

Model Carbyne Knots vs Ideal Knots[†]

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The structure and stability of model carbyne knots built from 60 to 120 carbon atoms with 0, 3, 4, ..., 7 crossings have been estimated by semiempirical AM1 calculations. The calculations have shown an increase of the knot-cycle energy difference (ΔE) with an increasing number of knot crossings and a decrease of ΔE with an increasing number of atoms constituting the molecule. The ΔE changes nonlinearly with the characteristics of the corresponding ideal knots such as the average crossing number (ACN) and the length-to-diameter ratio (L/D). The molecular mechanic strain energy of carbyne knots correlates similarly with ACN and L/D of ideal knots. The calculated energy of the model carbyne knots correlates also with the electrophoretic mobility or sedimentation coefficient of DNA knots. Thus, similarly to characteristics of ideal knots, the energy of carbyne knots is a rather easily available parameter which can be used for further correlations with some characteristics of DNA knots.

1. INTRODUCTION

Since the last 5 years we have been studying the structures of models for topological isomerism.^{1–10} Within the frame of that project, we studied carbyne structures, the compounds built solely with the $(C\equiv C)_n$ motif,^{1–8} and polycyclic aromatic hydrocarbons either in the belt form or twisted in the form of Moebius strip.^{9,10} So far, we analyzed carbyne knots,^{1–4,7,8} carbyne links (catenanes),^{3,5,8} carbyne hook-and-ladder structures,⁶ coronene isomers of the belt and Moebius type,⁹ and the number of belt and Moebius structures built from 3 to 14 catacondensed benzene rings.¹⁰ On the other hand, our studies on topological carbynes and PAHs are also a voice in discussion in a search for new forms of polycarbon systems^{11–16} and nonplanar PAHs.^{17–25}

The DNA topological structures are known since 1967 when Wang and Schwartz,²⁶ Hudson and Vinograd,²⁷ and Clayton and Vinograd²⁸ first observed DNA catenanes. Until the mid 1970s, the DNA catenanes were discovered in a majority of organisms: from viruses, through bacteria containing plasmids and cyclic salamander chomosomes, to mammal mitochondria, and human leucocytes.²⁹ The DNA knots and links (catenanes) can be obtained in vitro thanks to integrative recombination of a supercoiled DNA. For example, Mizuuchi et al. synthesized the 2^2_1 and 4^2_1 DNA links from pBP86 plasmid and the 3_1 and 5_1 DNA knots from pBP90 plasmid.³⁰ The recombination catalyzed by the site-specific resolvase Tn3 leads to very selective products: out of six possible stereoisomers of the six crossings knots (three prime knots 6_1 , 6_2 , and 6_3 , and three composed—one stereoisomer of square knot $3_1\#-3_1$ and two granny knots $3_1\#3_1$ and $-3_1\#-3_1$) only one DNA topological 6_2 isomer is

formed.³¹ On the other hand, a nonspecific action of the topoisomerase I on a nicked DNA duplex leads to a multitude of different knots.³² After topoisomerase I action, Dean et al. observed the 3_1 , 4_1 , 5_1 , 6_1 , 6_2 , 6_1 , square $6_c=3_1\#-3_1$, 7_2 , 7_5 , 7_6 , 7_7 , $9_c=5_1\#4_1$, and 9_1 DNA knots.³²

Owing to a variety of knots produced by topoisomerase I, it was possible to notice that electrophoretic mobility of DNA knots correlate with their number of crossings.³² In an electrophoretic band the majority of structures possess the same crossing number and the crossing numbers of neighboring electrophoretic bands differ by unit.³² Moreover, by using the high-resolution electrophoresis the torus DNA knots can be separated from the twist DNA knots.³³ An excellent example of electrophoretic separation of different topological DNA structures produced in integrative recombination by site-specific integrase is an isolation of right-handed torus DNA knots (3_1 , 5_1 , 7_1 , ..., 23_1) and right-handed DNA links (4^2_1 , 6^2_1 , 8^2_1 , 10^2_1 , ..., 20^2_1), which migrate according to an increasing crossings number.³⁴

After electrophoretic isolation, the topology of DNA structures can be observed by electron microscopy; however, this is an expensive and not easily available method in biochemical laboratories. Therefore, a lot of effort was made to characterize DNA topology by the interpretation of electrophoretic bands. The electrophoretic migration as well as sedimentation coefficient of DNA knots and catenanes were correlated with parameters of ideal knots and ideal links.^{35–39} The concept of ideal knots and links refers to ideal Plato's figures.⁴⁰ The geometry of physical knots is represented by images of torus in R^3 . The ideal knot or link is that with the smallest volume-to-surface ratio³⁶ or the shortest knotted tube with constant diameter.³⁷ Then, the length-to-diameter ratio (L/D) is constant and invariant for the actual, physical parameter of the knot or the link. For example for the 3_1 knot, the (L/D) is equal to 16.33, and for the 7_7 knot it is ca. twice as much, i.e., 32.76.⁴⁰ The shape of ideal knots can be interpreted as the sum of trajectories averaged over

[†] This paper is dedicated to Prof. Milan Randić on the occasion of his 70th birthday in recognition of his exceptional contribution in applications of graph theory in chemistry.

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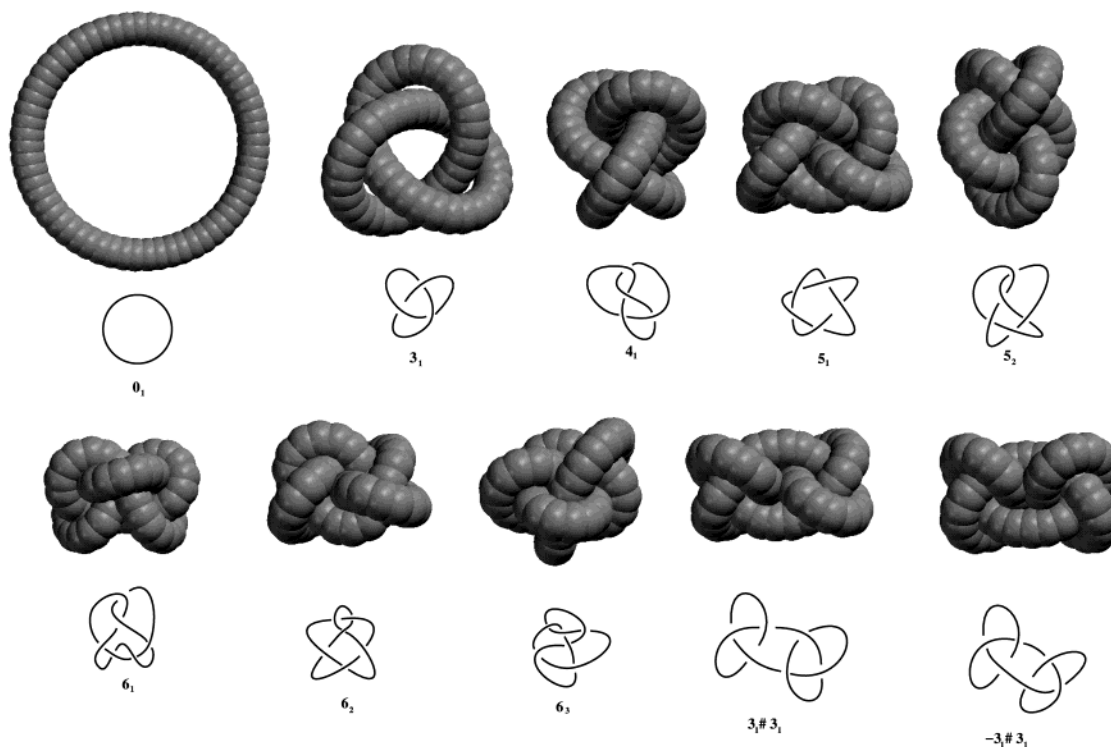


Figure 1. The AM1 optimized structures of C₆₀ carbyne knots with not more than six crossings, their regular diagrams, and notation.

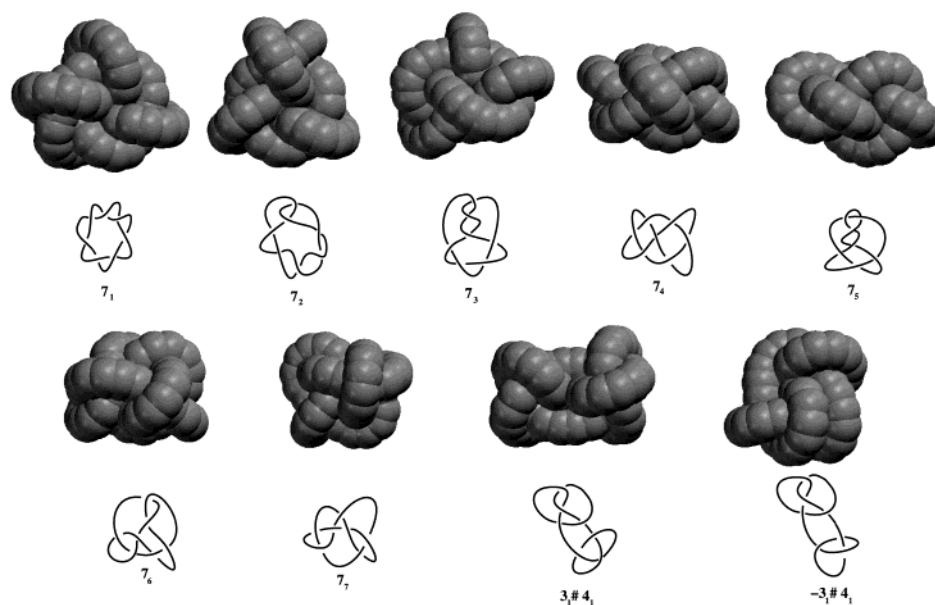


Figure 2. The AM1 optimized structures of C₆₀ carbyne knots with seven crossings, their regular diagrams, and notation.

time of the real knots moving stochastically. So far, there is no analytical description of the shape of ideal knots or links; however, the necessary conditions of such a class of ideal figures are known.⁴¹ Thus, the ideal knots and links are modeled numerically, though to find their optimal shape,⁴² even for the simplest nontrivial trefoil knot, is a complex task.⁴³

For the ideal knots an averaged wrighting number (AWN) and an averaged crossing number (ACN) are introduced, where the averaging is over all projections of the sphere to the plane.³⁶ The AWN is connected to (averaged) the Tait number^{38,44} and tells whether the wright is overbalanced to the left or to the right.⁴⁴ So, the AWN can be either positive or negative, for achiral knots (4₁, 6₃, 8₁₈, square 3₁#-3₁, 4₁#4₁)

the AWN is close to or equal to zero, and for various families of knots (torus, twisted, etc.) it changes linearly with the topological crossing number.^{37,38} The ACN is always positive and correlates with electrophoretic mobility or sedimentation coefficient.^{35,39,45} However, it was shown that ACN correlates linearly with the L/D ratio, in general such a relationship is not linear.⁴⁶⁻⁴⁸

The aim of this paper is to show correlations between energetics of model carbyne knots and parameters describing ideal knots, which do correlate with electrophoretic mobility and sedimentation coefficients of DNA knots. We also show correlations between electrophoretic mobility and sedimentation coefficients of DNA knots and energetics of carbyne knots, which thus can serve as a kind of easily available

Table 1. AM1 Heat-of-Formation (kcal/mol) for Cyclic Carbynes and Seven Crossings Carbyne Knots with 60, 70, ...,120 Carbon Atoms^a

knot type	ACN	L/D	EPM ref 40	SC ref 39	number of carbon atoms in the structure						
					60	70	80	90	100	110	120
0 ₁	0.00	6.28	0.0		1557.73	1809.57	2062.32	2315.66	2569.43	2823.50	3077.79
3 ₁	4.26	16.33	2.3	19.0	1664.31	1894.19	2132.60	2375.78	2621.95	2870.13	3119.73
4 ₁	6.47	20.99	3.2	20.1	1768.69	1972.00	2196.64	2430.92	2670.52	2913.59	3159.00
5 ₁	7.75	23.55	3.9	20.8	1878.00	2038.02	2240.77	2463.08	2692.40	2925.19	3163.88
5 ₂	8.21	24.68	4.1	21.0	1899.04	2051.37	2249.08	2469.80	2701.78	2939.92	3181.83
6 ₁	10.15	28.30	5.1	22.1	2124.51	2191.94	2345.39	2539.48	2754.46	2980.65	3214.69
6 ₂	10.39	28.47		22.4	2135.60	2199.86	2351.82	2545.76	2761.84	2989.18	3223.83
6 ₃	10.52	28.88		22.5	2187.32	2227.55	2370.57	2557.49	2770.01	2989.18	3223.26
3 ₁ #3 ₁	9.46	28.60			2117.56	2189.64	2345.71	2540.35	2756.90	2985.00	3220.10
-3 ₁ #3 ₁	9.51	28.60			2122.63	2193.54	2348.86	2543.50	2759.50	2987.33	3222.06
7 ₁	11.36	30.70	5.7	22.45	2431.98	2372.12	2472.42	2634.40	2830.94	3046.76	3272.20
7 ₂	12.18	32.41	5.9	23.0	2513.51	2400.30	2486.50	2640.67	2832.37	3046.35	3278.97
7 ₃	12.07	31.90			2572.44	2421.27	2501.16	2652.29	2841.71	3054.64	3280.04
7 ₄	12.61	32.53			2526.35	2407.44	2488.82	2640.95	2831.80	3044.36	3270.01
7 ₅	12.38	32.57			2610.34	2446.43	2518.44	2676.58	2850.22	3059.26	3282.43
7 ₆	12.76	32.82			2640.28	2454.90	2519.91	2662.25	2845.39	3053.09	3275.28
7 ₇	12.80	32.76			2603.06	2435.22	2503.35	2650.78	2838.20	3048.96	3273.14
3 ₁ #4 ₁	12.42	32.63			2594.88	2447.07	2521.45	2669.46	2857.05	3067.43	3290.90
-3 ₁ #4 ₁	12.42	32.63			2581.79	2433.57	2510.84	2660.67	2848.42	3059.00	3282.91

^a ACN — averaged crossing number of ideal knot, L/D — length-to-diameter ratio of ideal knot, EPM — electrophoretic mobility of DNA knots read from ref 40, SC — sedimentation coefficient of DNA knots read from ref 39.

Table 2. Molecular Mechanics Strain Energy (kcal/mol, Sybyl Force Field) for Knotted Carbynes with 40, 50, ...,120 Carbon Atoms

knot type	ACN	L/D	number of carbon atoms in the structure								
			40	50	60	70	80	90	100	110	120
0 ₁	0.00	6.28	60.99	44.76	37.17	30.04	24.44	19.87	16.02	12.69	9.75
3 ₁	4.26	16.33	343.52	230.72	174.89	139.00	112.25	92.37	75.66	61.46	49.33
4 ₁	6.47	20.99	687.79	412.35	315.95	258.30	217.31	186.38	161.95	142.10	125.58
5 ₁	7.75	23.55	1259.93	599.65	402.49	308.06	231.22	176.53	137.43	108.13	85.21
5 ₂	8.21	24.68	1448.28	681.24	421.71	325.66	268.18	227.84	197.01	172.34	151.89
6 ₁	10.15	28.30	2928.60	1324.42	713.13	514.33	356.09	288.63	242.19	207.00	179.12
6 ₂	10.39	28.47	2742.98	1237.08	666.54	472.29	376.25	312.11	259.54	217.82	185.72
6 ₃	10.52	28.88	2946.62	1288.62	683.50	468.25	366.21	300.05	251.28	213.16	182.35
3 ₁ #3 ₁	9.46	28.60	2679.60	1204.54	659.46	465.90	369.05	306.25	260.69	225.79	197.39
-3 ₁ #3 ₁	9.51	28.60	2676.30	1215.35	664.23	470.91	372.72	309.02	262.71	221.15	190.39
7 ₁	11.36	30.70	4027.60	1944.13	1001.10	650.04	453.74	424.30	350.35	258.14	222.80
7 ₂	12.18	32.41	4629.23	2160.60	1087.31	669.47	501.27	412.98	322.61	271.49	230.83
7 ₃	12.07	31.90	4623.59	2302.04	1141.90	694.21	518.77	430.12	366.78	260.52	225.07
7 ₄	12.61	32.53	4491.12	2237.91	1093.66	671.12	499.86	402.82	337.79	290.94	255.37
7 ₅	12.38	32.57	4821.73	2450.77	1193.15	724.15	534.25	434.18	362.05	306.18	263.26
7 ₆	12.76	32.82	4824.32	2460.63	1221.75	724.25	520.91	414.74	347.40	299.45	262.68
7 ₇	12.80	32.76	4818.39	2367.11	1169.09	694.06	508.24	413.59	349.54	301.06	263.09
3 ₁ #4 ₁	12.42	32.63	4771.45	2330.81	1202.65	739.57	553.17	454.36	386.65	335.38	294.59
-3 ₁ #4 ₁	12.42	32.63	4613.18	2332.38	1160.89	711.85	531.06	433.71	367.85	318.54	279.41

model structures yielding important parameters for analysis of DNA knots and links.

2. COMPUTATIONS

The structure building, preliminary molecular modeling using the Sybyl⁴⁹ and Merck^{50–54} force fields for the molecular mechanic method, and the semiempirical AM1⁵⁵ optimizations were performed by using the *Spartan 4* package of programs with a graphical interface.⁵⁶

3. RESULTS AND DISCUSSION

The AM1 optimized structures of C₆₀ carbyne knots are depicted in Figures 1 and 2. The heats of formation calculated semiempirically and strain energy calculated by two molecular mechanic methods are collected in Tables 1–3.

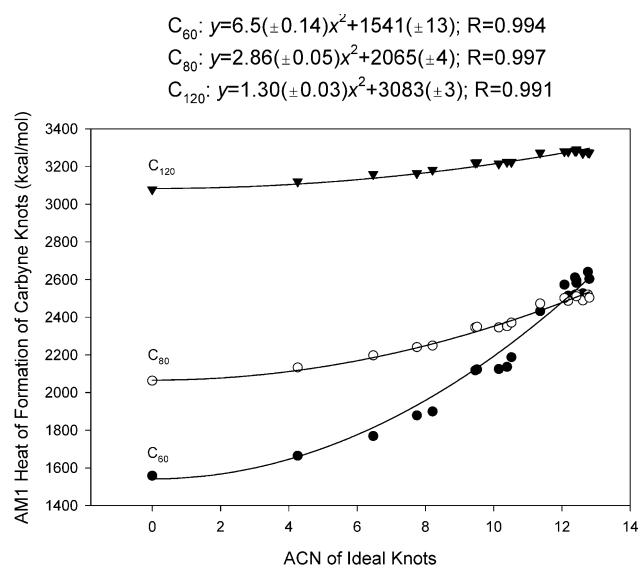
3.1. Energy Trends in Carbyne Knots. Two tendencies can be observed by inspection of Tables 1–3: one is connected with a change of energy in rows of Tables 1–3

(change of energy with an increase in the number of atoms in carbyne structure), while the other is associated with a variation of knot energy in the table columns (variation of energy with an increase in the number of crossings in knot structure of defined length).

With an increasing number of carbon atoms in knot structure, the difference between the carbyne knot and the cycle semiempirical heat of formation (difference between the *n*th and the first row in Table 1) asymptotically decreases. This phenomenon was previously shown for semiempirical and ab initio knot-cycle energy differences of the carbyne knots with a number of crossings not exceeding six.^{1–4} This tendency is easily explicable: for a given topological type of carbyne knot, the energetic strain in the knotted structure decreases as the length of carbyne structure increases. Qualitatively, the same tendency can be observed by examination of a particular row in Tables 2 or 3, where molecular mechanics strain energy is given. In this moment

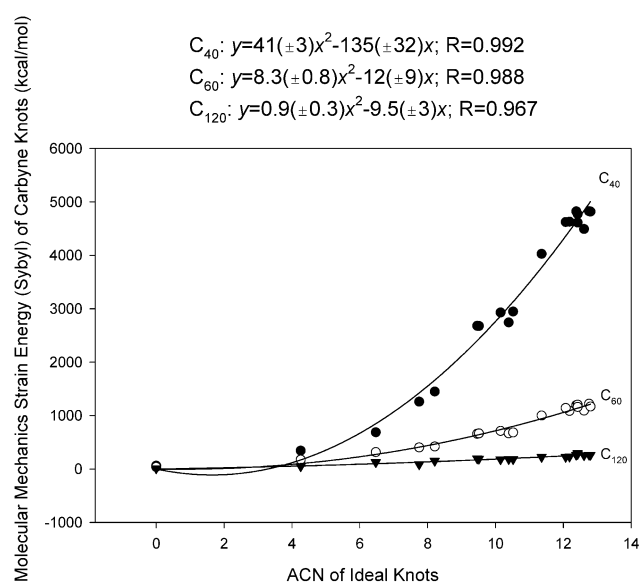
Table 3. Molecular Mechanics Strain Energy (kcal/mol, Merck Force Field) for Knotted Carbynes (kcal/mol) with 40, 50, ...,120 Carbon Atoms

knot type	ACN	L/D	number of carbon atoms in the structure								
			40	50	60	70	80	90	100	110	120
0 ₁	0.00	6.28	12.06	8.17	5.30	3.02	1.09	-0.59	-2.10	-3.48	-4.77
3 ₁	4.26	16.33	140.31	54.74	31.70	25.34	16.96	15.14	9.43	4.37	-0.22
4 ₁	6.47	20.99	664.20	193.16	71.63	47.41	37.16	29.54	23.23	17.85	13.15
5 ₁	7.75	23.55	1347.73	502.76	163.88	70.59	45.10	32.33	20.55	10.20	1.35
5 ₂	8.21	24.68	1532.13	609.77	198.71	80.38	49.03	35.73	26.81	19.65	13.52
6 ₁	10.15	28.30	2813.50	1448.58	620.17	236.78	92.27	59.93	45.90	34.03	25.17
6 ₂	10.39	28.47	2751.26	1405.96	582.96	217.00	94.33	61.39	46.50	37.35	25.19
6 ₃	10.52	28.88	2882.97	1456.09	625.69	233.28	99.12	57.97	41.28	29.85	20.18
3 ₁ #3 ₁	9.46	28.60	2607.80	1299.33	550.57	209.20	95.04	59.95	44.10	33.40	24.79
-3 ₁ #3 ₁	9.51	28.60	2585.88	1304.17	551.79	210.22	95.93	60.75	44.64	33.26	24.50
7 ₁	11.36	30.70	3754.14	2083.78	1031.58	437.69	182.80	91.39	60.26	38.55	27.10
7 ₂	12.18	32.41	4151.33	2335.80	1175.29	520.59	216.90	104.19	64.69	48.20	36.65
7 ₃	12.07	31.90	4266.00	2455.19	1279.47	572.70	238.25	110.87	67.50	49.81	39.07
7 ₄	12.61	32.53	4179.63	2408.28	1230.86	547.81	255.59	105.49	64.57	48.32	36.15
7 ₅	12.38	32.57	4405.59	2545.70	1322.81	596.79	249.70	117.50	71.85	53.40	38.61
7 ₆	12.76	32.82	4431.76	2598.96	1370.06	627.96	264.70	122.92	71.51	49.65	36.61
7 ₇	12.80	32.76	4454.30	2560.69	1348.82	609.85	250.71	113.52	66.32	48.72	38.83
3 ₁ #4 ₁	12.42	32.63	4262.10	2435.90	1301.66	611.20	260.61	123.81	76.89	55.16	44.28
-3 ₁ #4 ₁	12.42	32.63	4186.81	2444.05	1271.54	572.58	238.77	112.19	68.40	50.38	38.95

**Figure 3.** Quadratic correlations between AM1 heat of formation of carbyne knots of selected lengths and averaged crossing number (ACN) of ideal knots.

it is worth noticing that calculation of the AM1 energy for a C₁₂₀ knot with seven crossings takes ca. 3 days on a R8000 SGI computer, while the analogous calculation by a molecular mechanics method for the same structure takes less than a quarter of an hour.

The other tendency is connected with an increasing number of crossings for carbyne knots built in a constant number of carbon atoms: its energy increases as the number of crossings in the knotted structure increase. Again, this tendency was previously shown for the carbyne knots with a number of crossings not larger than six¹⁻⁴ and remains true when considering an additional nine carbyne knots with seven crossings, not studied before. It is remarkable that the molecular mechanics strain energy plotted against the number of crossings reproduces the same trend; however, for the carbyne knots composed of a greater number of carbon atoms (for example 100–120) the structure flexibility is larger and the strain energy discrepancy is greater. Moreover, energy values in Tables 1–3 show that this tendency has the same

**Figure 4.** Quadratic correlations between molecular mechanics strain energy (Sybyl force field) of carbyne knots of selected lengths and averaged crossing number (ACN) of ideal knots.

origin that the previous one has: with an increase in the number of crossings in the carbyne knot structure the molecular strain increases. As a result, molecular energy calculated either at the ab initio, or semiempirical, or even molecular mechanics level increases.

3.2. Correlations: Carbyne Knots vs Ideal Knots. The relationship between knot energy and the (topological) number of crossings is clear, yet it does not reveal differences between topologically different knots with the same number of crossings. For example, the energy of seven prime knots and two composed knots with seven crossings should be assigned to one crossing number—seven. The averaged crossing number of an ideal knot ACN³⁵⁻⁴⁰ is not an integer number, and usually for nonhomeomorphic knots with the same the (topological) crossings number is different³⁵⁻⁴⁰ (Tables 1–3). For a series of carbyne knots, Figures 3–5 demonstrate a type of relations between the heat of formation, calculated at semiempirical AM1 level, or molecular me-

Table 4. Parameters of the Linear and Quadratic (Binomial and Trinomial) Correlations between AM1 or Molecular Mechanics Energies, Calculated Using Sybyl and Merck Force Fields (y) and ACN of Ideal Knots (x , Averaged Crossing Numbers)^a

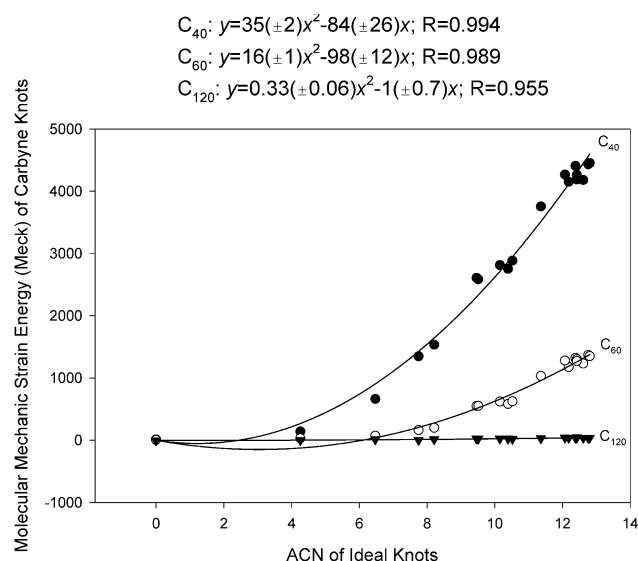
no. of C-at	semiempirical AM1 method										molecular mechanics, Sybyl force field										molecular mechanics, Merck force field									
	linear correlation $y = ax + b$			quadratic correlation $y = ax^2 + c$			quadratic correlation $y = ax^2 + bx + c$				linear correlation $y = ax + b$			quadratic correlation $y = ax^2 + c$			quadratic correlation $y = ax^2 + bx + c$				linear correlation $y = ax + b$			quadratic correlation $y = ax^2 + c$			quadratic correlation $y = ax^2 + bx + c$			
	a (Δa)	b (Δb)	Δy R	a (Δa)	c (Δc)	Δy R	a (Δa)	b (Δb)	c (Δc)	Δy R	a (Δa)	b (Δb)	Δy R	a (Δa)	c (Δc)	Δy R	a (Δa)	b (Δb)	c (Δc)	Δy R	a (Δa)	b (Δb)	Δy R	a (Δa)	c (Δc)	Δy R	a (Δa)	b (Δb)	c (Δc)	Δy R
40											463 (44)	-1446 (461)	634 0.930	32 (1)	-385 (140)	256 0.989	42 (4)	-149 (57)	66 (210)	220 0.992	427 (36)	-1299 (372)	512 0.945	29.5 (0.9)	-282 (103)	187 0.993	34 (3)	-66 (47)	-82 (173)	181 0.993
50											226 (24)	-714 (252)	346 0.915	16.0 (0.7)	-214 (87)	158 0.983	22 (2)	-107 (33)	107 (119)	125 0.990	254 (27)	-921 (281)	386 0.916	18.0 (0.7)	-362 (88)	162 0.986	26 (2)	-125 (30)	15 (109)	114 0.993
60	98 (73)	1263 (97)	133 0.932	6.89 (0.025)	1491 (30)	54 0.989	8.7 (0.8)	-28 (13)	1577 (47)	49 0.991	107 (10)	-263 (103)	142 0.933	7.4 (0.3)	-14 (35)	64 0.987	9 (1)	-26 (16)	63 (58)	61 0.989	134 (17)	-545 (182)	250 0.880	9.7 (0.6)	-275 (71)	129 0.986	17 (1)	-110 (21)	56 (76)	80 0.989
70	59 (5)	1663 (47)	65 0.952	4.0 (0.1)	1906 (14)	26 0.992	4.2 (0.5)	-2 (7)	1813 (26)	26 0.993	62 (4)	-96 (43)	59 0.963	4.2 (0.2)	62 (19)	34 0.988	3.5 (0.6)	10 (9)	30 (31)	34 0.989	60 (9)	-251 (91)	126 0.855	4.4 (0.3)	-136 (40)	74 0.952	8 (0.8)	-60 (13)	43 (47)	50 0.980
80	41 (3)	1972 (30)	41 0.961	2.79 (0.09)	2075 (11)	20 0.991	2.5 (0.3)	4 (5)	2063 (19)	20 0.991	44 (3)	-52 (28)	38 0.971	3.0 (0.1)	64 (15)	27 0.985	2.1 (0.4)	14 (6)	23 (23)	24 0.989	25 (4)	-96 (37)	50 0.861	1.8 (0.1)	-47 (16)	30 0.952	3.2 (0.4)	-22 (6)	19 (21)	22 0.976
90	31 (2)	2255 (21)	28 0.967	2.09 (0.08)	2335 (9)	17 0.988	1.7 (0.3)	7 (4)	2316 (16)	16 0.990	36 (2)	-40 (25)	35 0.964	2.4 (0.1)	56 (16)	29 0.975	1.6 (0.5)	13 (7)	16 (26)	27 0.979	11 (1)	-32 (12)	16 0.915	0.76 (0.04)	-8 (5)	9 0.976	1.0 (0.1)	-4 (2)	4 (8)	8 0.981
100	25 (1.5)	2528 (15)	20 0.973	1.64 (0.07)	2593 (8)	15 0.986	1.1 (0.2)	8 (3)	2568 (12)	13 0.990	30 (2)	-33 (22)	31 0.960	2.0 (0.1)	47 (15)	27 0.970	1.3 (0.4)	12 (7)	13 (24)	25 0.974	6.5 (0.5)	-16 (5)	7.5 0.950	0.44 (0.02)	0 (2.5)	5 0.981	0.41 (0.08)	0.5 (1)	1.5 (4.5)	4.7 0.981
110	21 (1)	2791 (12)	16 0.973	1.36 (0.06)	2846 (8)	14 0.982	0.86 (0.2)	8 (3)	2822 (11)	11 0.987	25 (2)	-28 (19)	26 0.958	1.7 (0.1)	40 (13)	23 0.968	1.1 (0.4)	9 (6)	11 (21)	22 0.973	4.9 (0.4)	-14 (4)	5.8 0.947	0.33 (0.02)	-1.6 (2.3)	4 0.974	0.29 (0.07)	0.7 (1)	-3.5 (4)	4.2 0.974
120	18 (1)	3051 (11)	15 0.973	1.18 (0.06)	3099 (7)	13 0.980	0.71 (0.2)	7 (3)	3076 (11)	11 0.986	22 (2)	-27 (18)	25 0.951	1.5 (0.1)	31 (12)	22 0.963	1.0 (0.4)	8 (5)	9 (20)	21 0.967	4.0 (0.4)	-15 (4)	5.8 0.922	0.28 (0.02)	-4.7 (2.4)	4 0.958	0.27 (0.08)	0.02 (1)	-4.7 (4.3)	4.5 0.958

^a a , b , and c denote coefficients of the fits, Δ denotes standard errors, and R denotes correlation coefficient.

Table 5. Parameters of the Triparameter Exponential Correlations between AM1 or Molecular Mechanics Energies, Calculated Using Sybyl and Merck Force Fields (y) and ACN of Ideal Knots (x , Averaged Crossing Numbers)^a

no. of C-at	semiempirical AM1 method				molecular mechanics Sybyl force field				molecular mechanics Merck force field			
	exponential correlation $y = ae^{bx} + c$				exponential correlation $y = ae^{bx} + c$				exponential correlation $y = ae^{bx} + c$			
	a (Δa)	b (Δb)	c (Δc)	Δy R	a (Δa)	b (Δb)	c (Δc)	Δy R	a (Δa)	b (Δb)	c (Δc)	Δy R
40					527 (210)	0.19 (0.03)	-743 (415)	264 0.989	777 (291)	0.16 (0.02)	-1092 (472)	233 0.990
50					144 (58)	0.23 (0.03)	-162 (152)	124 0.990	203 (85)	0.21 (0.03)	-888 (200)	149 0.989
60	98 (34)	0.20 (0.02)	1440 (72)	49 0.991	113 (44)	0.19 (0.03)	-84 (88)	58 0.990	39 (19)	0.29 (0.04)	-114 (80)	83 0.988
70	116 (39)	0.15 (0.02)	1680 (60)	28 0.991	205 (81)	0.12 (0.02)	-186 (107)	34 0.989	7.5 (4)	0.35 (0.04)	-22 (32)	39 0.987
80	113 (40)	0.13 (0.02)	1941 (56)	20 0.991	214 (88)	0.10 (0.02)	-197 (107)	25 0.988	3 (1.5)	0.36 (0.04)	0.7 (12)	15 0.988
90	116 (45)	0.11 (0.02)	2194 (58)	17 0.989	215 (126)	0.09 (0.03)	-204 (146)	28 0.979	7 (3)	0.23 (0.03)	-5 (9)	7 0.985
100	130 (52)	0.09 (0.02)	2435 (62)	13 0.989	186 (122)	0.08 (0.03)	-177 (141)	26 0.974	16 (8)	0.13 (0.03)	-19 (12)	5 0.981
110	126 (58)	0.08 (0.02)	2693 (67)	12 0.987	143 (93)	0.09 (0.03)	-134 (110)	22 0.973	15 (9)	0.12 (0.04)	-20 (12)	4 0.973
120	119 (59)	0.08 (0.02)	2955 (67)	11 0.985	114 (81)	0.09 (0.04)	-107 (97)	21 0.967	9 (7)	0.14 (0.05)	-15 (10)	5 0.957

^a a , b , and c denote coefficients of the fits, Δ denotes standard errors, and R denotes correlation coefficient.

**Figure 5.** Quadratic correlations between molecular mechanics strain energy (Merck force field) of carbyne knots of selected lengths and averaged crossing number (ACN) of ideal knots.

chanics strain energy (calculated by using two different, yet widely used, force fields: Sybyl and Merck) and ACNs of ideal knots. The correlations between carbyne knot energy and the ACN of an ideal knot is nonlinear, and generally the simplest, yet proper, fitting can be done by using second-order polynomial (Figures 3–5 demonstrate weighted correlations). The longer the carbyne knot is, the more linear the correlation seems to be (Figures 3–5). Once more, this is connected with a decrease of strain energy and asymptotic decay of the energy with knot length. On the other hand, the energy points are more scattered and goodness of quadratic correlation decreases.

Because of knots built in 120 carbon atoms, the linear model of correlation could possibly be applied, and we show that for the studied data set the quadratic model is always better than the linear one (Table 4). The goodness of the

quadratic correlation for the AM1 heats of formations with ACN, measured by correlation coefficient, R , decreases as the number of C-atoms in the carbyne knot increases. On the other hand, the goodness of the analogous linear correlation increases as the number of C-atoms in the carbyne knot increases. However, for the AM1 heats of formations, comparison of qualities (measured by R and the standard error of estimation Δy) of the linear and quadratic correlations, both two-parameter (binomial) and three parameter (trinomial), indicate that the quadratic model is always better than linear one (Table 4). Analysis of standard errors of a , b , and c coefficients (Table 4) shows that in many cases a binomial quadratic fit is methodologically more correct than a trinomial. This is the reason in Figures 3–5 that the fitting expressions presented are binomial rather than trinomial quadratic, although the latter (as a three-parameter fit) exhibits higher measures of fit goodness. Last but not least, the character of energy changes with ACN for carbynes of relatively small numbers of carbon atoms, e.g., 40–70, persuade that if we could calculate large carbyne knots (e.g., with 120 carbon atoms) with a sufficiently large crossing number, the correlation would become strongly nonlinear.

On one hand, for the large knots the correlation between energy and ACN flattens. On the other hand, for small knots the correlation is strongly nonlinear. Therefore, we also tested four-parameter cubic fits, and, in a few cases for the smallest knots, they were a bit better than quadratic. However, in our opinion fewer correlated parameters and a lower order of the fitted polynomial provide a kind of rational compromise between good fit and clear interpretation. Therefore, finally we correlate data with a three-parameter exponential expression (Table 5), in which the quality is practically the same as the three-parameter trinomial quadratic fit (Table 4). Thus, at this stage of study it is difficult to judge between whether the polynomial or exponential model is more exact to express the relationship between the carbyne knot energy and the ACN parameter of ideal knots.

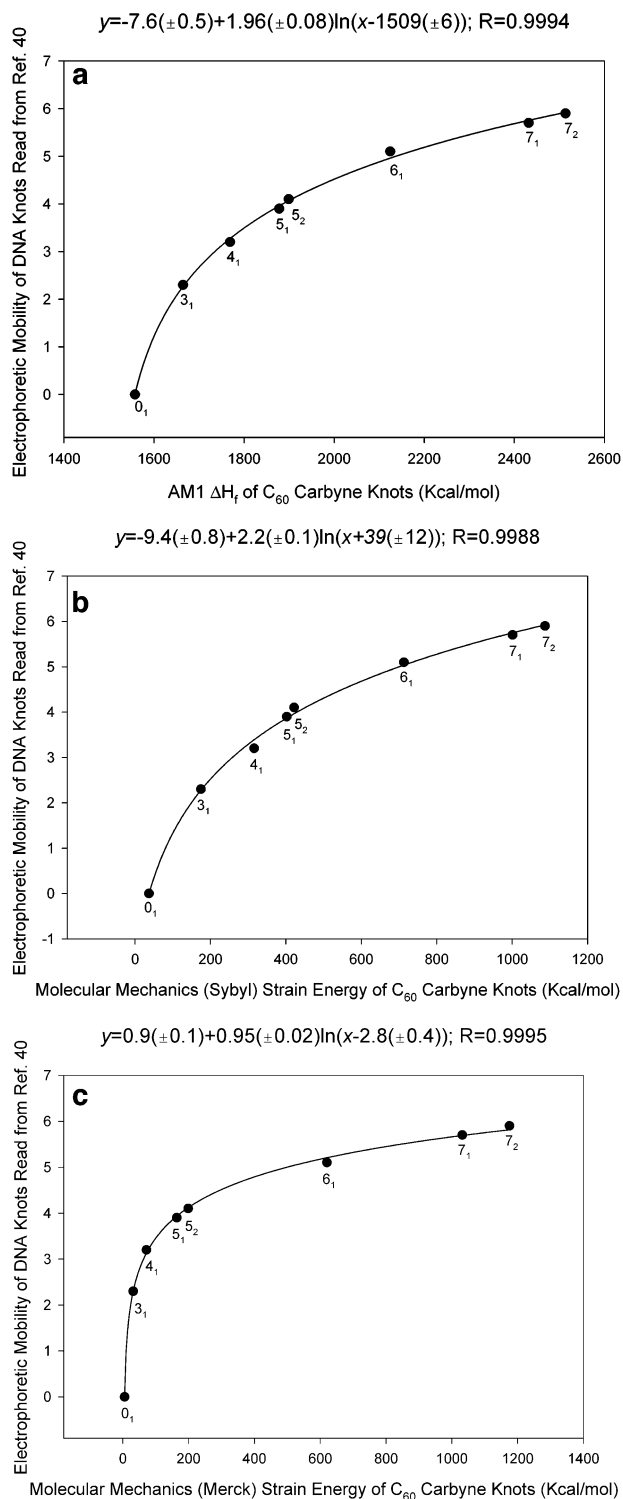


Figure 6. Correlations between the electrophoretic mobilities of DNA knots (read from ref 40) and energy calculated for carbyne knots (a) AM1 heat of formation, (b) MM Sybyl force field strain energy, and (c) MM Merck force field strain energy.

Data collected in Tables 4 and 5 can also serve for comparison of the calculation methods used in this paper. The correlations of molecular mechanics strain energies with ACN undergo similar trends (Tables 4 and 5). However, the qualities of quadratic (Table 4) and exponential (Table 5) correlations for the two molecular mechanics method are similar and none of them can be favored, while that for the AM1 semiempirical method is always better than them.

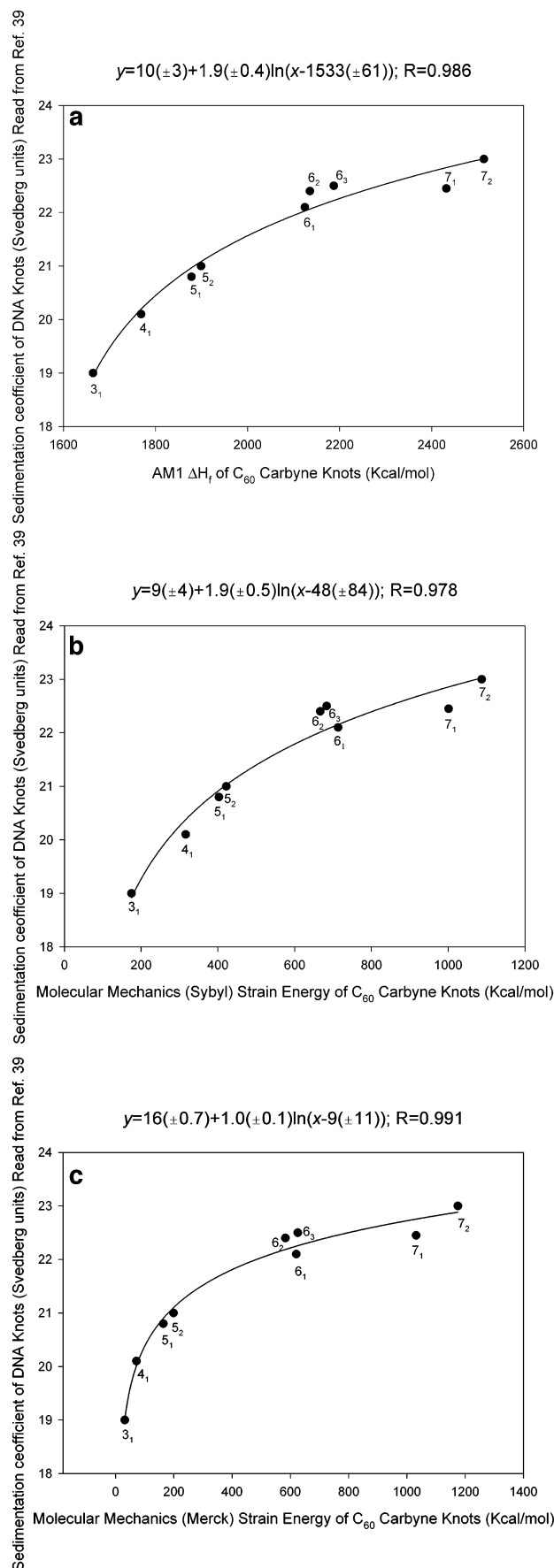


Figure 7. Correlations between the sedimentation coefficients of DNA knots (read from ref 39) and energy calculated for carbyne knots (a) AM1 heat of formation, (b) MM Sybyl force field strain energy, and (c) MM Merck force field strain energy.

In Tables 1–3 we show two characteristics of ideal knots ACN and L/D. Nevertheless, for the set of the ACN and L/D values collected here correlation between them is, with good precision, linear. Therefore, energies calculated in this paper correlate with L/D resembling correlations with ACN and therefore we shall not present them.

3.3. Correlations: Carbyne Knots vs DNA Knots. So far, we showed that the energies of carbyne knots, both calculated semiempirically and by molecular mechanics methods, correlate with parameters of ideal knots, ACN and L/D. On the other hand, we know that ACN and L/D correlate with parameters of DNA knots: electrophoretic mobility and sedimentation coefficient.^{35–40} So, based on supposed transitive property between correlations: if *A* correlates with *B* and *B* correlates with *C*, then *A* correlates with *C*, one could formulate a conclusion that DNA knots electrophoretic mobility and DNA knots sedimentation coefficients do correlate with carbyne knots energies. For experimental data correlations, such a transitive property has, however, its limitation which is connected with the magnitude of errors: if errors are too large then error propagation may release any correlation between *A* and *C*. The numerical values of electrophoretic mobility and sedimentation coefficients of DNA knots were not published and the plots against ACN were given, only.^{35,39,40} Therefore, we measured the corresponding values from the published pictures (Table 1) and correlated them with our energetic values of carbyne knots (Figures 6 and 7).

The correlations are undoubtedly nonlinear and meaningful (Figures 6 and 7). We used for them the logarithm model which is reciprocal to the previous exponential correlation between carbyne knot energy and ACN. The correlation coefficients for such correlations, especially for those between the carbyne knot energy and electrophoretic mobility, are striking (Figures 6 and 7).

Based on the quality of such a correlation one would formulate a hypothesis that

$$\Delta E = ae^{bX} \quad (1)$$

where ΔE is the calculated energy of carbyne knots, *a* and *b* are coefficients, and *X* is the parameter characterizing DNA knots properties or characteristic of ideal knots such as ACN or L/D. However, again taking into account a similar good quality of the quadratic models discussed before, at this stage of study the expression (1) should be treated only as a postulate. Finally, let us stress that easily available molecular mechanics energies yield quite acceptable energies for further correlations with DNA knot parameters.

4. CONCLUSIONS

In this study we calculated prime and composed carbyne knots built in 40, 50, ..., 120 carbon atoms, up to systems with seven crossings, using semiempirical AM1 and molecular mechanics methods. We showed that semiempirical AM1 and molecular mechanics energies correlate nonlinearly with characteristics of ideal knots. Finally, we presented correlations between parameters describing the electrophoretic mobilities and the sedimentation coefficients of DNA knots and the energies calculated for carbyne knots. Thus, we showed that model knots containing only carbon atoms can constitute a model for large DNA knots at least

for several important characteristics. Finally, we stress that simple and widely accessible approaches such as the molecular mechanics method may produce valuable data for further correlations.

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