

$C_{22}H_{46}$: The smallest open 3_1 -knotted alkane by computer-aided design

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Received 1 August 2007; received in revised form 15 October 2007; accepted 15 October 2007

Available online 9 November 2007

Abstract

The program MolKnot [Chem. Phys. Lett. 433 (2007) 422–426] has been used in order to detect the smallest ever-reported alkane configured to an open-knotted shape with three crossings (3_1). High level ab initio calculations support our findings that 22 carbon atoms are enough to create a knotted polyethylene strand with open ends. These tight open molecular knots exhibit unusually distorted geometric characteristics as multiple extended CC bonds (maximum bond length ~ 1.70 Å) and several large CCC bond angles (maximum bond angle $\sim 145^\circ$). The energy decomposition shows that the strain mainly affects the valence angles of the entangled structure. We observed that this 22-knotted carbon atoms' region remained almost intact as a part of alkanes with longer chain lengths.

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Keywords: Molecular knots; Ab initio calculations; Alkanes; BDE; Distorted geometries; Elongated CC bonds and CCC valence angles

1. Introduction

Knots [1–3] (Fig. 1a) are present everywhere in daily life (ropes, ties, art, etc.); nevertheless, these intertwining designs are also found at the extreme opposite boundaries of the universe as gigantic galactic knots [4,5] or nanoscience devices such as knotted proteins [6,7], synthesized molecular knots [8–10], etc. Landmark works were the introduction of knot topology in the field of chemistry [11], the thermodynamics [12] of knot formation and the first reported synthesis [13] of a molecular knot. Delbrück [14] conjectured and later Sumners and Whittington [15] proved that the probability of knotting should depend on the length of the polymer; so as the length of a polymer chain tends to infinity the probability of knotting approaches 1. However, at the opposite limit, a very short molecule could not wrap around itself far enough to form a knot at all, so the probability of locating the entanglement is almost zero. The usual model of sticks and balls for representing a

molecule has been employed by mathematicians to construct ideal minimal knots. So Diao [16] has shown that the smallest knots on the cubic lattice (\mathbb{Z}^3) are all trefoils of length 24 (Fig. 1d) while Huh and Oh [17] found that the minimum number of sticks required to construct a polygonal representation of the knot 3_1 in \mathbb{Z}^3 is 12. Lately, Cantarella and Johnston [18] has shown that the smallest open 3_1 knot in Cartesian space \mathbb{R}^3 requires five sticks and six vertices (Fig. 1c). Recent advances [19] produced classifications of open polygonal knots (polygonal chains) made up of six straight line segments in Cartesian space \mathbb{R}^3 . Existing knot construction methods [20–23] are efficiently applicable to chains longer than 50 methylene units, while these same methods are incapable to operate with small molecular chains. Contrarily, small knots are amenable to studies with high-level ab initio calculations, while this is not an available option for large knots. In a recent work, the $C_{27}H_{54}$ cyclic alkane trefoil knot [24] was found to be the smallest stable alkane knot using RHF/3-21G(*) level of theory. This work presents the tightest open (with unlinked ends, see Fig. 1b) molecular knot that can be constructed, using only 22 carbon atoms, by applying the findings from the mathematical field of open polygonal knots [18,19] to the homologous series n - C_nH_{2n+2} (small chains, $n < 50$). The existence of these knots was verified with high-level ab initio calculations.

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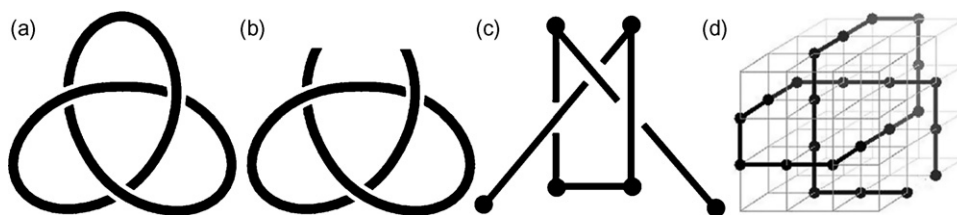


Fig. 1. (a) The trefoil knot. (b) The trefoil knot with open ends. (c) A polygonal chain with six vertices in open knot formation. (d) The open trefoil knot constructed with 24 vertices on the cubic lattice.

2. Computational details

Recently, [25,26] has been reported a de novo computer-aided systematic production of small molecular knots with three or more crossings and unlinked ends. Briefly the generalized molecular knotting (GMK) algorithm does the following four tasks: (a) Generates molecular conformations with inherent knot topology by applying the theory of open polygonal knots at dihedral space. Hence, the polyethylene strand is modeled as a finite number of straight line segments that are linked together with suitable turns. Extended pieces of $-(CH_2)_n-$ chains (contiguous 180° CCCC torsion angles) represent the line segments, while the turns are $-(CH_2)_5-$ fragments with two contiguous torsion angles such as to produce an appropriate bend between two successive straight molecular segments. (b) Evaluates knottiness for each structure using the Knot Program [27]. (c) Applies constrained molecular mechanics (MM) computation [28] to create tolerable initial conformations. (d) Verifies knottiness at various levels of theory.

Firstly, all resultant conformers are subjected to unconstrained geometry optimization with AM1 (a semiempirical, self consistent field molecular orbital method, developed by Dewar et al. [29]). In addition, some representative knotted conformers were reoptimized at Hartree-Fock level of theory (HF), density functional theory (using the hybrid exchange-correlation functional B3LYP [30]) and Møller-Plesset second order perturbation (MP2) that improves the HF method by adding a significant portion of the electron correlation effects. The 6-31G(d,p) basis set was employed for all HF,DFT-B3LYP,

MP2 computations. The semiempirical, ab initio and DFT calculations were executed using Gamess [31], PC GAMESS [32] and Gaussian98 [33] programs. The AM1 model seems to describe well the overall optimized knotted geometries since its carbon skeleton torsion angles are in good agreement with those derived from MP2/6-31G(d,p) optimizations (see supplementary information, RMS for CCCC torsion angles). It must be noted that the computational cost of performing an AM1 geometry optimization is smaller by at least two orders of magnitude in comparison to the required cost for an MP2 geometry optimization of the same conformer.

A graphical representation of the GMK algorithm application to alkanes $C_{23}H_{48}$ and $C_{30}H_{62}$ is shown at Figs. 2 and 3, respectively. The overall knot shape (expressed as a sequence of CCCC torsion angles) changes slightly beyond the AM1 optimization procedure.

The enumeration of local minima – total conformer space – (TCS) of a linear alkane C_nH_{2n+2} , is given by Tasi et al. [34] along with a set of rules for allowable double, triple and quadruple sequences of CCCC torsion angles. The fraction of the knotted conformers (total knotted conformational space—TKCS) over all permitted possibilities for the TCS is a measure of the Delbrück's [14] knotting probability. The construction of the 3D molecular shape by the application of the GMK algorithm has the advantage that a very small subset (compare columns two and three of Table 1) of the TCS is expected to have high probability to form a knot by belonging to the total knotted conformational space (TKCS).

The number of polygonal chains embedded in a 3_1 open knot curve is a measure of the TKCS [24] and it is defined as a

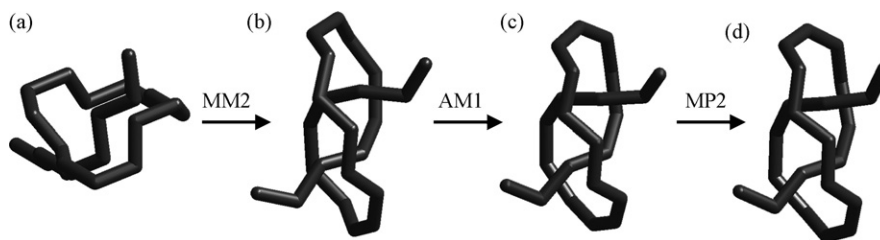


Fig. 2. Tube representation of the open knot $C_{23}H_{48}$ at the stage of: (a) initial building (MolKnot Program-GMK algorithm), the sequence of the CCCC backbone torsion angles is: $180.0^\circ, 180.0^\circ, 180.0^\circ, 60.0^\circ, 60.0^\circ, 180.0^\circ, 60.0^\circ, 60.0^\circ, 180.0^\circ, 180.0^\circ, -60.0^\circ, 95.0^\circ, 180.0^\circ, 95.0^\circ, -60.0^\circ, 180.0^\circ, 95.0^\circ, -60.0^\circ, 180.0^\circ, 180.0^\circ$. (b) After the MM2 optimization procedure, the sequence of the CCCC backbone torsion angles is: $149.3^\circ, 9.8^\circ, 59.7^\circ, -42.0^\circ, 81.4^\circ, -70.5^\circ, 28.3^\circ, 69.6^\circ, -142.4^\circ, 119.8^\circ, -145.7^\circ, 124.8^\circ, -114.6^\circ, 93.8^\circ, -67.9^\circ, 70.3^\circ, -36.0^\circ, 59.0^\circ, 132.4^\circ, -173.3^\circ$. (c) After AM1 optimization procedure, the sequence of the CCCC backbone torsion angles is: $140.7^\circ, 55.1^\circ, 39.7^\circ, -31.7^\circ, 46.2^\circ, -24.8^\circ, 15.6^\circ, 58.5^\circ, -132.9^\circ, 116.8^\circ, -156.6^\circ, 130.9^\circ, -109.0^\circ, 54.6^\circ, 40.9^\circ, -58.0^\circ, 28.9^\circ, 36.4^\circ, 130.7^\circ, -161.2^\circ$. (d) After MP2/6-31G(d,p) optimization procedure, the sequence of the CCCC backbone torsion angles is: $131.4^\circ, 60.2^\circ, 47.7^\circ, -58.7^\circ, 77.5^\circ, -48.3^\circ, 28.3^\circ, 53.0^\circ, -127.3^\circ, 119.1^\circ, -162.5^\circ, 123.3^\circ, -100.1^\circ, 49.1^\circ, 47.3^\circ, -66.7^\circ, 32.2^\circ, 40.9^\circ, 125.5^\circ, -161.9^\circ$. In all cases, hydrogen atoms are not shown for clarity.

Table 1

Number of structures generated and processed during the various levels of the computations

Alkane	Total number of conformations	Number of generated conformations	Knots detected by the Knot program	Knotted structures computed at different levels of theory				
				MM2	AM1 ^a	HF/6-31G(d,p)	B3LYP/6-31G(d,p)	MP2/6-31G(d,p)
C ₂₂ H ₄₆	1.0×10^{11}	754,272	486	2	N/A	1	1 ^b	1 ^b
C ₂₃ H ₄₈	3.2×10^{11}	933,120	N/A	2,454	3 ^b	1	1 ^b	1
C ₃₀ H ₆₂	9.9×10^{14}	16,656,192	45,204	17,808	210 ^b	1	1	N/A
C ₃₈ H ₇₈	9.6×10^{18}	600,000	2940	330	159 ^b	1	1	N/A

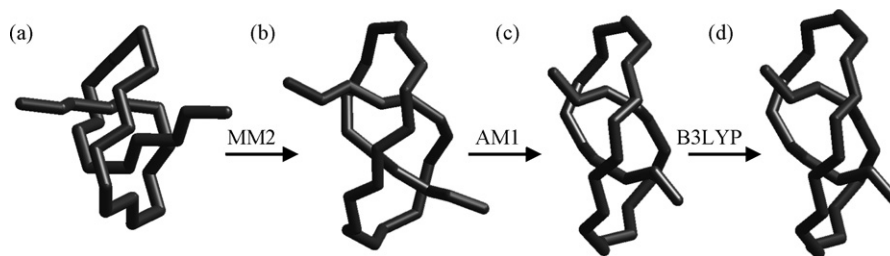
^a AM1 minimization followed by evaluation of knottiness using the Knot program. One conformer was further reoptimized at higher levels of theory.^b Frequency calculations confirmed the local minimum.

Fig. 3. Tube representation of the open knot C₃₀H₆₂ at the stage of: (a) initial building (MolKnot Program-GMK algorithm), the sequence of the CCCC backbone torsion angles is: 180.0°, 180.0°, 180.0°, 60.0°, 60.0°, 180.0°, 95.0°, –60.0°, 180.0°, 180.0°, 60.0°, –95.0°, 180.0°, 180.0°, –95.0°, 60.0°, 180.0°, 180.0°, –60.0°, 95.0°, 180.0°, 60.0°, 60.0°, 180.0°, 180.0°, 180.0°. (b) After the MM2 optimization procedure, the sequence of the CCCC backbone torsion angles is: –167.6°, 162.5°, –169.5°, 121.5°, –60.6°, –57.2°, 92.8°, –104.5°, 117.8°, –137.9°, 130.3°, –130.6°, 165.0°, –138.2°, 162.6°, –129.7°, 133.0°, –139.1°, 116.5°, –106.7°, 98.5°, –61.8°, –59.5°, 118.3°, –166.3°, 165.6°, –168.3°. (c) After AM1 optimization procedure, the sequence of the CCCC backbone torsion angles is: 170.4°, 121.3°, –143.2°, 113.0°, –74.7°, –61.8°, 135.9°, –141.7°, 123.4°, –124.2°, 136.3°, –168.5°, 166.3°, –100.1°, 166.7°, –168.7°, 136.5°, –123.4°, 124.1°, –142.6°, 135.2°, –61.1°, –75.3°, 114.6°, –141.2°, 118.6°, 171.5°. (d) After B3LYP/6-31G(d,p) optimization procedure, the sequence of the CCCC backbone torsion angles is: 172.3°, 123.7°, –145.7°, 111.4°, –75.0°, –65.3°, 137.4°, –136.8°, 121.7°, –127.9°, 136.8°, –169.3°, 166.3°, –94.4°, 167.8°, –170.0°, 136.8°, –127.4°, 123.1°, –137.7°, 135.7°, –64.9°, –74.9°, 115.1°, –140.5°, 117.8°, 172.2°. In all cases, hydrogen atoms are not shown for clarity.

function of two parameters (a) the number of carbon atoms: nc and (b) the number of linear molecular segments: k .

$$\text{TKCS}(nc, k) = \sum_{k=5}^{\lfloor (nc-1)/3 \rfloor} \left(\frac{(nc-2k-2)!}{(k-1)!(nc-3k-1)!} 6^{(k-1)} \right) \quad (1)$$

The representation $\lfloor (nc-1)/3 \rfloor$ denotes the integral part of the division.

In the current contribution, 18943584 n -C _{n} H_{2 n +2} ($n = 22, 23, 30$ and 38 , see Fig. 4) structures were evaluated for knottiness and a summary of the results are shown in Table 1.

3. Results and discussion

This work presents the construction of the most compact open polyethylene knot by using the MolKnot program. So, we focus first to find the smallest alkane that the knotted region contains the whole molecule. The shortest knotted polyethylene chain was found to be C₂₂H₄₆ (Fig. 4a), while recent work [35,36] predicted C₂₃H₄₈ as the minimum-knotted alkane. However, they did not confirm its existence either in vitro or in silico. The investigation for all possible k values of the linear segments for the C₂₂H₄₆ molecule is summarized in Table 2, where the total-knotted conformational space according to the GMK algorithm is 7.5×10^5 , while the total conformational

space [34] for C₂₂H₄₆ is 1.0×10^{11} ; the total number of knots found according to MolKnot program at the stage of the initial building is 486. The knotted C₂₂H₄₆ molecule was optimized at HF, B3LYP and MP2 level using 6-31G(d,p) basis set and frequency calculations (at B3LYP and MP2 level) confirmed the local minimum. The MP2 optimized structure is quite compact with the smallest C···C nonbonded distance at 2.42 Å; a very weak bond C₂₀–C₂₁ (1.675 Å) occurs just at the entrance of the knot while its associated CĈC bond angles are 143° and 133°. Similar weak CC bonds appear in regions very close to the entrance/exit. Table 3 summarizes the most distorted bonds and valence angles of the two shortest open molecular knots. It appears that there is a consistency of the recorded distortions across the various computational ab initio models.

The overall structure is quite deformed since 81% of its CC bonds are above 1.60 Å and the 70% of its CĈC bond angles are above 130°. The C₂₂H₄₆ open knot is depicted in Fig. 4a with graphic representation of bond dissociation energy (BDE) for

Table 2
The TKCS analysis for C₂₂H₄₆

k	Number of conformers built for each k	Knots according to Knot program
5	272,160	54
6	435,456	418
7	46,656	14

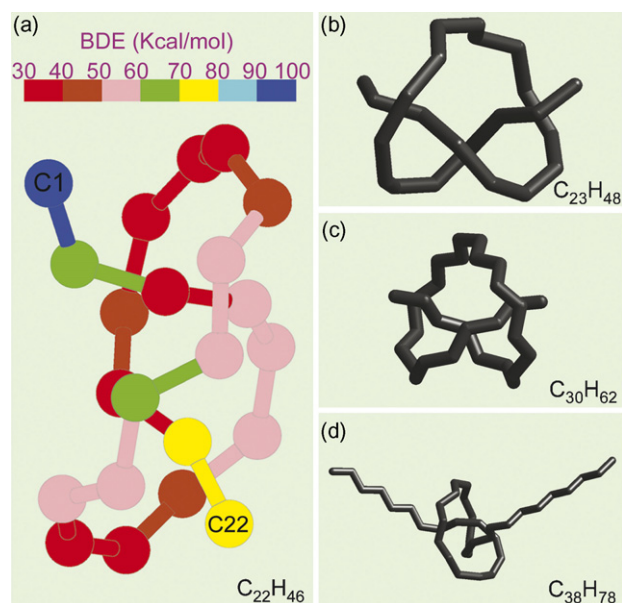


Fig. 4. (a) $C_{22}H_{46}$ open knot optimized at MP2/6-31G(d,p) with a color representation of bond dissociation energy (BDE). The geometry by means of CCCC torsion angles: -101.6° , -51.7° , -51.7° , 55.2° , -77.5° , 54.1° , -35.9° , -49.3° , 125.9° , -114.8° , 159.9° , -128.7° , 105.0° , -91.4° , 58.6° , -43.8° , 29.6° , -60.0° , -122.0° (the initial dihedral assignment was: 180.0° , 180.0° , 180.0° , -60.0° , -60.0° , 180.0° , -60.0° , -60.0° , 180.0° , 180.0° , $+60.0^\circ$, -95.0° , 180.0° , -95.0° , $+60.0^\circ$, 180.0° , $+60.0^\circ$, -95.0° , 180.0°). (b) $C_{23}H_{48}$ open knot optimized at MP2/6-31G(d,p). (c) $C_{30}H_{62}$ open knot optimized at B3LYP/6-31G(d,p). (d) $C_{38}H_{78}$ tightest open knot optimized at B3LYP/6-31G(d,p); In all cases, hydrogen atoms have been omitted for clarity.

its CC bonds. The later were calculated by applying Zavitsas' [37] equation

$$r = 1.748 - 0.002371 \times \text{BDE} \quad (2)$$

(r : CC bond length, optimized at MP2 level).

The weakest bond between carbon atoms 20 and 21 has a BDE value of 30.8 kcal/mol, while six more bonds have BDEs less than 40 kcal/mol. In addition, the smallest knot appears to show considerable decrease of its molar volume (20%) and molar surface in comparison to the fully extended conformer. The $C_{22}H_{46}$ knot is elongated as much as 16.1% (unknotting it by resetting all CCCC torsion angles to 180° ; this way we get a measure of the contour length for the $C_{22}H_{46}$ -knotted chain, see Fig. 5) compared to the extended n - $C_{22}H_{46}$ hydrocarbon due to its deformation. This amount of elongation is inevitable because the knot topology induces high bonds' and bond angles' distortions. Similar, but smaller deformation exhibits the $C_{23}H_{48}$ knot (overall elongation 14.2%), where 77% of the CC bonds are above 1.60 Å, while 71% of its $C\dot{C}C$ bond angles are above 130° (at MP2 level). The application of uniaxial strain by systematically increasing the separation between the terminal carbon atoms of the n -decane molecule has been reported [35] to produce a maximum elongation of 18.5% beyond its equilibrium length. A search at the Cambridge structural database (CSD) [38] located crystallographic structures with $(-CH_2-)_n$ chains where CC bonds and $C\dot{C}C$ angles are distorted; for example, the substance (2*E*,4*S*,5*S*,15*R*)-4,5-(isopropylidenedioxy)hexadec-2-en-15-olide [39] has a

Table 3

Most distorted geometric parameters at three levels of theory for the two shortest stable open hydrocarbon knots

Open knot	HF/6-31G(d,p)	B3LYP/6-31G(d,p)	MP2/6-31G(d,p)
Max CC (Å)			
$C_{22}H_{46}$	1.704 ^a	1.713 ^a	1.675 ^a
$C_{23}H_{48}$	1.727 ^a	1.745 ^a	1.697 ^a
Max CCC (°)			
$C_{22}H_{46}$	145.5 ^b	146.2 ^b	146.0 ^b
$C_{23}H_{48}$	145.1 ^c	144.9 ^c	144.7 ^c
%CC > 1.60 Å			
$C_{22}H_{46}$ (%)	90	90	81
$C_{23}H_{48}$ (%)	86	86	77
%CCC > 130°			
$C_{22}H_{46}$ (%)	70	70	70
$C_{23}H_{48}$ (%)	71	71	71

^a $C_{20}C_{21}$.

^b $C_2C_3C_4$.

^c $C_8C_9C_{10}$.

bicycle system with an elongated CC bond at 1.714 Å and the molecule syn,syn-diepoxy[6](9,10)anthracenophane [40] exhibits a bond angle $C\dot{C}C = 136.8^\circ$ as part of an eight-member ring. However, such a compound featuring multiple CC bonds and $C\dot{C}C$ bond angles more than 10% away from their equilibrium values has not been reported until now. Furthermore, by replacing one hydrogen atom with the $-(CH_2)_xCH_3$ group at each of the terminal methyls of the knotted $C_{22}H_{46}$ and subsequent energy minimization at AM1, HF, B3LYP levels of theory, we produced tight open knots with longer chain lengths; in all cases the geometric features of the knotted region remained nearly intact.

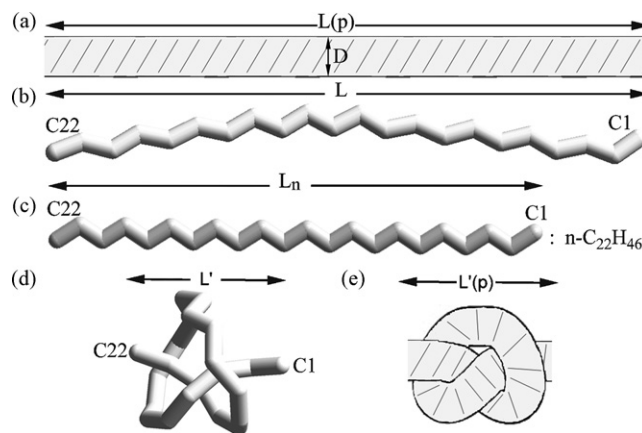


Fig. 5. (a) The perfect rope model (Pieranski) is depicted where $L(p)$ is the distance between the ends of the unknotted rope. (b) Tube representation of the $C_{22}H_{46}$ open trefoil knot (optimized at MP2/6-31G(d,p) level of theory) where all CCCC torsion angles assigned to value: 180.0° , $L = 31.01$ Å. (c) Tube representation of the n - $C_{22}H_{46}$ alkane where all the CCCC torsion angles were set initially to 180.0° and then performed geometry optimization at MP2/6-31G(d,p) level of theory, $L_n = 26.76$ Å. (d) Tube representation of the $C_{22}H_{46}$ open trefoil knot (optimized at MP2/6-31G(d,p) level of theory), where $L' = 6.59$ Å is its associated length of the knotted strand. (e) The perfect rope model is depicted in tight knot shape where $L'(p)$ is the distance between the ends of the knotted strand.

The question that arises now is whether the $C_{22}H_{46}$ knot is the smallest alkane that can be sustained in knot shape. A model of perfect ropes was sought to provide an estimate for the tightest molecular knot. According to Pieranski et al. [41] the perfect rope (Fig. 5a) has the following properties: (a) it is perfectly hard, (b) it is perfectly flexible and (c) it is perfectly slippery. It follows that the relation $\Lambda_o = (L - L')/D$ describes the tightness of a perfect open rope in knot shape (L : rope's length, L' : the length of the knotted strand, $\Delta L = L - L'$: the length of the rope engaged in the active region within the knot, D : the diameter of the rope). Fig. 5 shows the perfect open trefoil-knotted rope and its $C_{22}H_{46}$ counterpart. Therefore, we calculate the tightness Λ_o for each of the shorter molecules optimized at MP2/6-31G(d,p) level, using in each case the minimum C··C nonbonded distance as diameter (D). Fig. 5 exhibits the ΔL measurement of the $C_{22}H_{46}$ -knotted strand. Since the knotted alkanes are elongated, the L value refers to the molecule's contour length. The three molecular knots $C_{22}H_{46}$, $C_{23}H_{48}$, $C_{24}H_{50}$ have Λ_o values: 10.1, 10.5 and 10.6, respectively. It seems that the knotted $C_{22}H_{46}$ is the lowest limit, since its Λ_o value coincides with the tightest perfect open trefoils' value. However, the alkane molecules do not have the ideal behavior of the Pieranski's perfect ropes (since this ideal model refers to an 'inextensible' chain) but we used the previously mentioned model as an approximate measure of the tightness' lowest limit. So, we believe that an even smaller knotted alkane can be sustained in knot shape; for example, a hypothetical $C_{21}H_{44}$, with 18% total elongation has C1··C21 length about ~ 30 Å, which is sufficient to form an open knot. Thus, it might be possible that an even smaller polyethylene strand than $C_{22}H_{46}$ can be made to open knot shape, but our attempts to construct it were unsuccessful. Andrae [42] suggested a surface template technique as a possible experimental avenue to actually form molecular knots. This technique may pave the way to directed and controlled synthesis of knots, thus replacing present-day methods based on self-assembly of constituting monomers/oligomers. Since Andrae's procedure is based on a piecemeal build-up (albeit with a surface template) similar to the one proposed here, one could envisage that it might be achieved the appropriate positioning with proper functionalisation of the molecular segments, so as to form a knotted structure.

The energy of the i th-knotted conformer is defined as

$$\Delta E_i = E_i^K - E^E \quad (3)$$

where E_i^K is the molecular energy of the i th-knotted conformer and E^E is the molecular energy of the fully extended optimized molecular conformation (all CCCC torsion angles set initially at: 180°). Goodman [43] reported that the ground state of long alkanes is not the extended chain; however, we use it as a reference conformation. Another important feature of the knotted molecules' topology is the knot diameter (KD), defined as the maximum non-bonded C··C distance on the active-knotted region. We examined the set of the 210 $C_{30}H_{62}$ 3_1 knots with respect to KD and ΔE_i . The knot with the lowest ΔE_i energy exhibited the largest KD distance on the knot (~ 9.4 Å)

while the highest ΔE_i conformer had a knot diameter of about ~ 7.5 Å. This correlation is applicable to all high and low energy conformers, so it appears that the degree of compactness affects the knotted energy. Finally, we decided to investigate the construction of the tightest possible molecular knot within a polyethylene strand. By exploring the $C_{38}H_{78}$ conformational space we discovered 159 tight molecular knots at AM1 level with knotted energy ΔE_i taking values from 155 to 470 kcal/mol. Seventy-one percent of these structures recorded $\Delta E_i > 300$ kcal/mol and the number of carbon atoms involved in the active knot region was at least 22. The $C_{22}H_{46}$ and $C_{23}H_{48}$ knots exhibited the highest of all $\Delta E_i \sim 530$ kcal/mole. Saitta and Klein [44] in his work on the rupture of $C_{28}H_{58}$ knot found that slightly more than half of the total strain energy (~ 300 kcal/mol) is released into radical formation energy (2×83 kcal/mol). The remaining part is transformed into kinetic energy of the radicals $C_{28}H_{58} \rightarrow C_{19}H_{38} + C_3H_7^\bullet + C_6H_{13}^\bullet$.

The permanence of the knotted entanglement (locked configurations) can be secured with (i) appropriate capping, (ii) side chains, or (iii) inflexible molecular segments. Arteca [45] constructed stuck-polygonal molecular configurations Phe-(CH₂) n -Phe ($8 < n < 19$ the loop segment) where MM2 force field retained the knot because of the bulky capping; the longer the loop the smaller its corresponding ΔE_i energy.

The knotted energy is spreading all over the knotted region of the molecule and induces distortions in bond lengths, bond angles and torsion angles; it can be partitioned into meaningful contributions of geometric deformations with the following components:

$$\Delta E_i = (E_i^K - E_i^A) + (E_i^A - E_i^B) + (E_i^B - E_i^C) + (E_i^C - E_i^D) + (E_i^D - E^E) \quad (4)$$

where E_i^K and E^E are the energy of the i th knotted and the energy of the fully extended optimized conformer, respectively. The components E_i^A , E_i^B , E_i^C , E_i^D , are energy values of the knotted molecule by setting step by step specific geometric parameters to the extended conformer's values: E_i^A : CCCC torsion angles, E_i^B : CCCC torsions and CĈC angles, E_i^C : CCCC torsions, CĈC, CĈH and HĈH angles, E_i^D : CCCC torsions, CĈC, CĈH, HĈH angles and CH bonds. The fifth term ($E_i^D - E^E$) shows the energy contribution due to CC bonds deformation. In all cases, the molecular energy is calculated performing single point energy calculation at the same level of theory where the energies E_i^K and E^E were obtained. So, Eq. (4) can be rewritten as

$$\Delta E_i = \Delta E_i^{CCCC} + \Delta E_i^{CCC} + \Delta E_i^{CCH,HCH} + \Delta E_i^{CH} + \Delta E_i^{CC} \quad (5)$$

Table 4 sums up the energy decomposition of $C_{22}H_{46}$, selected $C_{30}H_{62}$ conformers and the tightest $C_{38}H_{78}$ knot. It appears that most of the knottiness' energy strain (over 50%, whatever the method used: MP2, B3LYP, HF, AM1) affects the valence angles CĈC, CĈH, HĈH. Each carbon atom of an extended aliphatic chain has $\theta = C_{i-1}\hat{C}_iC_{i+1} + C_{i-1}\hat{C}_iH_j + C_{i+1}\hat{C}_iH_j = 331.0^\circ$, while most of carbon atoms

Table 4

Energy decomposition of the knotted energy (ΔE_i) due to geometric deformations calculated at different levels of theory (all energy values are in kcal/mol)

Alkane/level of theory	ΔE_i^{CCCC}	ΔE_i^{CCC}	$\Delta E_i^{\text{CCH,HCH}}$	ΔE_i^{CH}	ΔE_i^{CC}	ΔE_i
C ₂₂ H ₄₆ /HF/6-31G(d,p)	107.6	144.4	187.6	5.3	88.6	533.5
C ₂₂ H ₄₆ /B3LYP/6-31G(d,p)	94.8	120.0	158.4	3.4	81.4	458.0
C ₂₂ H ₄₆ /MP2/6-31G(d,p)	60.5	123.7	163.5	3.0	71.6	422.3
C ₃₀ H ₆₂ /AM1 ^a	93.2	69.7	71.4	1.9	18.3	254.5
C ₃₀ H ₆₂ /HF/6-31G(d,p) ^a	123.8	61.0	70.6	3.9	30.4	289.7
C ₃₀ H ₆₂ /B3LYP/6-31G(d,p) ^a	112.3	47.4	53.3	2.7	26.9	242.6
C ₃₀ H ₆₂ /AM1 ^b	72.8	130.7	123.5	1.4	34.9	363.3
C ₃₀ H ₆₂ /B3LYP/6-31G(d,p) ^b	61.2	93.2	128.4	1.7	41.6	326.1
C ₃₀ H ₆₂ /AM1 ^c	95.5	166.9	162.6	1.4	67.0	493.4
C ₃₀ H ₆₂ /B3LYP/6-31G(d,p) ^c	74.5	118.9	162.8	2.7	67.2	426.1
C ₃₈ H ₇₈ /B3LYP/6-31G(d,p) ^d	99.0	106.8	127.9	2.3	67.3	403.3

^a Low ΔE_i conformer.^b Medium ΔE_i conformer.^c High ΔE_i conformer.^d The tightest C₃₈H₇₈ knot.

in a tight-knotted loop are severe distorted tetrahedrons since the internal carbon tend to approach the face HCC, e.g. the atoms C₃ and C₁₉ with their $\theta = 349.4^\circ$ are nearly coplanar to C₂C₄H₂₈ and C₁₈C₂₀H₆₀, respectively.

Moreover, using the initial build for the knotted structure C₂₂H₄₆ as template, we created the conformational space that each torsion could take a value $\pm 10^\circ$ from the initial dihedral sequence and we randomly sample 10,000 conformers. Then, by applying the GMK algorithm (omitting the first step), we ended up with three additional AM1-knotted conformers all with ΔE_i values over 500 kcal/mol. This method can locate additional conformers at the vicinity of a successful find. Accordingly, we arrived to the conclusion that the order of magnitude of the unique C₂₂H₄₆-knotted conformers is about 1000. The construction of longer chain tight knots by adding $-(\text{CH}_2)_n\text{CH}_3$ groups to those C₂₂H₄₆ estimated tight conformations, using them as templates, could lead to the building of all possible tight open knots C_nH_{2n+2} of length $n > 22$.

4. Conclusions

By applying the theory of open polygonal knots in dihedral space, we were able to construct a C₂₂H₄₆ knot that, to the best of our knowledge is the smallest open-knotted polyethylene strand ever reported. Furthermore, a 22 carbon atoms' segment is the smallest chain that appears to participate in the tightest possible active-knotted region of a longer polyethylene strand. It is estimated that the 22 carbon-knotted region with 3₁ shape can exist at about 1000 different conformations. Since this molecular-knotted topology has been demonstrated that it can be accomplished in silico, it is expected to provide a stimulus and a challenge to synthetic chemists for its implementation in the lab as it is, or with some substitutions/modifications if necessary. The unique feature of multiple elongated CC bonds and extended C $\hat{\text{C}}\text{C}$ bond angles that was induced to a single compound by these intertwining patterns, presents substantial interest in the design of new high-tech materials with specific properties.

Acknowledgment

The research Project is co-funded by the European Union—European Social Fund (ESF) & National Sources, in the framework of the program “HRAKLEITOS” of the “Operational Program for Education and Initial Vocational Training” of the third Community Support Framework of the Hellenic Ministry of Education. Two anonymous referees provided important suggestions on how to enhance the manuscript. The authors gratefully acknowledge the computer time provided by: (a) the Computational Materials Science Laboratory at the Dept. of Materials Science and Engineering, (b) the Computer Center and (c) the Research Center for Scientific Simulations (RCSS) of Ioannina University, Greece.

Appendix A. Supplementary data

Supplementary information available: MP2/6-31G(d,p) optimized Cartesian xyz coordinates for the open knots: C₂₂H₄₆, C₂₃H₄₈. B3LYP/6-31G(d,p) optimized Cartesian xyz coordinates for the open knots: C₂₂H₄₆, C₂₃H₄₈, C₃₀H₆₂, C₃₈H₇₈. Calculated frequencies for the knotted alkane C₂₂H₄₆ at MP2 and B3LYP level of theory. Evaluation of the AM1 geometry optimized knotted alkanes C₂₂H₄₆ and C₂₃H₄₈ using as reference structures the corresponding MP2/6-31G(d,p) optimized knotted molecules. Detailed explanation of the knotted energy decomposition scheme's terms.

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jmngm.2007.10.010](https://doi.org/10.1016/j.jmngm.2007.10.010).

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