

Energetics of methyl branches in hydrocarbon crystals

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Semi-empirical energy calculations are reported for methyl branched hydrocarbon molecules in orthorhombic and monoclinic crystalline arrays of linear molecules. The 19 molecules in the array are flexible and twenty methylene units long. Two modes of packing the defect molecule in the crystals are found and for each the mechanical relaxation criterion of there being two or more sites available to the molecule is met. However, there is no significant relaxation strength because the differences in site energies are too large. This result holds for all cases because the unfavourable orientation of the molecular stem in one of the sites makes the energy much greater than in the other for which the stem has a favourable orientation. For the case with the lowest defect energy, the unit cell dimensions are comparable to those found experimentally for the same methyl group concentration. Drawings showing the molecular distortion are presented.

INTRODUCTION

The results of semi-empirical energy calculations on the effects of methyl branched hydrocarbon molecules in a crystalline array of linear molecules have been reported previously^{1,2}. They were obtained using a model consisting of nineteen conformationally rigid chain segments with lengths of eight methylene groups. The results indicated that such methyl branch defects could be incorporated in various modes in the crystalline array at a reasonable energetic cost. Further, in one mode of inclusion, multiple orientational sites of similar energies were available to the branched molecule. Calculations of the effects of a stress applied to this mode indicated that a mechanical relaxation might be possible through a redistribution of molecules among these orientational sites. When the calculated relaxation strength, time and activation enthalpy were corrected to the corresponding values for twenty methylene chains, they were similar to those observed experimentally for n-icosane containing a small amount of 10-methylnonadecane³.

The present paper reports the results of improved calculations eliminating the previous limitations of short rigid molecules. Energies are presented for methyl branch defects in the several orientations available using flexible molecules of twenty methylene units each.

COMPUTATIONAL METHOD

The method used is a combination of the array energy minimization scheme used in the previous calculations^{1,2} and the molecular energy minimization technique employed in the computer program MOLBD3⁴, modified to utilize the non-bonded interactions used previously^{1,2} and to increase to C—C—C bond angle to 112 deg. The chain positions and orientations determined in the previous calculations were used for the initial crystal model. The molecules were extended to twenty methylene units in length

(by adding on the end atoms in their rigid chain geometry) and the minimum energy cell dimensions were determined for the nineteen chain array shown in basal projection in *Figure 1*. Next, the energy of the branched molecule was minimized by allowing full geometric freedom to each of its atoms using a further slight modification of MOLBD3. During this conformational/geometric minimization the branched molecule was surrounded by its six closest neighbouring chains, so that appropriate intermolecular non-bonded interactions had their due influence. Each neighbour was then allowed in turn to minimize its energy while surrounded by its own set of neighbours which were constrained to their most recently determined geometry (i.e., to their energy-minimized geometry if such had already been determined). After the six neighbours had been minimized, the branch molecule was once again allowed to adjust its atomic positions. Finally, the minimum energy cell dimensions were determined¹, while holding the molecules in their minimum energy conformations. To be certain that the

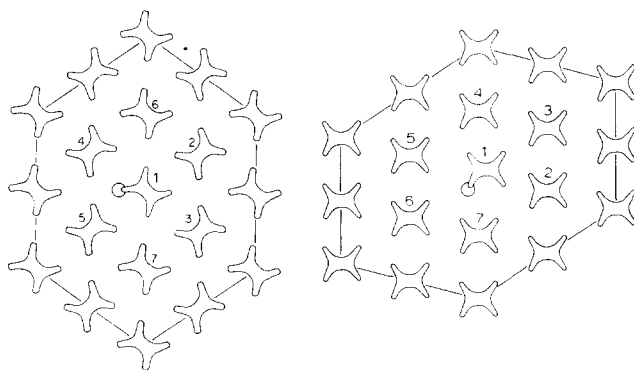


Figure 1 Schematic representation of the basal projection of the 19 molecule array. Case III-1 (see text) is illustrated for the orthorhombic array on the left and for the monoclinic array on the right

Table 1 Orthorhombic cell dimensions, defect energies and difference in site energies

Case	Cell dimension		Defect energy ^a	Difference in site energies ^a
	a (Å)	b (Å)		
I-1	7.23	4.94	0 ^b	23
I-2	7.22	4.98	23	
II-1	7.25	4.97	27	11
II-2	7.25	4.99	38	
III-1	7.27	4.95	23	31
III-2	7.25	5.01	54	

^a In kJ/mol of defects

^b As noted in the text, I-1 corresponds to the perfect orthorhombic crystal

system was at a minimum energy, this entire process was repeated. Changes during the last cycle were very slight.

This minimization scheme offered two benefits. First, it made the problem computationally reasonable. Otherwise, the computer time and storage required to allow full flexibility to all seven interior molecules simultaneously would have been prohibitive. Furthermore, the small changes upon recycling of the present calculations suggested that the coupling of intra- and intermolecular energies between neighbouring chains was less than might have been expected, and that simultaneous minimization was not essential. Second, the combination of the two computational techniques allowed the model to settle into a low energy state fairly rapidly. The program MOLBD3 did not allow for direct determination of the minimum energy cell dimensions of the model crystal—parameters that were especially crucial in determining the defect energy. While several cycles of the MOLBD3 technique would allow the requisite expansion of the crystalline array, one might expect the process to be somewhat longer since the expansion can only proceed by defect-caused perturbations propagating from the centre outward.

RESULTS AND DISCUSSION

Preliminary calculations for flexible linear molecules 8 and 20 carbon atoms long showed that there are substantial end effects for the shorter branched molecule. These would introduce errors to the results obtained by extrapolations to molecules of different lengths^{1,2}. All results reported here were calculated for a chain length of twenty carbon atoms.

Table 1 lists the cell dimensions, defect energies and differences in site energies for linear and branched chains containing twenty carbon atoms packed in an orthorhombic array. Defect energy is the extra energy required to pack a molecule with a central methyl branch into the crystal in place of a linear one. It does not include the extra intramolecular energy of about 8 kJ/mol associated with a branched molecule in comparison to a linear molecule when both are in their isolated state conformations. The latter is the inherent intramolecular cost of adding a branch to the molecule. The site terminology is that adapted previously^{1,2} for rigid molecules. Case I refers to the linear central chain, Case II to the branched molecule and Case III, to the branched molecule with the methyl branch substituted on the same carbon atom but on the opposite side of the carbon backbone plane. Arabic numeral I refers to the low energy site

for which the molecule stem is oriented approximately as it is in the perfect crystal of linear molecules and numeral 2 to another low energy site in which the chain is rotated from site 1 by about 90 deg. about its axis. As a result of the symmetry of the crystal there are pairs of equivalent sites related to these two by a rotation about the chain axis of $n \cdot 180$ deg. and a translation parallel to the axis by n carbon atoms (n is an integer). Of course, for flexible molecules, the orientation of the stem becomes somewhat ill defined near the branch while regaining its normal meaning at the ends of the molecule.

Case I-1 representing the perfect crystal, exhibits the lowest energy and is taken as the reference value. The cell dimensions for this case agree reasonably well with experimental results⁵ at 200K, a temperature representative of those for the data from which the potential energy parameters were derived. As estimated previously^{1,2}, III-1 exhibits the lowest defect energy because both the methyl branch and chain stem are in favourable orientations. Case III-2 exhibits the highest energy because both the branch and the stem are in an unfavourable orientation. The energies of II-1 and II-2 are more similar to one another and intermediate to those of III-1 and III-2 because, as noted^{1,2} when the stem is favourably oriented (Case II-1) the branch is not, and vice versa (Case II-2). While previous work using rigid, eight-methylene chains suggested the possibility of a mechanical relaxation process associated with methyl branches in a crystalline environment, the present results for the longer flexible chains indicate that in all three cases the difference in site energies is too large to permit a significant mechanical relaxation strength below the melting temperature. As noted, this difference is smallest for Case II. However, the effects of the adverse stem orientation in II-2 is greater than estimated previously^{1,2}. Indeed, it is the energetic cost of this adverse orientation which makes the defect energy of site 2 too great in all three cases. The results given for Cases II and III in Table 1 can be converted for 10-methylnonadecane in n-eicosane by increasing the defect energies to allow for the vacancy caused by the shorter stem of the branched molecule. The energy is approximately 10 kJ/mol but varies slightly from case to case. This correction does not qualitatively change the conclusions above. (Note also that the model does not assure that the ends of the molecules are arranged in the fashion found experimentally in paraffin crystals.)

While the defect energies seem high and while the concentration of the various cases in a crystal might be determined more by the crystallization kinetics than by equilibrium considerations, it could be expected that the lowest energy III-1 would dominate. In that event, comparison of the III-1 cell dimensions with those of I-1 shows that a increases more than b , a result in agreement with experiment^{6,7}. Moreover, the calculated increments in a and b are close to the experimental ones for comparable methyl concentration. Figure 2 shows the branched molecule and the two adjacent linear ones in the 110 plane for III-1. In the branched molecule, the departures from a linear planar zig-zag conformation are not very large. Generally, there is some very slight opening of bond angles and conformational twisting in the vicinity of the branch. The distortions gradually disappear and become extremely small at the ends of the molecule. The distortions induced by the branch in neighbouring molecules were likewise slight with the maximum occurring in those molecules toward which the branch protrudes. These effects show in the energies given in Table 2 for the molecules involved. Thus, the greatest increase in energy

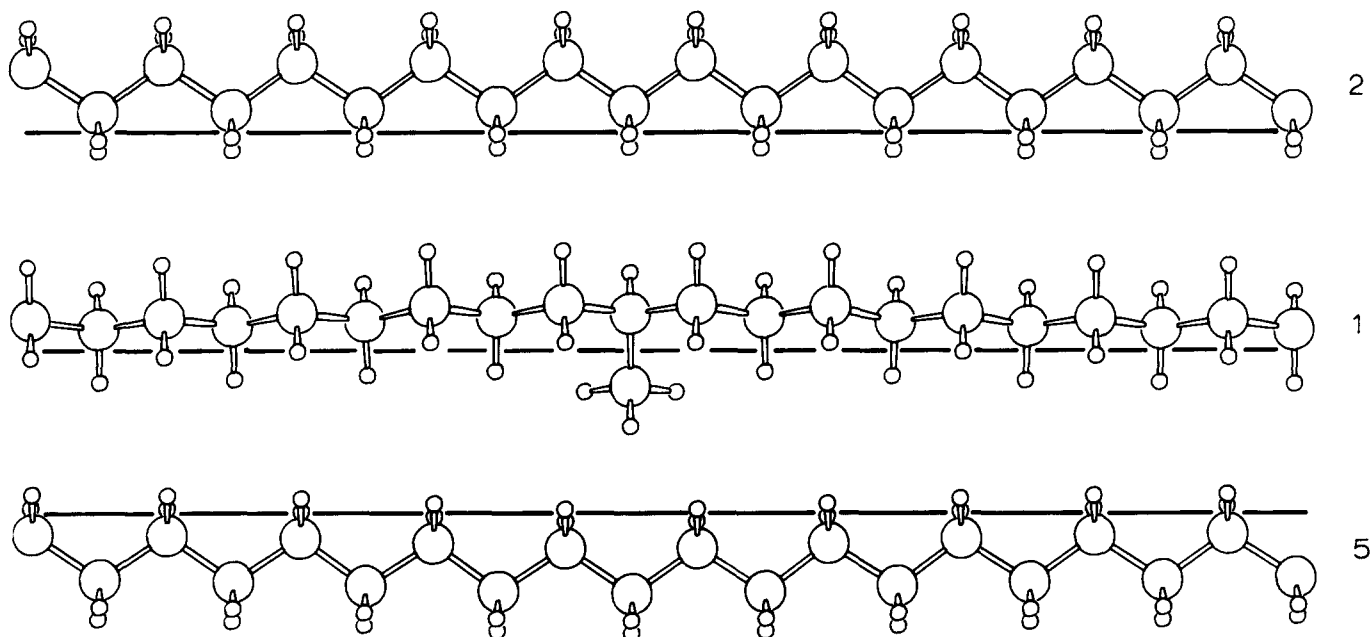


Figure 2 The branched molecule and the two adjacent linear ones in the 110 plane for orthorhombic Case III-1. The numbers identify the molecules in terms of Figure 1 and the straight lines are used to guide the eye

Table 2 Individual chain energies for Case III-1

	Chain	Approximate energy ^a (kJ/mol)	
		Intramolecular	Intermolecular ^b
Orthorhombic	1	9	13
	4	1	7
	5	1	13
Monoclinic	1	9	15
	5	1	5
	6	1	4
	7	2	12

^a Relative to the corresponding chain in a perfect crystal

^b Calculated for interactions between the indicated chain and its six immediate neighbours

over that for the corresponding molecule in the perfect crystal occurs in the branched molecule¹. The increase was almost negligible for all other molecules except 4 and 5 which are the ones toward which the branch protrudes. (Note that the energy of interaction between a given pair of molecules is counted twice in this manner of presentation).

Table 3 lists the cell parameters, defect energies, and differences in site energies for packing in a monoclinic array. Again Case I-1 represents the perfect crystal and exhibits cell parameters which agree reasonably well with experimental data for the monoclinic phase of polyethylene⁸. If the experimentally determined mode of molecular staggering along the *c* axis is assumed, the parameters can be converted to others which compare favourably with those observed for triclinic n-eicosane⁹. For the same reasons discussed above, Cases III-1 and III-2 exhibit the largest differences in site energies and II-1 and II-2 the smallest. Again, however, the energetic cost of the unfavourable stem orientation for site 2 makes the site energy differences too large to permit a significant mechanical relaxation in any of the cases. Figure 3 shows the 100 plane for III-1. The

Table 3 Monoclinic cell parameters, defect energies and difference in site energies

Case	Cell parameters			Defect energy ^a	Difference in site energies ^a
	<i>a</i> (Å)	<i>b</i> (Å)	γ (deg)		
I-1	4.52	8.14	104.0	0 ^b	28
I-2	4.51	8.24	104.1	28	
II-2	4.55	8.18	104.0	32	14
II-2	4.53	8.26	104.1	46	
III-1	4.54	8.18	104.0	25	26
III-2	4.53	8.26	104.1	51	

^a In kJ/mol of defects

^b As noted in the text, I-1 corresponds to the perfect monoclinic crystal

distortions are qualitatively similar to those for orthorhombic packing. Energies given in the lower half of Table 2 show the increases for the branched molecule and those toward which the branch protrudes. Again the energy increases for the other molecules are much smaller.

CONCLUSIONS

Although the defect energies seem high, the results indicate for both the orthorhombic and the monoclinic modes of packing, methyl branches might be incorporated to some extent as defects during the kinetic crystallization process. The mechanical relaxation criterion of there being two or more sites available to the defect is met. Nevertheless, the relaxation will exhibit no significant strength because the differences in the site energies are too large. The cause of this is the same one that applies to the unbranched Case I; that is, the energy of the unfavourable stem orientation makes the energy of site 2 too large compared to site 1. Although this difference is reduced for shorter molecules;

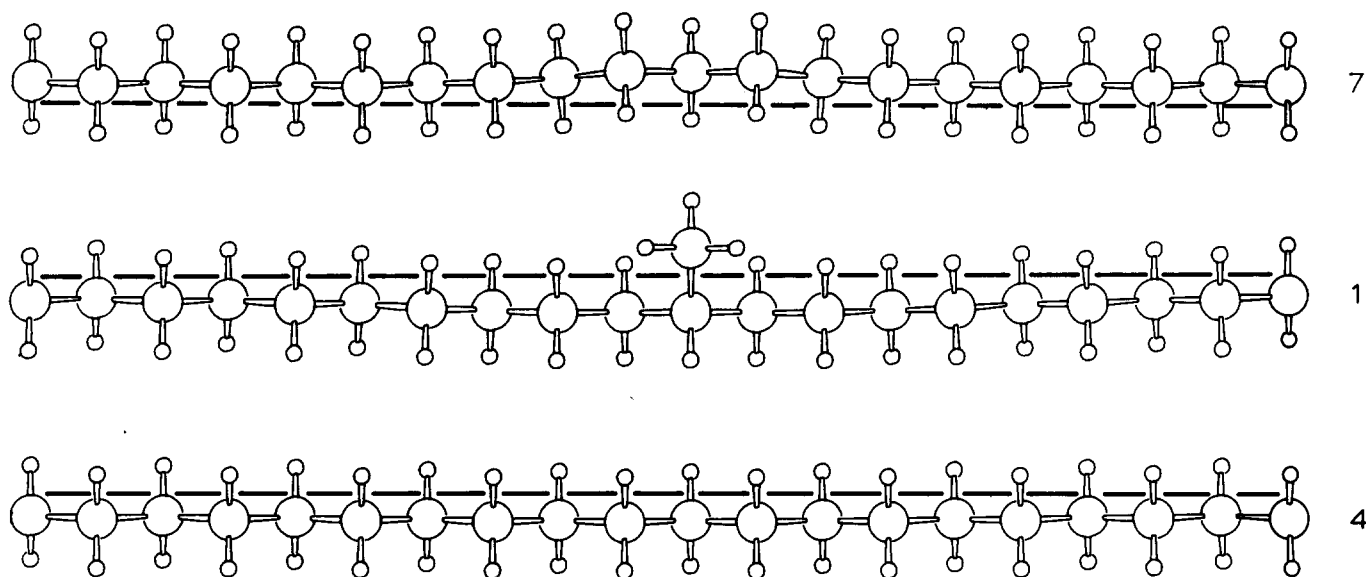


Figure 3 The branched molecule and the two adjacent linear ones in the 100 plane for monoclinic Case III-1. The numbers identify the molecules in terms of Figure 1 and the straight lines are used to guide the eye

by branch incorporation (Case II) and by a vacancy adjacent to the relaxing molecule¹⁰, none of these result in a significant relaxation strength. Further, this problem will be worsened by the long stem lengths encountered in polyethylene. These results suggest that isolated defects in a crystal of linear molecules might not lead to relaxations. In view of the experimental evidence indicating a correlation between methyl branch content and a mechanical relaxation process, it can therefore be reasonably speculated that some combination of disorders may give rise to such relaxations. There are, of course, many possible defects to be combined: branches, vacancies, folds and Reneker defects to name a few. Also, the branch defects might be located in more disordered regions of the crystal and there, with suitably altered site energies, play a role in the relaxation processes.

The atomic coordinates for the cases discussed here are available on magnetic tape.

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