Molecular mechanics calculations of deformation of paraffin chains

[a]T. BLEHA and [b]J. GAJDOŠ

[a]*Polymer Institute, Centre for Chemical Research,*
Slovak Academy of Sciences, CS-842 36 Bratislava

[b]*Institute of Chemistry, Centre for Chemical Research,*
Slovak Academy of Sciences, CS-842 38 Bratislava

Received 20 May 1988

Dedicated to Academician V Kellö, in honour of his 70th birthday

The variation of the potential energy and of the valence geometry accompanying the elongation and compression of paraffin molecules was calculated. The distribution of the stored elastic energy into the individual valence coordinates was determined for an all-*trans* chain and for the molecules involving the conformational defects. The computations provide the energy parameters for the conformational transitions induced by the extension of a chain with the *gauche* defect and by the compression of the all-*trans* molecule. The range of applicability of the Hooke's law for a single paraffin chain was established and Young's moduli determined at various strains were compared.

Рассчитаны изменения потенциальной энергии и валентной геометрии, сопровождающие удлинение и сжатие молекул парафинов. Распределение накопленной эластической энергии по отдельным валентным координатам было определено для молекул с исключительно *транс*-конфигурацией цепи и молекул с конформационными дефектами. Были рассчитаны энергетические параметры для конформационных переходов, вызванных удлинением цепи с *гош*-дефектом и сокращением цепи у молекул с исключительно *транс*-конфигурацией. Определен интервал применимости закона Гука для одиночной парафиновой цепи, а также сопоставлены значения модулей Янга для разных величин деформации.

The recent interest in the description of deformation of paraffinic molecules originates from two sources. Firstly, the paraffinic compounds are frequently used in the situations where fairly high deformational fields exist, for example as lubricants. Secondly, paraffin chains are also the suitable models for the study of chain deformation of the structurally related synthetic polymers.

At present two theoretical approaches are available for the energetical and structural characterization of the paraffin deformation, namely, the quantum-

-chemical [1, 2] or molecular-mechanical [3, 4] computations. For complex hydrocarbon molecules and macromolecules the molecular mechanics represents the sole sufficiently reliable and economically feasible method of theoretical chemistry. Molecular mechanics is inherently well suited for the description of molecular deformation because it expresses [5] the "strain" energy of a molecule relative to a "strainless" reference state even in the absence of external force. We have used this method in our previous papers [6, 7] dealing with the mechanism of deformation of macromolecules in the solid state and in solution from the standpoint of polymer physics. In this paper we concentrate on the changes of the valence geometry and on the distribution of stored elastic energy in simple models from the perspective of the structural chemistry. We have also determined the Young's elastic modulus of single chains and its dependence on the strain and the method of evaluation.

Method and model

In molecular mechanics the total potential energy of a molecule is expressed as a sum of several contributions [5]

$$V = V_r + V_\Theta + V_\varphi + V_{\mathrm{nb}} \qquad (1)$$

The energy of bond length deformation is expressed in harmonic approximation as $V_r = (1/2)k_r(r_{ij} - r_{ij}^\circ)^2$, where r_{ij} is the bond length between atoms i and j and r_{ij}° is an analogous reference (relaxed) bond length and k_r is the bond stretching force constant. The energy of deformation of bond angles is $V_\Theta = (1/2)k_\Theta(\Theta_{ijk} - \Theta_{ijk}^\circ)^2$ where the symbols have the meaning in analogy with the V_r term. The inherent torsional energy of ethane-like type in the form $V_\varphi = (1/2)V_0(1 + \cos 3\varphi_i)$ exhibits minima at 180° for the *trans* (t) state and in the vicinity of 60° and 300° for the *gauche* (g^+ and g^-) states. The term V_{nb} accounts for nonbonded interactions of atoms in the molecule. The Boyd's version of the method we used [5] was extensively applied in the calculation of conformational energetics and dynamics of hydrocarbon chain molecules [3—10] and is easily adaptable for calculation of molecular deformation by an external force.

The calculations were carried out for hexadecane in three forms (Fig. 1), for the extended zig-zag conformation, for a molecule with the *gauche* defect formed by the torsion by angle φ_3 and for a molecule which involves the two *gauche* φ_3 and φ_5 defects of opposite sign coupled in a kink $\ldots g^+ t g^-$ The single *gauche* defects are frequently assumed in the interpretation of liquid-state properties of chain molecules whereas the kink defect is believed to be a characteristics of the solid state. The external stretching force was simulated in all three cases by an additional deformational term in eqn (*1*) $V_{\mathrm{ex}} = (1/2)k_{\mathrm{ex}}$

$(h^s - h)^2$ where k_{ex} is the parameter, h^s is the preset distance of the terminal carbon atoms C-1 and C-16 in the molecule and h is an analogous distance after optimization by the Newton—Raphson method. The extra deformational term serves only as a constraint at optimization and does not contribute to the total potential energy V The chain elongation (strain) is $\varepsilon = (h - h_0)/h_0$ where h_0 is the distance of end-carbon atoms in an undeformed molecule. For the all-*trans* molecule, in addition to stretching, the compression by the forced reduction of the distance of end-atoms was investigated, too.

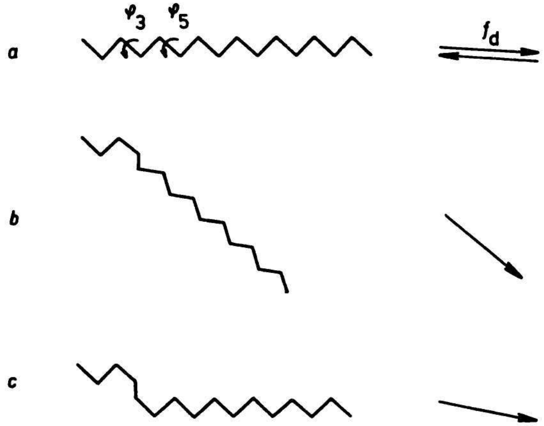

Fig. 1. Hexadecane chain (*a*) in the all-*trans* form, (*b*) with a *gauche* defect and (*c*) with a kink defect.

Results and discussion

One of the obvious questions to address in the study of chain deformation relates to the applicability of Hooke's law $f_d = EA_0\varepsilon$ to individual chains, where f_d is the deformation force, E is the Young's modulus in unilateral elongation and A_0 is the cross-sectional area of an undeformed chain. For the deformation energy this law gives

$$V = (1/2)Eh_0A_0\varepsilon^2 \qquad (2)$$

In accordance with this equation we plotted in Fig. 2 the potential energy as a function of square of strain for all four investigated models. It is seen that only the deformation of the zig-zag chain obeys the Hooke's law in the whole range of strain studied up to 5 %. The quadratic dependence of energy on strain for the all-*trans* chain could be expected since the bond angle and the bond length deformations are expressed in eqn (1) in the harmonic approximation. Torsional contribution is zero in this case and the term V_{nb}, decreasing with the increase of ε as the unfavourable repulsion of neighbour nonbonded atoms is reduced, is also apparently a quadratic function of ε.

Distribution of stored elastic energy

The detailed analysis of the changes of the valence geometry with deformation showed the linear increase of the CC bond lengths and CCC bond angles with ε and only a minor change in the CH bond lengths. The widening of the CCC bond angles by the chain stretching brings about a slight change of the orbital hybridization on carbon atoms, which results in the reduction of the CCH and HCH bond angles. In other words, the effective "thickness" of the zig-zag ribbon is reduced by its stretching. The both modes, the deformation of bond lengths and of bond angles contribute about equally to the total stored deformation energy V and to the overall chain strain ε.

In a chain involving one or more bonds in the *gauche* state a part of mechanical energy due to stretching is allocated into the torsional mode. The equilibrium *gauche* torsion angle $\varphi = 66°$ increases gradually with the increase of ε. The elongation of molecule by this mechanism is the prevailing contribution to the overall strain ε in molecules involving a torsional defect. Since the torsional contribution V_φ seems not to be a quadratic function of ε, it brings about the deviation of curves in Fig. 2 from straight lines at small strains (up to 1.5 %).

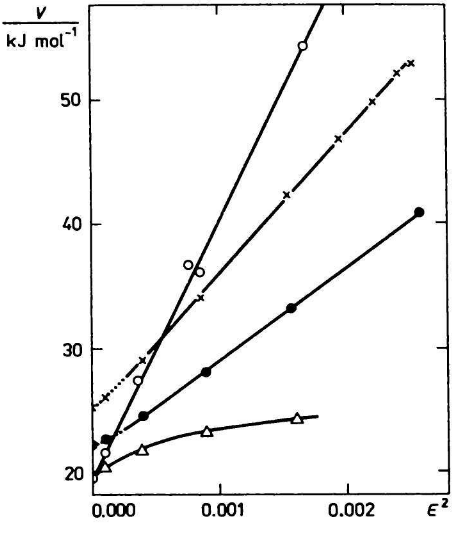

Fig. 2. Variation of the potential energy V with the square of strain for the structures: all-*trans* (○), with a *gauche* defect (●), with a kink defect (×), for the compression of all-*trans* unit (△).

The torsional mode is relatively soft and thus in a chain with the *gauche* defect its contribution to the stored energy (Fig. 3) is minor at small strain. In addition to the φ_3 angle, the deviations of φ_2 and φ_4 angles from the *trans* position, which are for example $-9°$ and $-6°$ at 2 % strain, also contribute to the term V_φ. In the previous paper [7] we documented the conspicuous changes which occur in the valence geometry of deformed chain in the vicinity of the *gauche* defect. The changes of bond angles, bond lengths, and torsion angles induced by stretching gradually dampened when moving away from the defect along the chain and the odd-even alternation was observed. The more facile deformability of the CCC bond angles in the vicinity of the torsional defect also contributes to the predominance of the V_Θ term over the V_r term in Fig. 3.

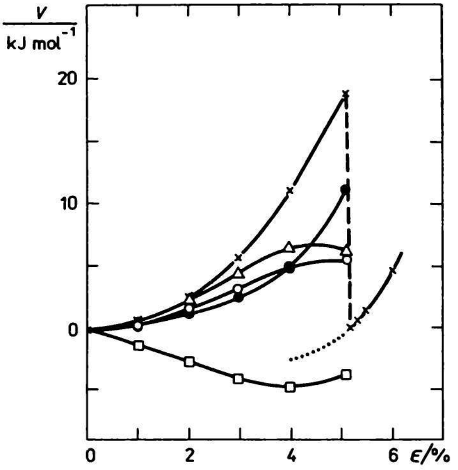

Fig. 3. Decomposition of the potential energy V according to eqn (*1*) for a chain with a *gauche* defect. Total energy V (×), the term V_φ (●), the term V_{nb} (□), the term V_r (○), and the term V_Θ (△). A hypothetical region of small deformation of the all-*trans* form is shown by dotted line.

The distribution of the stored elastic energy in a chain with the kink displays the similar features as shown already in Fig. 3 for the *gauche* chain. Obviously, the individual terms in eqn (*1*) can be further decomposed to find the contribution of each of r_i, Θ_i, and φ_i valence coordinates. For example, in an undeformed chain with the kink, the CC bonds located within the defect have about the same bond lengths, however, considerably higher than the remaining CC bond in the chain. The stretching of chain elongates mainly the C-3C-4 and C-5C-6 bonds subjected to torsion and to much less degree the C-4C-5 bond as seen for example from their lengths 156.0, 155.9, and 155.2 pm at 5 % strain, respectively. This result may suggest that the two "outer" bonds in the kink are the weakest link in a chain, liable to the scission at higher strains. Overall, the structural data for the deformation of chains with torsional defects show the partial delocalization of the defect and its coupling with the adjoining parts of the chain. Hence, the summation of properties of "defect" and "all-*trans*" parts in evaluation of the properties of the whole chain can serve just as a first approximation. It also turned out in accord with the previous reports [3, 4, 6, 7] that the presence of the "soft" torsional variable in a chain does not mean that the response of "hard" parameters r_i and Θ_i to the stress can be neglected.

Stress-induced conformational interconversions

By stretching the chain with the *gauche* defect to about 5 %, the torsion angle φ_3 increases abruptly and the molecule transforms to the all-*trans* conformation with the concomitant decrease of the potential energy. The maximum elastic energy stored in the *gauche* chain relative to the undeformed state is denoted as the activation energy ΔV^{+} and the strain at the transition as $\varepsilon_{\mathrm{tr}}$ (Table 1). At the transition point, the further conservation of the *gauche* chain destabilized by the energy stored in the deformed valence coordinates is unfavourable and the accumulated energy is released. This mechanism of dissipation of the stored elastic energy is believed to play an important role in the mechanical deformations of the oriented polymer fibres by drawing [11].

Table 1

The characteristics of the deformational behaviour of n-hexadecane. E and E_1 are the Young's moduli determined from Fig. 2 and from eqn (*3*) for 1 % strain, respectively, ΔV^{+} is the activation energy of strain-induced *gauche-trans* transition occurring at strain $\varepsilon_{\mathrm{tr}}$

Chain	E/GPa	E_1/GPa	ΔV^{+}/kJ mol^{-1}	$\varepsilon_{\mathrm{tr}}$/%
all-*trans*	200.4	192.2^{a}	—	—
all-*trans*^{b}	—	65.8	37.5^{c}	8.5
with *gauche* defect	70.1	55.5	18.7	5.1
with kink defect	110.5	84.2^{a}	28.2^{a}	5.1^{a}

a) Ref. [6]; *b*) compressional deformation; *c*) barrier of transition *trans-gauche*.

The similar stress-induced *gauche-trans* conformational transition was observed earlier [6] for a chain with the kink defect and data are listed in Table 1. It should be pointed out that the activation energy of transition depends on the chain length. The *gauche-trans* barrier in an isolated undeformed alkane chain is about 8.2 kJ mol^{-1} [10] and the remaining part in ΔV^{+} is mainly due to the energy stored in the valence parameters of the all-*trans* part and is proportional to the number of methylene groups. The subsequent stretching of the chain after the transition obeys again the Hookean energetics of the zig-zag unit. Fig. 3 shows that the length of the undeformed all-*trans* chain is actually reached at

4 % strain and the transition might occur already at this point. Seemingly the region between 4 and 5.1 % strain corresponds to the energy "oversaturation" of deformed molecule.

In addition to the stretching, we have also investigated the energetics of compression (bending) of an all-*trans* chain due to the gradual drawing the end-carbon atoms closer from their equilibrium distance in an undeformed chain. The resulting energetic curve is shown in Fig. 4 and for comparison it also includes the data for the uniaxial extension. A marked asymmetry of the deformational potential for the two modes of deformation is evident. The same data plotted in coordinates of Fig. 2 show that the compressional deformation of the all-*trans* unit cannot be described by the Hooke's law.

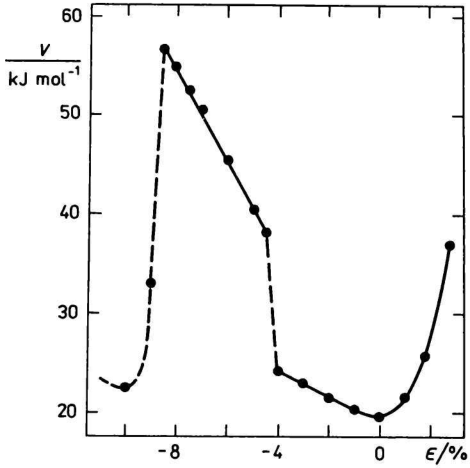

Fig. 4. The energy of deformation of the all-*trans* segment in extension and in compression.

The chain compression is accompanied by a gradual buckling of the originally rod-like molecule by two mechanisms. The chain distortion can be achieved by a small change of the all torsion angles from 180° and in our case this mechanism operates at small strains only. The other possibility to distort a chain relies on variations of the bond angles since the zig-zag unit is planar only when the two neighbour skeletal bond angles are identical. The molecule jumps to this mechanism of buckling at compressional strain of about 4 % when the torsional deformational energy reaches a high value. At small strain the torsional term V_φ is small, for example the deviation of one torsion angle from ideal 180° position to 170° requires about 0.59 kJ mol^{-1} assuming the value 8.8 kJ mol^{-1} for V_0 parameter in the V_φ term [5]. However, since there are 15 possible C—C torsional axes in hexadecane, when all torsion angles are distorted by 10°, the torsional term could be as much as 8.85 kJ mol^{-1}. For the ± 20° and ± 30° distortions, the torsional term could be 33.0 and 66.0 kJ mol^{-1}, respectively, and the deformation of bond angles may become more favourable.

The further increase of compression to about of 8.5 % strain brings about the drop of energy due to the formation of the *gauche* defect at the CC bond located fourth from the chain end. The stored elastic energy is thus released again by the conformation interconversion, this time however in the opposite, *trans-gauche* direction. The remaining torsion angles relax to 180° and also the bond angles and bond lengths return to the equilibrium values. The compressional transition can be compared with the inverse process due to stretching shown in Fig. 3 even if the latter data refer to the transition at the third bond from the chain end. The comparison of data (Table 1) shows the large difference in the barrier ΔV^{+} and strain ε_{tr} for these two processes indicating the existence of the large hysteresis in the path of mechanically-induced conformational transitions.

Chain modulus

For all the four cases of deformation studied we have also evaluated the Young's modulus. The exact value of modulus is however dependent to some degree on the procedure used in its determination. For example, the choice of cross-sectional area A_0 is unambiguous just for the all-*trans* form where the crystallographic value of about 0.18 nm^2 is used. Due to the absence of other data this value is used also for the chains containing conformational defects, where a slightly higher value should be anticipated.

The Young's modulus of the chain E can be evaluated using eqn (*2*), from the linear part of curves shown in Fig. 2 and the results are listed in Table 1. The modulus can be calculated also directly from the stretching force f_d proportional to the distance of the C-1 and C-16 atoms h or to the difference $h - h_0$. The force f_{ex}, corresponding to the extra (deformational) term we have used, is given as $f_{ex} = k_{ex}(h^s - h)$ and represents the retractive force which brings the preset end atom distance h^s to the value h reached after optimization. The corresponding expression for the modulus is

$$E = k_{ex}(h^s - h)/\varepsilon A_0 \qquad (3)$$

and its value for a given structure is the same regardless of using the stretching force f_d or retraction force f_{ex}.

The numerical procedure was used to calculate the moduli in nonlinear parts of curves shown in Fig. 2 and Table 1 lists the values E_1 corresponding to 1 % strain; their comparison with E values documents a fairly large variation of the chain modulus with the strain. The numerical procedure enables the determination of the chain modulus at any strain, it suffers, however, from the drawback of exaggerated sensitivity of results to the error in the computed difference $h^s - h$ which has to be known with the precision of pm [6]. In the language of energy hypersurfaces, the calculations of the modulus require the exact localization of minima and their curvature (second derivative of energy). This stipulation is hard to be satisfied in paraffin-like molecules where energy minima based on eqn (*1*) are unconspicuous and form the large shallow regions. Therefore, the graphical determination of the modulus should be preferred for the practical reasons even if that procedure does not provide the initial modulus ($\varepsilon \to 0$).

The calculated moduli correspond to the force acting in the direction of the line connecting the end carbon atoms of the chain. Even for the all-*trans* form this direction is not exactly colinear with the long axis of molecule. The deviation is more noticeable for chains with conformational defects. As concerns the modulus the main factor is the mutual orientation of the acting force and of the torsional axis, for example the bond C-3C-4 or C-5C-6 in Fig. 1. If the orientation of the force and the torsional axis is identical, a minimal value of modulus results. On the other hand, in situations where the force acts almost perpendicularly on the axis of torsion as in our case, the modulus attains a fairly large value.

The data from Table 1 suggest that an introduction of a kink or a *gauche* defect into the chain considerably diminishes its modulus, to about one half or one third of value of the zig-zag unit, respectively. Such a relative measure of the effect of defect on the modulus should be preferred over the absolute values. The absolute values of the calculated chain modulus for polymethylene chains differ considerably depending on the method used and are in the range of about 200 to 400 GPa [1—3]. Our calculations (Table 1) suggest that the Boyd parametrization of molecular mechanics gives the modulus in the lower limit of the above range. Recently, the modulus 267 GPa was reported [4] for the paraffinic zig-zag using the Boyd's method with an unspecified modification of the original parameters, presumably in the V_Θ term. Very few information is available on the modulus of chains with conformational defects. An unrealistically high modulus 245 GPa was calculated [12] for the three-bond kink defect assuming a strictly symmetrical (*i.e.* $\varphi_3 = -\varphi_5$) deformation of torsion angles. Using the Boyd's method *Reneker* and *Mazur* [13] calculated moduli in the range from 30 to 70 GPa for several six- or seven-bond crystallographic defects characterized by the full reentry of the chain ends into lattice points of the original all-*trans* chain.

Similarly to the modulus, the distribution of stored elastic energy into individual valence coordinates depends to some degree on the parameters of the method. However, the different parametrization of the molecular force-field yielded the similar distribution of the stored energy in the all-*trans* form [14] as our results. Nevertheless, the future developments of the reliable force-fields in molecular mechanics would certainly benefit by the inclusion of the stress-strain properties of single molecules into the process of selection and fitting of parameters.

References

1. Karpfen, A., *J. Chem. Phys. 75*, 238 (1981).
2. Suhai, S., *J. Chem. Phys. 84*, 5071 (1986).
3. Wool, R. P. and Boyd, R. H., *J. Appl. Phy. 51*, 5116 (1980).
4. Wool, R. P., Bretzlaff, R. S., Li, B. Y., Wang, C. H., and Boyd, R. H., *J. Polym. Sci., Polym. Phys. Ed. 24*, 1039 (1986).
5. Boyd, R. H., Breitling, S. M., and Mansfield, M., *AIChE J. 19*, 1016 (1973).
6. Gajdoš, J. and Bleha, T., *Mater. Chem. Phy.. 17*, 405 (1987).
7. Bleha, T. and Gajdoš, J., *Colloid Polym. Sci. 266*, 405 (1988).
8. Boyd, R. H. and Breitling, S. M., *Macromolecules 7*, 855 (1974).
9. Bleha, T., Gajdoš, J., and Šebek, J., *J. Mol. Struct. (Theochem) 139*, 35 (1986).
10. Gajdoš, J. and Bleha, T., *Collect. Czechoslov. Chem. Commun. 47*, 2323 (1982).
11. Kausch, H. H., *Polym. Eng. Sci. 19*, 140 (1979).
12. McCullough, R. L., Eisenstein, A. J., and Weikart, F., *J. Polym. Sci., Polym. Phys. Ed. 15*, 1837 (1977).
13. Reneker, D. H. and Mazur, J., *Polymer 25*, 1549 (1984).
14. Tashiro, K., Kobayashi, M., and Tadokoro, H., *Macromolecules 11*, 914 (1978).

Translated by T. Bleha