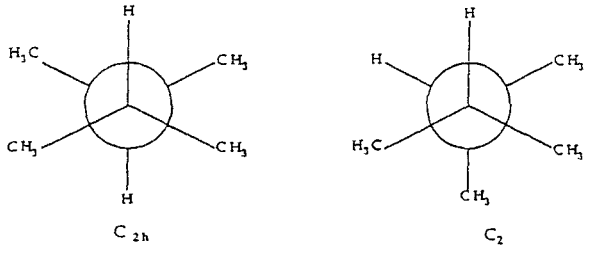

Figure 1. Newman projection for minima of 2,3-dimethylbutane

There are also two unique transition-state structures in 23DMB; the C_2' structure lies between the C_{2h} and the C_2 equilibrium conformers and the C_{2v} structure lies between the two C_2 conformers. Figure 2 shows these two transition states.

In MB there are also two equilibrium conformers, designated as C_1 and C_s and two unique transition states designated as C_s' and C_1'. The C_s' structure represents the barrier between the two C_1 equilibrium structures, and the C_1' transition state represents a barrier between a C_1 conformer and the C_s conformer. All other molecules studied here have one unique staggered equilibrium structure and one unique eclipsed transition state structure. In Table 1 the barriers between equilibrium structures for all molecules studies are reported for the MNDO, AM1 and PM3 theoretical methods and for experiment. Also included are the types and numbers of interactions between the groups on two central carbon atoms involved in the rotation; these have been identified as H–H, H–Me and Me–Me.

In general, the AM1 barriers tend to be lower than the MNDO value and further away from experiment. Increasing substitution on propane and butane gives higher barriers, as expected. The only cases observed where the AM1 barriers are higher than the MNDO involve barriers between *ganche* and *anti*-like conformers in BU, MB and 23DMB. In every case examined here, the PM3 method produces rotational barriers higher than the MNDO method. Except for 23DMB, where PM3 drastically overemphasizes the barrier, this method yields better agreement with experiment than either MNDO or AM1. On further examination of Table 1 for trends in barrier heights that could be applicable for the extension to polymer systems, there appears to be an additivity factor which could be derived. In the case of branched alkanes, the presence of multiple maxima and minima makes the task of finding a simple empirical relationship impossible. Deformation energies in polymers need to be fitted to model alkanes which are very nearly equal in structure.

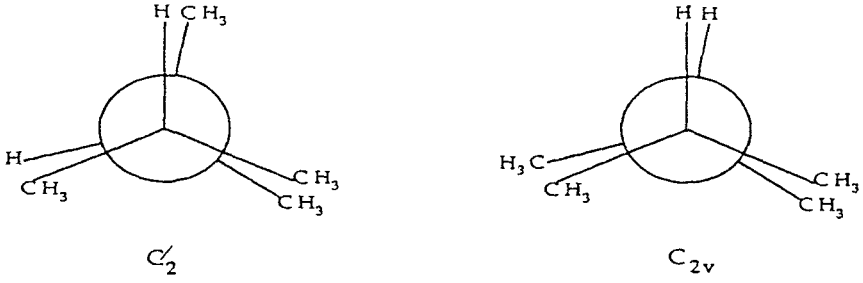

Figure 2. Newman projection for transition states of 2,3-dimethylbutane

Table 1. Number of *gauche* (eclipsing) interactions and torsional barriers (kcal mol^{-1}) between conformers

Molecule	Equilibrium conformation	Transition-state structure	Interactions			Barriers			
			H–H	H–Me	Me–Me	MNDO	AM1	PM3	Experimental
ET	*S*	*E*	6(3)	0(0)	0(0)	1·01	1·25	1·46	3·0[8]
MP	*S*	*E*	2(1)	4(2)	0(0)	1·56	1·42	1·66	3·9[9]
DMP	*E*	*E*	0(0)	6(3)	0(0)	2·20	1·60	1·74	4·7[9]
BU	*a*	C_2	2(1)	4(2)	0(0)	1·42	1·53	1·71	
	g	C_{2v}	3(2)	2(0)	1(1)	2·65	2·55	3·57	
	a	C_{2v}	2(2)	4(0)	0(1)	3·23	3·28	4·14	4·5[10]
MB	C_1	C_s'	1(0)	4(3)	1(0)	0·72	0·95	1·20	
	C_1	C_1'	1(1)	4(1)	1(1)	3·01	2·85	3·92	
	C_s	C_1'	2(1)	2(1)	2(1)	2·64	1·99	3·11	
22DMB	*S*	*E*	0(0)	4(2)	2(1)	2·95	2·23	3·34	4·9[12]
23DMB	C_{2h}	C_2'	0(0)	4(2)	2(1)	0·90	1·76	3·37	
	C_2	C_{2v}	1(1)	2(0)	3(2)	5·90	4·10	5·08	
	C_{2h}	C_{2v}	0(0)	4(2)	2(1)	4·60	4·16	5·61	4·3[11]
	C_2	C_2'	1(0)	2(2)	3(1)	2·20	1·70	2·85	
TRB	*S*	*E*	0(0)	2(1)	4(2)	4·14	3·08	5·32	
TTB	*S*	*E*	0(0)	0(0)	6(3)	6·75	4·14	7·39	8·8[12]

The AM1 and PM3 parameterization were designed to give better heats of formation and give a better accounting for hydrogen bonding, which is a major weakness in the MNDO method.[13] Further, the AM1 parameterization was found to give a better agreement with *ab inito* calculations in predicting cyclization reaction transition states where long-range interactions between carbon atoms are important. Dewar *et al.*'s explanation for this was the tendency to overestimate repulsive interactions between atoms of a distance 1·5–2 times the length of a covalent bond in the MNDO method.[14] If the AM1 parameterization further reduces these long-range interactions, this might well be the case of the lower barrier heights in most cases.

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