

Model Carbyne vs Ideal and DNA Catenanes

Jan Cz. Dobrowolski^{*,†,‡} and Aleksander P. Mazurek[‡]

Industrial Chemistry Research Institute, 8, Rydygiera Street, 01-793 Warsaw, Poland, and National Institute of Public Health, 30-34, Chełmska Street, 00-725 Warsaw, Poland

Received January 8, 2005

The structure and stability of two-component carbyne catenanes, viewed as model compounds for DNA catenanes, have been estimated by molecular mechanics (MM) calculations. The carbyne catenane molecules studied were composed from intertwined cyclic molecules constituted solely from carbon atoms bonded by alternating single and triple bonds. The total number of carbon atoms in molecules studied was set to 60, and the complementary sizes of the catenane components varied. The component cycles were entangled by 2, 4, ..., 11 crossings. For the catenanes with the number of crossings equal to six and seven more than one catenane topological type was considered. The calculated MM strain energy of carbyne catenanes was correlated with the averaged crossing number and length-to-diameter ratio of ideal catenanes as well as the electrophoretic mobility and sedimentation coefficient of DNA catenanes. To observe these correlations, for each topological type of carbyne catenane, it was necessary to find the proportion of the sizes of the two catenane components at which the MM strain energy is the lowest. Then, the values of these energies were correlated with characteristics of ideal and real DNA catenanes. The fits are significant and nonlinear.

1. INTRODUCTION

Ten years after the structure of DNA was solved by Watson and Crick,¹ Vinograd and co-workers discovered a circular double-stranded DNA.^{2,3} The circular double-stranded DNA can be present in three main forms:⁴ relaxed, partially unreleased, and superhelical (or supercoiled), and it is widespread: it appears in plant chloroplasts as chromosomal DNA and in viruses and bacteria. The circular double stranded DNA has an important property—it cannot be disentangled without breaking one of the strands. Each circular DNA duplex is simultaneously a catenane (a link structure), i.e., a molecule composed of two or more cycles (or generally knots) linked together.^{5–7} A circular DNA structure can be characterized by three numbers Lk (the linking number which is two times larger than the number of crossings of the two strands), Tw (the twisting number which is the number of turns of ribbon borders about the helix axis), and Wr (the writhing number which is the number of self-crossings of the helix axis).⁴ These numbers were introduced by Fuller based on the analysis of orientable ribbon homeomorphic with $S^1 \times [-1,1]$,^{8,9} and, as was found by White,¹⁰ for cyclic ribbons to be interrelated: $Lk = Tw + Wr$.^{4,11} If one strand of a circular DNA duplex is nicked and then ligated with a ligase, a nonhomogeneous mixture is produced, and by using electrophoretic separation, one can distinguish a variety of circular DNA isomers which differ by Lk numbers.^{12–17}

In 1967 a catenane of two circular single strand DNAs ([2]-catenane or catenane of the type 2^2_1) were synthesized from phage DNA by Wang and Schwartz¹⁸ and [2]-, [3]-, ..., [7]-catenanes of circular DNA duplexes were isolated from the mitochondria of human cells by Hudson and

Vinograd¹⁹ and Clayton and Vinograd.²⁰ Mitochondrial DNA exists in the form of the circular duplex in most eukaryotes, and till the mid 1970s, the DNA catenanes were found in most organisms: in viruses, bacterial plasmids, circular salamander chromosomes, mammals mitochondria, and human leucocytes.⁶ It is also possible to synthesize DNA catenanes (as well as knots) in vitro by integrative recombination of superhelical DNA.^{21–26} In this way, Mizuuchi and co-workers obtained 2^2_1 and 4^2_1 DNA catenanes (where the notation N^C_S means that the number of crossings in the catenane is equal to N ; it is composed of C components; and its serial number in catenane classification tables is S). Kreutzer and Cozzarelli's investigation of gyrase, which is a topoisomerase of type 2, i.e., cuts the two DNA strands, has shown that [2]-, [3]-, and [4]-catenanes were formed.²³ The other enzyme, resolvase Tn3, produces mainly the 2^2_1 catenane and only 1% of catenanes with a greater number of crossings²⁶ such as 5^2_1 .²⁷ Unlike resolvase, topoisomerase I, generates a variety of different DNA catenanes (as well as DNA knots).^{28,29} DNA catenanes and knots can be observed by electron microscopy;²⁸ however, it appears that by electrophoresis one can separate topological DNA isomers which differ in the number of crossings³⁰ and even in the torus and nontorus topology.³¹ In this way, the right-handed catenanes, 4^2_1 , 6^2_1 , 8^2_1 , ..., 20^2_1 , products of site specific integrase action on the circular DNA, were separated electrophoretically, and it was shown that the greater the crossing number the faster they migrate.³⁰ Probably the most impressive examples of the DNA catenanes may be found in mitochondrial kinetoplasts of a unicellular parasite of the Kinetoplastidae order of the Flagellata class: they are composed of thousands of linked circular DNA.^{32–40}

Electrophoretic mobilities as well as sedimentation coefficients of the DNA knots and catenanes were linearly correlated with characteristics of ideal knots and links

* Corresponding author e-mail: janek@il.waw.pl.

[†] Industrial Chemistry Research Institute.

[‡] National Institute of Public Health.

Table 1. Variations of the Molecular Mechanics (MMFF94) Strain Energy (kcal/mol) of the C₆₀ Carbyne Catenanes with Change of the Size of the Two Components and Topological Catenane Type^a

	topological type of carbyne catenane															
ΔC	$0^1_1+0^1_1$	221	421	521	621	622	623		721	724		821	921	1021	1121	
40	126.97	338.48	1004.99	1145.09	1797.18	1843.54			1975.66	1407.93		1457.99	2822.30	3329.92	4306.03	
36	109.82	193.36	642.82	815.15	1194.90	1257.98			1424.45	1139.71		1180.26	2037.47	2699.25	3472.88	
32	98.01	117.08	418.19	668.33	825.32	905.98			1125.93	1022.77	2253.74	1073.82	1595.84	2383.69	3003.08	
28	89.49	87.18	272.67	603.22	596.24	698.49			997.30	988.50	1920.09	1031.67	1378.96	2281.28	2851.07	
24	83.16	76.95	188.30	609.32	462.74	580.43	823.22		972.03	1006.11	1703.76	1050.13	1342.98	2284.64	2830.55	4887.13
20	78.44	72.00	145.50	594.27	422.02	527.62	757.25		932.17	994.61	1516.78	1075.38	1365.39	2280.43	2882.51	4588.24
16	74.95	68.57	124.95	543.75	433.13	529.25	672.48		939.72	1001.83	1451.51	1150.89	1371.05	2302.14	2870.08	4360.97
12	72.41	65.90	116.11	471.61	427.09	549.00	615.55	1107.72	968.42	1045.31	1315.05	1217.15	1377.89	2280.48	2846.74	4215.52
8	70.69	63.59	119.06	416.28	438.13	536.06	562.64	980.98	925.34	1126.67	1250.59	1328.35	1353.65	2264.18	2859.01	4122.30
4	69.69	61.04	123.32	366.18	425.71	488.19	540.12	871.23	952.20	1268.90	1136.80	1435.30	1352.86	2255.77	2887.23	4130.00
0	70.04	58.49	124.90	332.17	438.13	469.02	534.44	778.73	1002.37	1431.45	1000.97	1566.36	1373.19	2244.03	2893.98	4171.90
-4	69.69	61.04	123.32	301.48	425.71	488.19	540.12	716.33	1074.30	1701.84	1031.53	1659.66	1352.86	2250.16	2887.23	4154.65
-8	70.69	63.59	119.06	279.50	438.31	536.03	562.64	661.33	1155.44	1981.30	994.73	1794.04	1353.65	2272.84	2859.01	4113.97
-12	72.41	65.90	116.11	258.99	427.09	552.55	615.55	623.90	1258.46	2295.09	974.56	1988.40	1377.89	2470.74	2846.74	4177.65
-16	74.95	68.57	124.95	244.93	433.13	529.25	672.48	586.47	1384.44	2690.96	1009.98	2143.59	1371.05	2638.08	2870.08	4154.65
-20	78.44	72.00	145.50	238.14	422.02	529.11	757.25	554.82	1519.90	3454.65	1050.86	2339.83	1365.39	2861.86	2882.51	4153.35
-24	83.16	76.95	188.30	262.67	462.74	580.43	823.22	536.28	972.03		1125.02	2581.20	1342.98	3114.76	2830.55	4138.40
-28	89.49	87.18	272.67	331.37	596.24	698.49		557.47			1157.72		1378.96	2281.28	2851.07	4133.87
-32	98.01	117.08	418.19	469.00	825.32	905.98		646.78			1205.79		1595.84		3003.08	4240.83
-36	109.82	193.36	642.82	685.61	1194.90	1257.98		830.13			1271.91		2037.47		3472.88	4645.70
-40	126.97	338.48	1004.99	1044.41	1797.18	1856.35		1147.31			1479.26		2822.30		4306.03	

^a ΔC stands for the difference in number of the C atoms in the two catenane components.**Table 2.** Variations of the Molecular Mechanics (SYBYL) Strain Energy (kcal/mol) of the C₆₀ Carbyne Catenanes with Change of the Size of the Two Components and Topological Catenane Type^a

	topological type of carbyne catenane															
ΔC	$0^1_1+0^1_1$	221	421	521	621	622	623	721	724		821	921	1021	1121		
40	303.96	476.13	1540.10	1184.93	2740.37	2796.75		2954.06	2055.32		2120.28	4214.18	4847.43	6297.41		
36	262.93	292.85	891.37	1193.07	1725.35	1806.53		1972.77	1470.47		1541.03	2917.54	3746.17	4935.84		
32	234.55	230.79	554.93	902.52	1137.28	1226.16		1438.10	1227.46		1317.60	2134.82	3212.10	4212.58		
28	214.08	206.35	398.27	806.09	816.04	912.84		1213.79	1177.92	2813.27	1253.74	1737.59	3036.65	3954.64		
24	198.97	191.03	329.20	825.22	657.87	749.75	1028.45	1166.44	1218.45	2361.87	1272.15	1651.25	3084.67	3982.33		
20	187.73	179.93	297.38	824.39	614.35	695.45	971.10	1124.20	1203.40	2018.05	1303.28	1701.08	3031.84	4093.29	7418.13	
16	179.44	172.09	282.36	786.28	637.95	719.57	864.40	1140.53	1203.33	1819.91	1401.72	1711.74	3104.24	4008.33	6902.23	
12	173.45	165.39	273.82	702.84	636.71	744.51	790.67	1148.34	1267.75	1684.80	1513.19	1699.29	3048.38	4044.22	6504.45	
8	169.40	159.92	265.47	629.25	642.34	723.77	733.68	1275.41	1108.97	1391.00	1528.26	1679.65	1666.51	3012.38	4028.72	6280.95
4	167.06	155.35	261.08	575.37	624.89	670.22	709.79	1117.74	1144.07	1628.33	1411.26	1846.46	1671.32	3000.34	4065.82	6168.83
0	166.30	150.94	260.18	539.11	604.93	640.22	700.99	989.55	1216.41	1918.02	1317.75	2062.76	1709.74	2990.41	4056.41	6191.15
-4	167.06	155.35	261.08	505.89	624.89	670.22	709.79	906.77	1316.51	2361.08	1242.27	2226.50	1671.32	3001.86	4065.82	6275.92
-8	169.40	159.92	265.47	475.96	642.34	723.77	733.68	838.72	1442.47	2869.80	1199.34	2482.21	1666.51	3177.46	4028.72	6285.32
-12	173.45	165.39	273.82	454.48	636.71	744.51	790.67	795.49	1602.01	3557.98	1167.94	2863.95	1699.29	3396.34	4044.22	6109.17
-16	179.44	172.09	282.36	441.90	637.95	719.57	864.40	765.48	1825.50	4177.65	1214.69	3113.08	1711.74	3709.26	4008.33	6233.60
-20	187.73	179.93	297.38	436.54	614.35	695.45	971.10	735.20	2042.79		1278.32	3516.66	1701.08	4110.53	4093.29	6166.85
-24	198.97	191.03	329.20	451.97	657.87	749.75	1028.45	719.26	1166.44		1378.32	1378.32	1651.25	4611.32	3982.33	6207.78
-28	214.08	206.35	398.27	511.80	816.04	912.84		736.18			1398.87		1737.59	3036.65	3954.64	6194.71
-32	234.55	230.79	554.93	662.36	1137.28	1226.16		852.20			1433.02		2134.82		4212.58	6237.37
-36	262.93	292.85	891.37	990.69	1725.35	1806.53		1163.78			1593.17		2917.54		4935.84	6296.29
-40	303.96	476.13	1540.10	1635.92	2740.37	2796.75		1776.60			2105.06		4214.18		6297.41	6763.38

^a ΔC stands for the difference in number of the C atoms in the two catenane components.

(catenanes).^{41–46} An ideal knot is a knotted torus which has minimal length-to-diameter ratio (or minimal volume-to-surface ratio), and an ideal n-component link (n-component catenane) is a system of n-interwined toruses of minimal length-to-diameter ratio.^{41–46} The ideal knots or links can be understood as solids formed from the corresponding DNA knots or catenanes, averaged over all trajectories of stochastic movements of the molecule.⁴³ The geometrical formulas describing shapes of ideal knots or links have not been found; however, necessary conditions that should be satisfied by the formulas are known.⁴⁸ So far, the numerical determination of the shape of an ideal knot or link is still a difficult task.^{49,50} To characterize ideal knots and links, the averaged crossings number (ACN) and averaged writhing number (AWN) were

introduced.^{41–49} These numbers are found by averaging crossing numbers over all projections of an ideal figure on a sphere and either ignoring or taking into account the sign of a crossing in the case of ACN or AWN, respectively. In contrast to the topological crossing number and the topological writhing number, ACN and AWN are not necessarily integers. Thus, knowing ACNs for a series of the ideal knots or catenanes, linearly correlated with their length-to-diameter ratios, one can predict the electrophoretic mobilities or sedimentation coefficients of the DNA knots or catenanes.^{41–47}

Despite living organisms easily synthesizing a multitude of topological structures, a chemical catenane was first reported in 1960 by a chemist—Wasserman⁵¹—who proved the presence of the catenane synthesized “statistically” by

using both IR monitoring of deuterated molecules and chromatographical analysis. Microamounts of catenanes were next synthesized by olefin metathesis.^{52–54} More rational synthesis proposed by Frish and Wasserman⁵⁵ and modified by Schill⁵⁶ was to synthesize first a doubly twisted chemical Möbius strip which next can be selectively transformed into catenane. Such a synthesis became possible when Walba synthesized a chemical Möbius strip for the first time.⁵⁷ First, fully controlled synthesis of a [2]catenane was introduced by Shill and Lüttringause in 1964^{58,59} and a [3]catenane by Schill and co-workers.^{60,61} However, a real breakthrough in catenane synthesis was a template synthesis by Dietrich-Buchecker and Sauvage in 1984 which enabled in obtaining catenanes with high yields.⁶² Nowadays, catenane synthesis is a well-known field of chemistry, yet its importance seems to increase permanently.^{63–70}

For a few years we have been studying model topological isomers,^{71–83} which in the case of knots and catenanes (links) have had the form of compounds built solely from $(C\equiv C-)_n$ motifs.^{72–75} Unlike diamond and graphite which have been known for a millenia and which are comprised solely from the sp^3 and sp^2 carbon atoms, respectively, carbon allotrope built only from the sp carbon atoms is a matter of debate till now.⁸⁴ According to Heimann et al.,⁸⁵ *chaoite*^{86,87} is just a mineral form of carbynes. However, on one hand, in the early 1980s assignment of the carbyne structure to chaoite was still a matter of serious controversy,⁸⁸ and, on the other hand, carbon IX was discovered by Whittaker et al.⁸⁹ and interpreted as built from “crystal forms containing triple bonds”. Moreover, according to Kudryavtsev et al.,⁹⁰ in 1969 polymers with long $(C\equiv C-)_n$ chains were synthesized and named carbynes, yet a well-proven synthesis of long carbynes with chain lengths in excess of 300 C-atoms was done as late as in 1995.⁹¹ After all, studies on the mobility of cationic and anionic carbon clusters have shown that in carbon plasmas there are besides fullerenes also linear, cyclic, bicyclic, and tricyclic carbynes.^{92,93} It appears that for an even number of carbon atoms, carbynes are more stable as the cyclic singlets than the linear triplets, while for the odd numbers of carbon atoms they are more stable as the cummulenic singlets than the cyclic triplets.^{93,94} Many $(C\equiv C-)_n$ carbynes are identifiable in interstellar space, as well.^{95–97} Also, there is an increasing number of reports on the syntheses of compounds including long $(C\equiv C-)_n$ moieties.^{98–106} Last but not least, carbon clusters, carbynes included, have been intensively studied by mathematical chemistry methods.^{107–118}

The aim of this paper is to show correlations between energetics of the model carbyne catenanes and parameters describing the ideal catenanes and the DNA catenanes. Recently, we have shown such a correlation between the energy of carbyne knots and the averaged crossing number (ACN) of the ideal knots and the electrophoretic mobility as well as the sedimentation coefficient of DNA knots.⁸¹ We have shown also that the correlations obtained by using the molecular mechanics (MM) force fields are quite comparable to those obtained by using the much more time-consuming AM1 semiempirical method.⁸¹ This type of correlation indicates a relatively easily available computational model which can support experimental separation analysis of DNA knots. However, for the carbyne catenanes composed from two cyclic components the problem is more complicated.

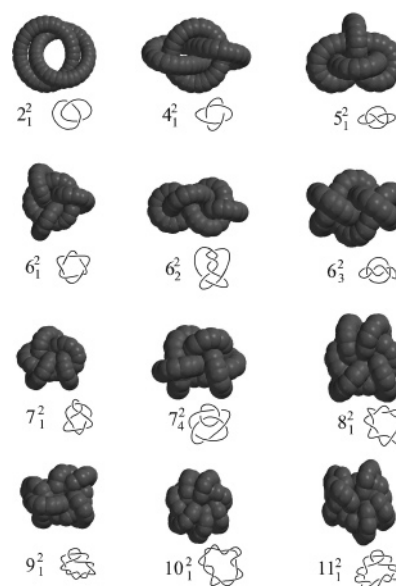


Figure 1. The MM optimized structures of C_{60} carbyne catenanes studied, their regular diagrams, and notation.

For the same total number of carbon atoms and the same topological type, there are several isomers of different component sizes and energies.⁷⁵ The graph presenting energy changing as a function of the component size difference was called the catenamer potential.⁷⁵ Here, we show that by selection of the lowest energy isomer from each set of isomers of the constant overall number of atoms and the same topological type (i.e., the selection of the minimum of the catenamer potential), one can obtain statistically significant, nonlinear correlations between the MM strain energy of carbyne catenane and ACN of the ideal catenanes as well as the electrophoretic mobilities and the sedimentation coefficients of the DNA catenanes.

2. COMPUTATIONS

The construction of structures and molecular modeling using the MMFF94^{119–125} and Sybyl^{125,126} force fields for the molecular mechanics (MM) optimizations were performed using the Spartan 4 package of programs with a graphical interface.¹²⁷ Data correlations were done by using SigmaPlot 2000 software.¹²⁸

3. RESULTS AND DISCUSSION

The MMFF94 force fields optimized structures of the lowest energy C_{60} carbyne catenanes are depicted in Figure 1. The strain energies calculated by using the two MM force fields are collected in Tables 1 and 2. The exemplary catenamer potentials are presented in Figure 2, and correlations between the MM strain energy of carbyne catenanes and ACNs of the ideal catenanes and the DNA electrophoretic mobilities and sedimentation coefficients are shown in Figure 4. Data displaying goodness of fits between the strain energy and parameters of the ideal catenanes are gathered in Table 4.

3.1. Energy Trends in Carbyne Catenanes. Two main tendencies can be observed for the MM strain energy of carbyne knotted or linked structures: it increases with the number of crossings and decreases with the number of atoms constituting the molecule.^{71–75,79,81} However, in one yet

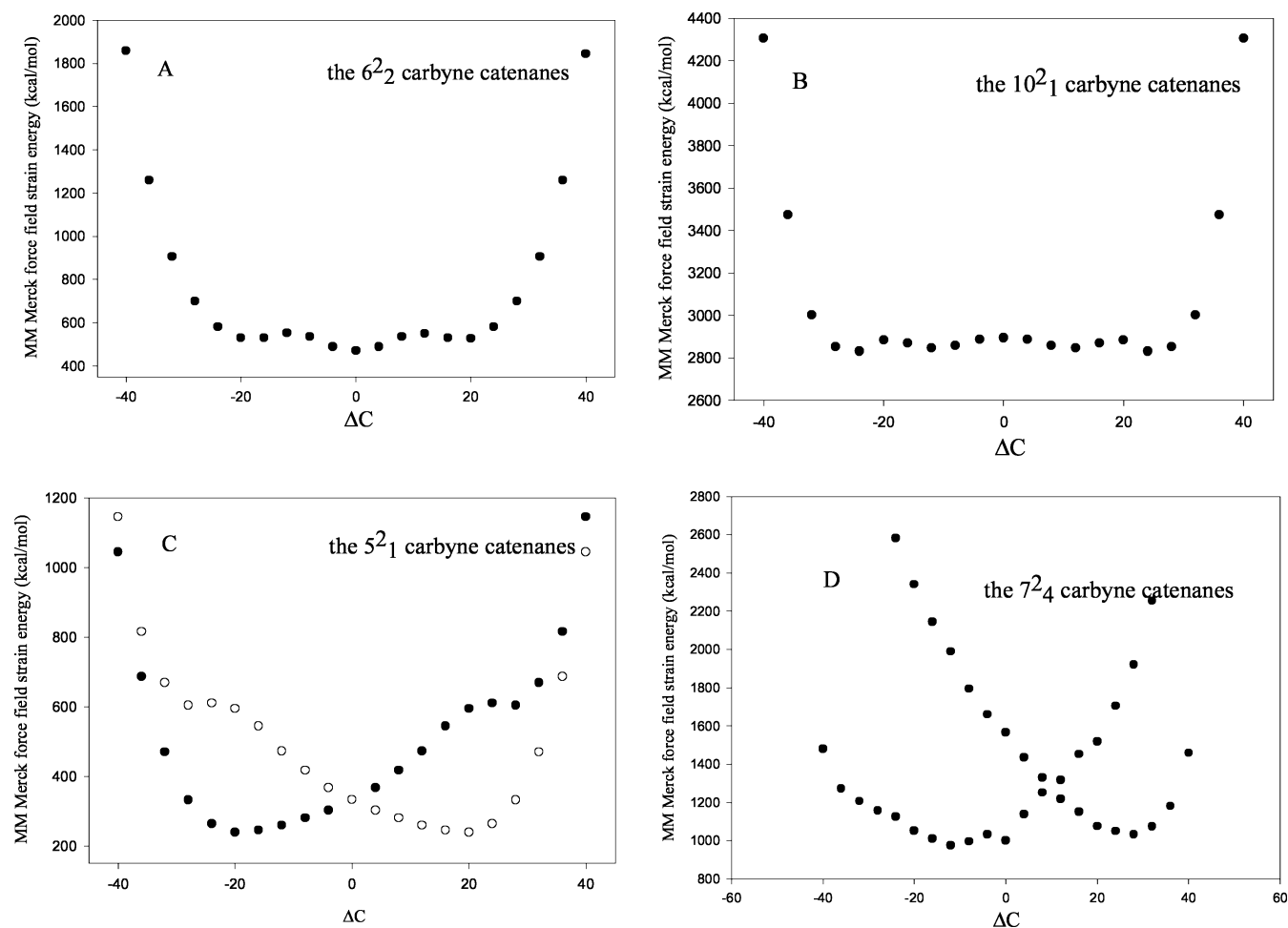


Figure 2. The catenamer potentials for 5^2_1 (top), 6^2_2 (middle), and 10^2_1 (bottom) C_{60} carbyne catenanes optimized by using MM strain energy and MMFF94 force field.

Table 3. Juxtaposition of the MM Strain Energies of the Lowest Energy Catenamers of Given Topological Type with the Length-to-Diameter (L/D) Ratio and the Averaged Crossing Number (ACN) of the Ideal Catenanes and Electrophoretic Mobility (EM) and the Sedimentation Coefficient (SC) of DNA Catenanes

topological type	MM strain energy (kcal/mol)		ideal catenane parameter ⁴⁷		DNA catenane parameter	
	MMFF94	SYBYL	L/D	ACN	EM ¹¹⁰	SC ⁴⁵
221	58.49	150.94	12.7	2.4	0.95	23.5
421	116.11	260.18	20.6	6.2	2.55	25.3
521	238.14	436.54	26.0	8.6		
621	422.02	604.93	28.7	9.9	4.60	26.8
622	527.62	640.22	29.7	10.1		
623	534.44	700.99	32.3	11.2		
721	925.34	1108.97	34.1	12.4		
724	974.56	1167.94	35.2	12.8		
821	1342.98	1651.25	37.2	14.0	6.70	28.2
921	2244.03	2990.41	42.7	16.8		
1021	2830.55	3954.64	46.1	18.6		29.4
1121	4113.97	6109.17	52.1	22.1		

important detail, the tendencies for the knots differ from those for the catenanes. This results from a specific catenane isomerism that arises with the presence of at least two components in their structures: Such catenanes can have several constitutional isomers of the same topological type but simply differing in component sizes. Such isomers we have called catenamers.⁷⁵ Interestingly, they are simultaneously constitutional isomers and topological isomers;⁸³ the latter are usually considered as a specific type of stereoisomers.^{129,130}

Obviously, two catenamers differ in their strain energy because of differences in the strain energies of individual cycles and in the strain energy originated from the crossings between cycles. For example, at the HF/STO-3G level, two C_{60} Hopf's links 2^2_1 , $C_{10}C_{50}$ and $C_{30}C_{30}$, differ in energy by as much as 320 kcal/mol.⁷⁵ The plot which displays the catenamer energy changes against the difference in the component size we have named the catenamer potential.⁷⁵ Here, we illustrate the same kind of tendency arising with the molecular mechanics MMFF94 force field calculations (Figure 2, Tables 1 and 2). The graphs displaying the MM energies obtained by using the Sybyl force field are similar.

The most important feature of the graphs of Figure 2 are the minima present in each of them. These minima correspond to the most stable molecule out of the group of catenanes of the same topological type and of diverse component cycle sizes. The catenamer potentials are expected to be symmetric with respect to the vertical axis when the difference between the cycle sizes equals zero, $\Delta C = 0$. This kind of catenamer potentials were found, inter alia, for the 6^2_2 and 10^2_1 C_{60} carbyne catenanes, parts A and B of Figure 2, respectively.

For the 5^2_1 C_{60} carbyne catenanes (as an example), the catenamer potential (Figure 2C) demonstrates two asymmetric graphs that cross each other at $\Delta C = 0$. The two curves demonstrate the fact that the calculations often do

Table 4. Parameters of the Model Correlations between the MM Strain Energies of the Lowest Energy Catenamers and the Length-to-Diameter (L/D) Ratio or the Averaged Crossing Number (ACN) of the Ideal Catenanes^a

fitting model	fitting parameters							
	MMFF94				SYBYL			
	<i>a</i>	<i>b</i>	<i>c</i>	(Δy)	<i>a</i>	<i>b</i>	<i>c</i>	(Δy)
$y=ax^2+bx+c$	(Δa)	(Δb)	(Δc)	R	(Δa)	(Δb)	(Δc)	R
$x=L/D$	3.6	-130	1171	(250).	5.8	-235	2390	(508).
	(0.2)	(1)	(187)	0.9964	(0.4)	(24)	(380)	0.9929
$y=ax^2+c$	1.68		-831	(958)	2.39		-1232	(1748)
$x=L/D$	(0.13)		(175)	0.9469	(0.23)		(320)	0.9155
$y=ae^{bx}+c$	146	0.067	-489	(460)	95	0.081	-335	(570)
$x=L/D$	(62)	(0.008)	(212)	0.9877	(37)	(0.007)	(200)	0.9910
$y=ae^{bx}$	48	0.086		(642)	49	0.093		(680)
$x=L/D$	(12)	(0.005)		0.9761	(10)	(0.004)		0.9973
$y=ax^2+bx+c$	12.7	-9.9	197	(254)	21.3	-223	668	(331)
$x=aCN$	(0.7)	(1.8)	(110)	0.9963	(0.9)	(24)	(144)	0.9970
$y=ax^2+c$	9.0		-358	(520)	12.9		-578	(1073)
$x=aCN$	(0.4)		(78)	0.9843	(0.7)		(161)	0.9681
$y=ae^{bx}+c$	431	0.111	-751	(496)	327	0.138	-584	(624)
$x=aCN$	(164)	(0.015)	(303)	0.9858	(113)	(0.014)	(273)	0.9892
$y=ae^{bx}$	128	0.160		(763)	144	0.172		(834)
$x=aCN$	(28)	(0.011)		0.9664	(26)	(0.009)		0.9808

^a Δ denotes standard error; R stands for the correlation coefficient.

not converge to the conformer of lowest energy at a given component size difference (ΔC value), and, instead of symmetric graphs, two asymmetric ones appear. The asymmetric graphs are, however; symmetric to each other about the vertical axis at $\Delta C = 0$, and the pair of symmetric graphs correspond to the molecules which structures are essentially the same, yet the first cyclic component of the first molecule corresponds to the second cyclic component of the second molecule and oppositely. These structures are symmetrical “by cyclic component exchange” if the cycles are distinguished. The two symmetric graphs may appear inequivalent in our computations because a failing of the convergence algorithm and/or a “real” structure freezing as a higher energy local-minimum conformer. In searching for the optimal structures, in this study the calculations were performed by using two different MM force fields, yet they both lead to the same qualitative picture of the catenamer potentials. Nevertheless, we cannot arbitrate univocally between the two possibilities for the graph asymmetries, because a third factor may also perturb the symmetry of the potentials. Relatively small sizes of the carbyne compounds considered may result in difficulties in relaxation of the optimized structure; however, this very factor enables calculations in a reasonable time.

Despite conformers originating from “the cyclic component exchange”, other conformers can coexist, too.⁷⁵ Examples for such a coexistence can be found in the 6^2_3 and 7^2_4 catenanes (Tables 1 and 2, Figure 2D). To make Tables 1 and 2 more compact, we show there the symmetric potentials and only one of the two branches of asymmetric potentials.

For the purpose of this study, we focus our attention on the minima at the catenamer potentials, only. Energies of the structures corresponding to these minima will be further correlated to the properties of the ideal and DNA catenanes.

Because majority of oriented links (catenanes) is chiral¹³¹ it is important to point out finally that the energies obtained by quantum or MM calculations for enantiomers are identical.¹³² This is why here the chirality of the catenanes studied

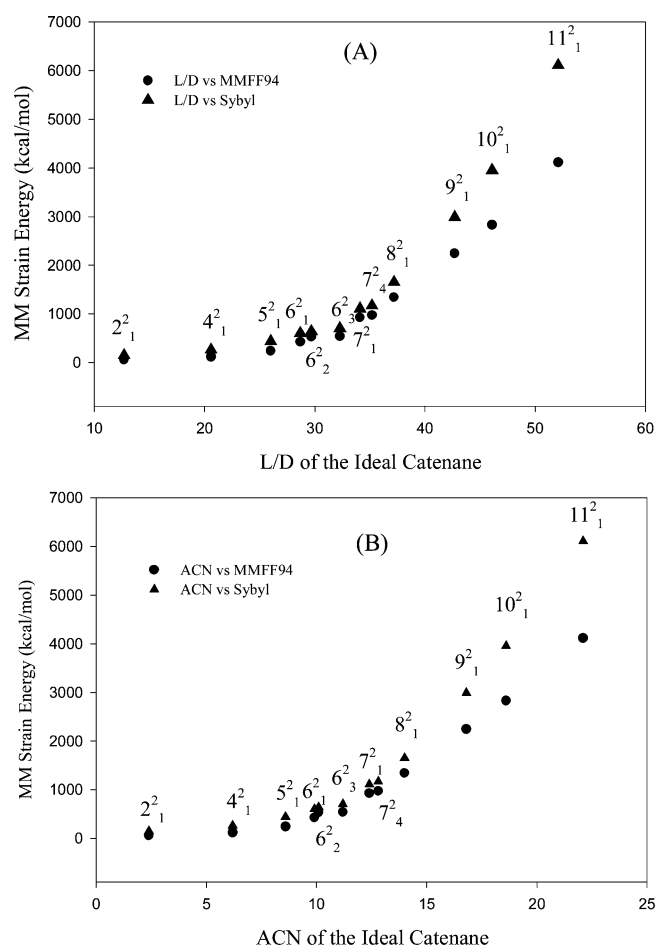


Figure 3. Plot of MM strain energy of the lowest energy carbyne catenanes against (A) length-to-diameter ratio (L/D) and (B) averaged crossing number (ACN) of the ideal catenanes.

is not addressed. Nevertheless, topological chirality of knots and links is an important notion not only of chemistry and physics but also of modern topology, since so far, there are not many general theorems concerning the notion.¹³³ Indeed, using appropriate polynomials assigned to a given link or

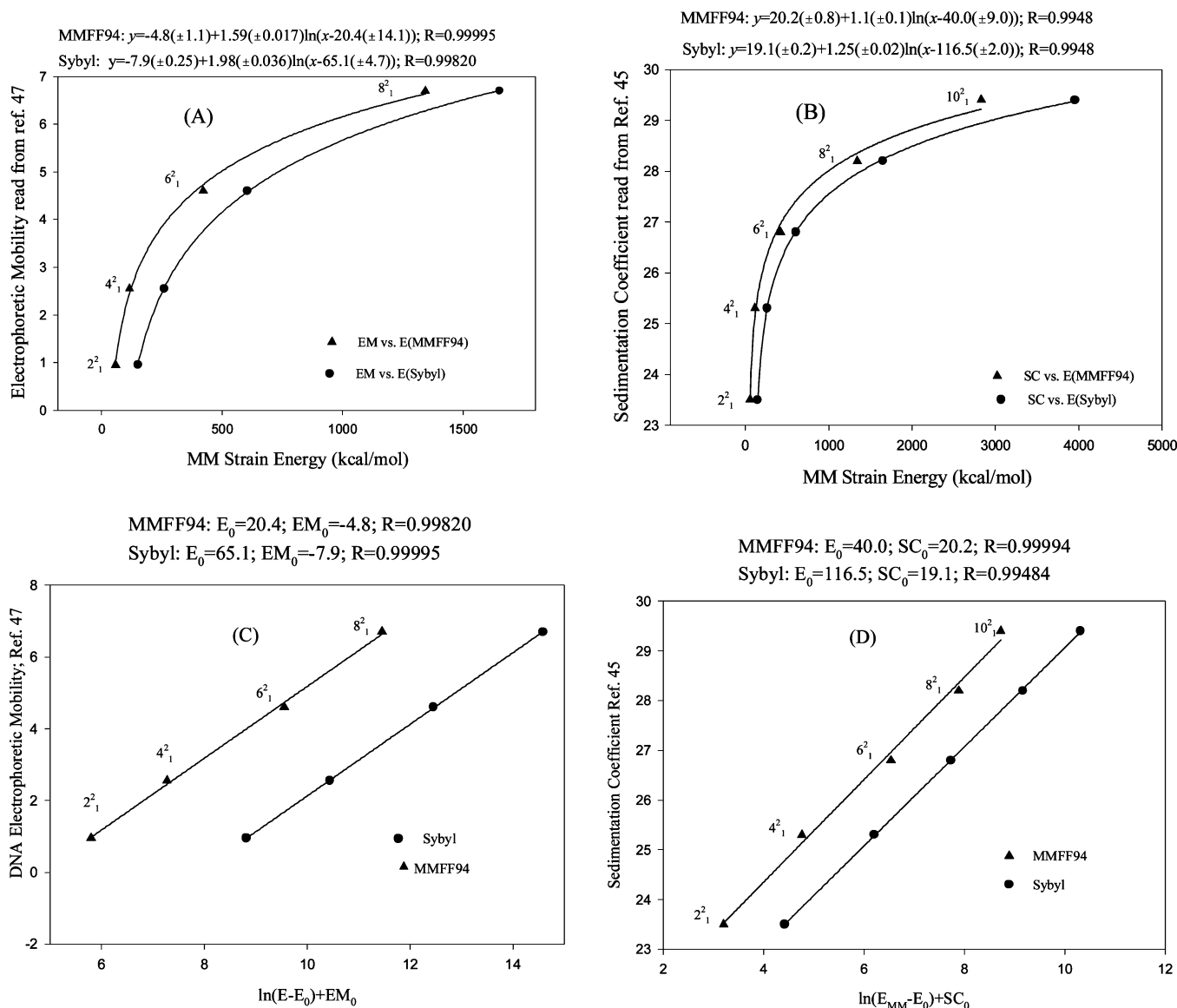


Figure 4. Correlations between the electrophoretic mobilities of DNA catenanes (read from ref 47 (A, C)) and sedimentation coefficients of DNA catenanes (read from ref 45 (B, D)) and MM strain energies of carbyne catenanes.

knot, usually one can distinguish whether it is chiral or not.¹³⁴ Also, based on chirality combined with invertibility of oriented links in some cases one can deduce chirality or achirality properties of unoriented links.¹³⁵ However, a general theorem is not known.

3.2. Correlations: Carbyne Catenanes vs Ideal Catenanes. The relationship between the MM strain energy of the minimal carbyne catenane (topological) number of crossings is clear (Table 3); however, it does not reveal differences between topologically different catenanes with the same number of crossings. For example, the energy of the three different prime catenanes with six crossings should be assigned to one crossing number—six. The averaged crossing number of an ideal catenane, ACN, is not an integer number, and usually for nonhomeomorphic catenanes with the same (topological) crossings number it is different^{45–48} (Tables 3). For a series of carbyne catenanes, Figure 2 demonstrates the type of relations between the MM strain energy (calculated by using two different, yet widely used, force fields: MMFF94 and Sybyl) and ACNs of the ideal catenanes. Analogous relations are known for the MM strain

energy and the length-to-diameter ratio (L/D) of the ideal catenanes.^{45–48} The correlations between the carbyne catenane strain energy and ACN or L/D of the ideal catenanes is nonlinear and generally the simplest, yet proper, fitting can be done by using a second-order polynomial (Figure 3, Table 4). The two-parameter linear, two-parameter quadratic (Table 4), and four-parameter cubic fits were found to describe the relations demonstrated in Figure 3 less accurately than the three-parameter quadratic fits do. As for correlation between the carbyne knots and ACN or L/D we demonstrated that the three-parameter exponential fit was of practically the same quality as the three-parameter trinomial quadratic fits.⁸¹ Here, the two- and three-parameter exponential fits were checked, too (Table 4). They seem to be a bit less exact than the quadratic fit, yet they cannot be ruled out from consideration. There is one important reason for this: the quadratic fit is the worst for the small ACNs and L/D s (the fit curve enters simply into the next branch of the parabola), whereas for this very interval the exponential fit performs well. Thus as for knots,⁸¹ we state that at this stage of study it is difficult to judge whether the polynomial or exponential

model is more exact in expressing the relationship between the carbyne catenane MM strain energy and the ACN or L/D parameter of ideal catenane.

3.3. Correlations: Carbyne Knots vs DNA Catenanes. So far, we showed that the energies of carbyne catenanes calculated by the molecular mechanics methods do correlate with parameters of the ideal catenanes, ACN and L/D. On the other hand, we know that ACN and L/D correlate with parameters of the DNA catenanes: the electrophoretic mobility and the sedimentation coefficient.^{45,47} So next, we consider whether a correlation between the DNA catenane electrophoretic mobility or DNA catenane sedimentation coefficients and the carbyne catenane MM energy exists or not. The numerical values of the electrophoretic mobility and sedimentation coefficients of DNA catenanes were not published, and only the plots against ACN were given.^{45,47} Therefore, we have measured the corresponding values from the published pictures (Table 3) and correlated them with our energetic values of the carbyne catenanes (Figure 4).

The correlations are evidently nonlinear but meaningful (Figure 4A,B). As previously for knots,⁸¹ we have used here the logarithm model to correlate between the carbyne catenane energy and ACN or L/D, the model which is reciprocal to the exponential correlation. Although, the correlation coefficients for such correlations are strikingly high, for the sake of clarity, we also demonstrate the fits in the appropriate linear forms (Figure 4C,D). Thus as for knots, we can state that for catenanes the following expression seems to hold

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

where ΔE is the calculated (MM strain) energy of the carbyne catenane, a and b are coefficients, and X is a parameter characterizing DNA catenane property or ideal catenane ACN or L/D.

As it was pointed out by one of the reviewers of this paper, the hypothesis of the exponential increase of energy with the ACN may seem counterintuitive. Indeed, the strain energy usually follows a Hooke's energy relation of a displacement parameter squared and thermodynamic energy follows a logarithmic relationship. However, increase in the averaged crossing number produces probably much complex, and much greater, changes in a catenane structure than does a simple displacement, and therefore, the energetic effect is multiplied. On the other hand, we propose here a statistical hypothesis which, in fact, does not necessarily explain definitely, yet correlates, and the correlation can be verified by considering more events. This goes, however, beyond the present study.

Finally, let us accentuate that from the point of view of laboratory practice, the most important fact is probably that by using commonly available molecular mechanics one can quite easily generate parameters that can be further correlated with the DNA catenane parameters.

4. CONCLUSIONS

In this study we have treated prime carbyne catenanes built from 60 carbon atoms, with up to 11 crossings, by using molecular mechanics (MM) methods. We have shown that MM energies do correlate, nonlinearly, with the averaged crossing number of the ideal catenanes. Finally, we have

presented correlations between parameters describing the electrophoretic mobilities and the sedimentation coefficients of the DNA catenanes and the MM strain energies calculated for the carbyne catenanes. Thus, by using the widely accessible molecular mechanics method we have shown that the model catenanes containing only carbon atoms can constitute a model for the large DNA catenanes at least for several important characteristics.

ACKNOWLEDGMENT

Financial support from State Committee for Scientific Research (KBN) for statutory activity of the National Institute of Public Health (Warsaw) is gratefully acknowledged.

REFERENCES AND NOTES

- (1) Watson, J. D.; Crick, F. H. C. Molecular structure of Nucleic Acids. A Structure for Deoxyribose Nucleic Acid. *Nature* **1953**, *171*, 737–738.
- (2) Vinograd, J.; Bruner, R.; Kent, R.; Weigle, J. Band-Centrifugation of Macromolecules and Viruses in Self-Generating Density Gradient. *Proc. Natl. Acad. Sci. U.S.A.* **1963**, *49*, 902–910.
- (3) Vinograd, J.; Lebowitz, J.; Radloff, R.; Watson, R.; Laipis, P. The Twisted Circular Form of Polyoma Viral DNA. *Proc. Natl. Acad. Sci. U.S.A.* **1965**, *53*, 1104–1111.
- (4) Streyer, L. *Biochemistry*, 4th ed.; W. H. Freeman and Co.: New York, 1995.
- (5) Murasugi, K. *Knot Theory and Its Applications*; Birkhäuser, Boston, Basel, Berlin, 1996.
- (6) Wasserman, S. A.; Cozzarelli, N. R. Biochemical Topology: Applications to DNA Recombination and Replication. *Science* **1986**, *232*, 951–960.
- (7) White, J. H.; Millett, K. C.; Cozzarelli, N. R. Description of the Topological Entanglement of DNA Catenanes and Knots by a Powerful Method Involving Strand Passage and Recombination. *J. Mol. Biol.* **1987**, *197*, 585–603.
- (8) Fuller, F. B. The Writhing Number of a Space Curve. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 815–819.
- (9) Fuller, F. B. Composition of the linking number of a closed ribbon: A problem of molecular biology. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3557–3561.
- (10) White, J. H. Self-Linking and the Gauss Integral in Higher Dimensions. *Am. J. Math.* **1969**, *9*, 693–728.
- (11) White, J. H.; Cozzarelli, N. R.; Bauer, W. R. Helical Repeat and Linking Number of Surface-Wrapped DNA. *Science* **1988**, *241*, 323–327.
- (12) Depew, R. E.; Wang, J. C. Conformational fluctuations of DNA helix. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4275–4279.
- (13) Pulleyblank, D. E.; Shure, M.; Tang, D.; Vinograd, J.; Vosberg, H.-P. Action of nicking-closing enzyme on supercoiled and nonsupercoiled closed circular DNA: Formation of a Boltzmann distribution of topological isomers. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4280–4284.
- (14) Geider, K.; Hoffman-Berling, H. Proteins Controlling the Helical Structure of DNA. *Annu. Rev. Biochem.* **1981**, *50*, 233–260.
- (15) Gellert, M. DNA Topoisomerases. *Annu. Rev. Biochem.* **1981**, *50*, 879–910.
- (16) Dean, F.; Krasnow, M. A.; Otter, R.; Matzuk, M. M.; Spengler, S. J.; Cozzarelli, N. R. *Escherichia coli* Type-1 Topoisomerases: Identification, Mechanism, and Role in Recombination. *Cold Spring Harb. Symp. Quantum Biol.* **1982**, *47*, 769–777.
- (17) Mizuuchi, K.; Gellert, M.; Weisberg, R. A.; Nash, H. A. Catenation and Supercoiling in the Products of Bacteriophage λ Integrative Recombination *In Vitro*. *J. Mol. Biol.* **1980**, *141*, 485–494.
- (18) Wang, J. C.; Schwartz, H. Noncomplementarity in Base Sequences Between the Cohesive Ends in Coliphages 186 and λ and the Formation of Interlocked Rings between the Two DNA's. *Biopolymers* **1967**, *5*, 953–966.
- (19) Hudson, B.; Vinograd, J. Catenated Circular DNA Molecules in HeLa Cell Mitochondria. *Nature* **1967**, *216*, 647–652.
- (20) Clayton, D. A.; Vinograd, J. Circular Dimer and Catenate Forms of Mitochondrial DNA in Human Leukaemic Leucocytes. *Nature* **1967**, *216*, 652–657.
- (21) Mizuuchi, K.; Gellert, M.; Weisberg, R. A.; Nash, H. A. Catenation and Supercoiling in the Products of Bacteriophage λ Integrative Recombination *In Vitro*. *J. Mol. Biol.* **1980**, *141*, 485–494.

- (22) Mizuuchi, K.; Fisher, L. M.; O'Dea, M. H.; Gellert, M. DNA gyrase involves the introduction of transient double-strand breaks into DNA. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *77*, 1847–1851.
- (23) Kreuzer, K. N.; Cozzarelli, N. R. Formation and Resolution of DNA Catenanes by DNA Gyrase. *Cell* **1981**, *20*, 245–254.
- (24) Read, R. R. Transposon-Mediated Site-Specific Recombination: A Defined in Vitro System. *Cell* **1981**, *25*, 713–719.
- (25) Read, R. R.; Grindley, N. D. F. Transposon-Mediated Site-Specific Recombination: DNA Cleavage and Protein-DNA Linkage at the Recombination Site. *Cell* **1981**, *25*, 721–728.
- (26) Krasnow, M. A.; Cozzarelli, N. R. Site-Specific Relaxation and Recombination by the Tn3 Resolvase: Recognition of the DNA Path between Oriented *res* Sites. *Cell* **1983**, *32*, 1313–1324.
- (27) Wasserman, S. A.; Cozzarelli, N. R. Determination of the stereostructure of the product of Tn3 resolvase by a general method. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 1079–1083.
- (28) Dean, F. B.; Stasiak, A.; Koller, T.; Cozzarelli, N. R. Duplex DNA Knots Produced by *Escherichia coli* Topoisomerase I. *J. Biol. Chem.* **1985**, *260*, 4975–4983.
- (29) Dean, F. B.; Cozzarelli, N. R. Mechanism of Strand Passage by *Escherichia coli* Topoisomerase I. *J. Biol. Chem.* **1985**, *260*, 4984–4994.
- (30) Spengler, S. J.; Stasiak, A.; Cozzarelli, N. R. The Stereostructure of Knots and Catenanes Produced by Phage λ Integrative Recombination: Implications for Mechanism and DNA Structure. *Cell* **1985**, *42*, 325–334.
- (31) Crisona, N. J.; Kanaar, R.; Gonzalez, T. N.; Zechiedrich, E. L.; Klippel, A.; Cozzarelli, N. Processive Recombination by Wild-type Gin and an Enhancer-independent Mutant. Insight into the Mechanisms of Recombination Selectivity and Strand Exchange. *J. Mol. Biol.* **1994**, *243*, 437–457.
- (32) Brewster, S.; Aslett, M.; Barker, D. C. Kinetoplast DNA Minicircle Database. *Parasitol. Today* **1998**, *14*, 437–438.
- (33) Simpson, L. The mitochondrial genome of kinetoplastid protozoa: genomic organization, transcription, replication, and evolution. *Annu. Rev. Microbiol.* **1987**, *41*, 363–382.
- (34) Ryan, K. A.; Shapiro, T. A.; Rauch, C. A.; Englund, P. T. Replication of kinetoplast DNA in trypanosomes. *Annu. Rev. Microbiol.* **1988**, *42*, 339–358.
- (35) Ryan, K. A.; Shapiro, T. A.; Rauch, C. A.; Griffith, J. D.; Englund, P. T. A knotted free minicircle in kinetoplast DNA. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 5844–5848.
- (36) Shapiro, T. A. Kinetoplast DNA maxicircles: Networks within networks. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 7809–7813.
- (37) Chen, J.; Rauch, C. A.; White, J. H.; Englund, P. T.; Cozzarelli, N. R. The topology of the kinetoplast DNA network. *Cell* **1995**, *80*, 61–69.
- (38) Rauch, C. A.; Perez-Morga, D.; Cozzarelli, N. R.; Englund, P. T. The absence of supercoiling in kinetoplast DNA minicircles. *EMBO J.* **1993**, *12*, 403–411.
- (39) Shapiro, T. A.; Englund, P. T. The structure and replication of kinetoplast DNA. *Annu. Rev. Microbiol.* **1995**, *49*, 117–143.
- (40) Chen, J.; Englund, P. T.; Cozzarelli, N. R. Changes in network topology during the replication of kinetoplast DNA. *EMBO J.* **1995**, *14*, 6339–6347.
- (41) Stasiak, A.; Katritch, V.; Bednar, J.; Michoud, D.; Dubochet, J.; Electrophoretic mobility of DNA knots. *Nature* **1996**, *384*, 122–122.
- (42) Katritch, V.; Bednar, J.; Michoud, D.; Scharein, R. G.; Dubochet, J.; Stasiak, A. Geometry and physics of knots. *Nature* **1996**, *384*, 142–145.
- (43) Katritch, V.; Olson, W. K.; Pieranski, P.; Dubochet, J.; Stasiak, A. Properties of ideal composite knots. *Nature* **1997**, *388*, 148–151.
- (44) Cerf, C.; Stasiak, A. A topological invariant to predict the three-dimensional writhe of ideal configurations of knots and links. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 3795–3798.
- (45) Vologodskii, A. V.; Crisona, N.; Laurie, B.; Pieranski, P.; Katritch, V.; Dubochet, J.; Stasiak, A. Sedimentation and electrophoretic migration of DNA knots and catenanes. *J. Mol. Biol.* **1998**, *278*, 1–3.
- (46) Stasiak, A.; Dubochet, J.; Katritch, V.; Pieranski, P. *Ideal knots and their relation to the physics of real knots*, in *Ideal Knots*; Stasiak, A., Katritch, V., Kauffman, L. H., Eds.; World Scientific: Singapore, New Jersey, London, Hong Kong, 1998; Series on Knots and Everything Vol. 19.
- (47) Laurie, B.; Katritch, V.; Sogo, J.; Koller, T.; Dubochet, J.; Stasiak, A. Geometry and Physics of Catenanes Applied to the Study of DNA Replication. *Biophys. J.* **1998**, *74*, 2815–2822.
- (48) Gonzalez, O.; Maddocks, J. H. Global curvature, thickness, and ideal shapes of knots. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 4769–4773.
- (49) Pieranski, P. In *Search of Ideal Knots*, in *Ideal Knots*; Stasiak, A., Katritch, V., Kauffman, L. H., Eds.; World Scientific: Singapore, New Jersey, London, Hong Kong, 1998; Series on Knots and Everything Vol. 19.
- (50) Pieranski, P.; Przybyl, S. Ideal trefoil knot. *Phys. Rev. E* **2001**, *64*, 031801-1-031801-5.
- (51) Wasserman, E. The Preparation of Interlocking Rings: A Catenane. *J. Am. Chem. Soc.* **1960**, *82*, 4433–4434.
- (52) Wasserman, E.; Ben-Efraim, D. A.; Wolovsky, R. The Synthesis of Carbon Macrocycles to C₁₂₀. *J. Am. Chem. Soc.* **1968**, *90*, 3286–3287.
- (53) Wolovsky, R. Interlocked Ring Systems Obtained by the Metathesis Reaction of Cyclododecene. *J. Am. Chem. Soc.* **1970**, *92*, 2132–2133.
- (54) Ben-Efraim, D. A.; Batich, C.; Wasserman, E. Mass Spectral Evidence for Catenanes Formed via “Möbius-Strip” Approach. *J. Am. Chem. Soc.* **1970**, *92*, 2133–2135.
- (55) Frish, H. L.; Wasserman, E. Chemical Topology. *J. Am. Chem. Soc.* **1961**, *83*, 3789–3795.
- (56) Schill, G. *Catenanes, Rotaxanes, and Knots*; Academic: New York, 1971.
- (57) Walba, D. M.; Richards, R. M.; Halftiwanger, R. C. Total Synthesis of the First Molecular Möbius Strip. *J. Am. Chem. Soc.* **1982**, *104*, 3219–3221.
- (58) Schill, G.; Lüttringhaus, A. Directed synthesis of catena compounds (in German). *Angew. Chem.* **1964**, *76*, 567–568.
- (59) Schill, G. Transformation of a triansa compound into a catena compound (in German). *Chem. Ber.* **1967**, *100*, 2021–2037.
- (60) Schill, G.; Murjahn, K. Directed synthesis of catena compounds. Part XI. Bis-diansa compounds of 5-aminobenzodioxol as models for the synthesis of [3]-catenanes (in German). *Liebigs Ann. Chem.* **1970**, *740*, 18–30.
- (61) Schill, G.; Rissler, A. K.; Fritz, H.; Vetter, W. Synthesis, Isolation, and Identification of Translationally Isomeric [3]Catenanes. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 187–189.
- (62) Schill, G. *Catenanes, Rotaxanes, and Knots*; Academic: New York, 1971.
- (63) Walba, D. M. Topological Stereochemistry. *Tetrahedron* **1985**, *41*, 3161–3212.
- (64) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kern, J. M. Templated Synthesis of Interlocked Macrocyclic Ligands: The Catenands. *J. Am. Chem. Soc.* **1984**, *106*, 3043–3045.
- (65) Dietrich-Buchecker, C. O.; Sauvage, J.-P. Interlocking of Molecular Threads: From the Statistical Approach to the Templated Synthesis of Catenands. *Chem. Rev.* **1987**, *87*, 795–810.
- (66) Sauvage, J.-P. Interlacing Molecular Threads on Transition Metals: Catenands, Catenates, and Knots. *Acc. Chem. Res.* **1990**, *23*, 319–327.
- (67) Amabilino, D. B.; Stoddart, J. F. Interlocked and Intertwined Structures and Superstructures. *Chem. Rev.* **1995**, *95*, 2725–2828.
- (68) Bělohradský, B., M.; Raymo, F. M.; Stoddart, J. F. Template-Directed Synthesis of Catenanes. *Collect. Czech. Chem. Commun.* **1997**, *62*, 527–557.
- (69) *Molecular Catenanes, Rotaxanes and Knots. A Journey Through the World of Molecular Topology*; Sauvage, J.-P., Dietrich-Buchecker, C., Eds.; Wiley-VCH: Weinheim, 1999.
- (70) Flappen, E. *When Topology Meets Chemistry*; Cambridge University Press: 1999.
- (71) Dobrowolski, J. Cz.; Mazurek, A. P. Carbyne Trefoil Knots – Are They Stable Enough to Exist. *Pol. J. Chem.* **1998**, *72*, N.7S, 1593–1603.
- (72) Dobrowolski, J. Cz.; Mazurek, A. P. C₆₀ Carbyne Knots (from 0₁ to 6₃): Theoretical NMR Spectra. *Int. J. Quantum Chem.* **1998**, *70*, 1009–1015.
- (73) Dobrowolski, J. Cz.; Mazurek, A. P. C₆₀ Topological Isomers: Other Carbon Allotropes. *J. Phys. Chem.* **1998**, *A 102*, 5260–5262.
- (74) Dobrowolski, J. Cz.; Mazurek, A. P. The Granny and Square Carbyne Knots: Theoretical NMR Spectra. *J. Mol. Struct.* **1999**, *482*–483, 339–342.
- (75) Dobrowolski, J. Cz.; Mazurek, A. P. On the C₆₀ Carbyne Links (from 2₂¹ to 6₃³). *Int. J. Quantum Chem.* **1999**, *75*, 839–846.
- (76) Dobrowolski, J. Cz.; Mazurek, A. P. On the C₆₀ Cyclized Hook and Ladder Carbynes. *Int. J. Quantum Chem.* **2000**, *80*, 1087–1098.
- (77) Dobrowolski, J. Cz.; Mazurek, A. P. On Theoretical VCD, IR and Raman Spectra of Model Chiral Trefoil Knots. *J. Mol. Struct.* **2001**, *563*–564, 309–313.
- (78) Dobrowolski, J. Cz.; Mazurek, A. P. Erratum to “On theoretical VCD, IR and Raman spectra of model chiral right-hand trefoil knots”. *J. Mol. Struct.* **2001**, *563*–564, 309–313, *J. Mol. Struct.* **2002**, *616*, 267.
- (79) Dobrowolski, J. Cz.; Mazurek, A. P. On the qualitative theoretical NMR chemical shifts of model carbyne catenanes and knots. *Chem. Phys. Lett.* **2001**, *348*, 60–66.
- (80) Dobrowolski, J. Cz. On the Belt and Möbius Isomers of the Coronene Molecule. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 490–499.
- (81) Dobrowolski, J. Cz.; Mazurek, A. P. Model Carbyne Knots vs Ideal Knots. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 861–869.
- (82) Dobrowolski, J. Cz. DNA knots and links (in Polish). *Polimery* **4820033**–15.

- (83) Dobrowolski, J. Cz. On the Classification of Topological Isomers: Knots, Links, Rotaxanes, etc. *Croat. Chem. Acta* **2003**, *76*, 145–152.
- (84) Li, S.-Y.; Zhou, H.-H.; Gu, J.-L.; Zhu, J. Does carbyne really exist? – carbynes in expanded graphite. *Carbon* **2000**, *38*, 934–937.
- (85) Heimann, R. B.; Evsyukov, S. E.; Koga, Y. Carbon allotropes: a suggested classifications scheme based on valence orbital hybridization. *Carbon* **1997**, *35*, 1654–1658.
- (86) El Goresy, A. E.; Donnay, G. A New Allotropic Form of Carbon from the Ries Crater. *Science* **1968**, *161*, 363–364.
- (87) El Goresy, A. A new modification of carbon from Nördlinger Ries (in German). *Naturwissenschaften* **1969**, *56*, 493–494.
- (88) Smith, P. P. K.; Buseck, P. R. Carbyne Forms of Carbon: Do They Exist? *Science* **1982**, *216*, 984–986.
- (89) Whittaker, A. G.; Neudorffer, M. E.; Watts, E. J. Carbon: a rhombohedral carbyne form. *Carbon* **1983**, *21*, 597–599.
- (90) Yu. Kudryavtsev, P.; Heinman, R. B.; Evsukov, S. E. Carbynes: advances in the field of linear carbon chain compounds. *J. Mater. Sci.* **1996**, *31*, 5557–5571.
- (91) Lagow, R. J.; Kampa, J. J.; Wei, H.-C.; Battle, S. L.; Genge, J. W.; Laude, D. A.; Harper, C. J.; Bau, R.; Stevens, R. C.; Haw, J. F.; Munson, E. Synthesis of Linear Acetylenic Carbon: The “sp” Carbon Allotrope. *Science* **1995**, *267*, 362–367.
- (92) Van Orden, A.; Saykally, R. J. Small Carbon Clusters: Spectroscopy, Structure, and Energetics. *Chem. Rev.* **1998**, *98*, 2313–2357.
- (93) Gotts, N. G.; van Helden, G.; Bowers, M. T. Carbon cluster anions: structure and growth from C_5^- to C_{62}^- . *Int. J. Mass Spectrom. Ion Processes* **1995**, *149–150*, 217–229.
- (94) Weltner, W., Jr.; Van Zee, R. J. Carbon Molecules, Ions, and Clusters. *Chem. Rev.* **1989**, *89*, 1713–1747.
- (95) McCarthy, M. C.; Thaddeus, P. Microwave and laser spectroscopy of carbon chains and rings. *Chem. Soc. Rev.* **2001**, *30*, 177–185.
- (96) Shindo, Fr.; Bénilan, Y.; Chaquin, P.; Guillemain, J.-C.; Jolly, A.; Raulin, Fr. IR Spectrum of C₈H₂: Integrated Band Intensities and Some Observational Implications. *J. Mol. Spectrosc.* **2001**, *210*, 191–195.
- (97) Henning, Th.; Salama, F. Carbon in the Universe. *Science* **1998**, *282*, 2204–2210.
- (98) Gibtnier, T.; Hampel, F.; Gisselbrecht, J. P.; Hirsch, A. End-Cap Stabilized Oligoynes: Model Compounds for Linear sp Carbon Allotrope Carbyne. *Chem. Eur. J.* **2002**, *8*, 408–432.
- (99) Tobe, Y.; Furukawa, R.; Sonoda, M.; Wakabayashi, T. [12.12]-Paracyclophanedodecynes C₃₆H₈ and C₃₆Cl₈: The smallest Paracyclophynes and Their Transformation into the Carbon Cluster Ion C₃₆⁺. *Angew. Chem., Int. Ed.* **2001**, *40*, 4072–4074.
- (100) Pschurer, N. G.; Vaughn, M. E.; Dong, Y. B.; zur Loye, H.-C.; Bunz, U. H. F. Novel liquid-crystalline PPE-naphthalene copolymers displaying blue solid-state fluorescence. *Chem. Commun.* **2000**, 85–86.
- (101) Unno, M.; Saito, T.; Matsumoto, H. Synthesis and Crystal Structures of Silapericyclines. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2407–2413.
- (102) Rosseli, S.; Ramminger, A.-D.; Wagner, T.; Siler, B.; Wiegand, S.; Häussler, W.; Lieser, G.; Scheumann, V.; Höger, S. Coil-Ring-Coil Block Copolymers as Building Blocks for Supramolecular Hollow Cylindrical Brushes. *Angew. Chem., Int. Ed.* **2001**, *40*, 3138–3141.
- (103) Diederrich, F. Functional acetylenic molecular architecture. *Pure Appl. Chem.* **1999**, *71*, 265–273.
- (104) Ohkita, M.; Ando, K.; K.-i. Yamamoto, Suzuki, T.; Tsuji, T. First Dewar benzene approach to acetylenic oligophenylene macrocycles: synthesis and structure of a molecular rectangle bearing two spindles. *Chem. Commun.* **2000**, 83–84.
- (105) Sarker, A.; Haley, M. M. Synthesis and Characterisation of dehydrothieno [18]annulenes. *Chem. Commun.* **2000**, 1733–1734.
- (106) Boydston, A. J.; Bondarenko, L.; Dix, I.; Weakley, T. J. R.; Hopf, H.; Haley, M. M. [2.2]Paracyclophane/Dehydrobenzoanulene Hybrids: Transannular Delocalization in Open-Circuited Conjugated Macrocycles. *Angew. Chem. Int. Ed.* **2001**, *40*, 2986–2989.
- (107) Ünsal, Ö.; Godt, A. Synthesis of a [2]Catenane with Functionalities and 87-Membered Rings. *Chem. Eur. J.* **1999**, *5*, 1728–1733.
- (108) Szafert, S.; Gladysz, J. A. Carbon in One Dimension: Structural Analysis of the Higher Conjugated Polyynes. *Chem. Rev.* **2003**, *103*, 4175–4205.
- (109) Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. Elemental Carbon Cages. *J. Am. Chem. Soc.* **1988**, *110*, 1113–1127.
- (110) Klein, D. J.; Liu, X. Theorems for Carbon Cages. *J. Math. Chem.* **1992**, *11*, 199–205.
- (111) Klein, D. J.; Liu, X. Elemental Carbon Isomerism. *Int. J. Quantum Chem. Quantum Chem. Symp.* **1994**, *28*, 501–523.
- (112) Klein, D. J.; Zhu, H. All-Conjugated Carbon Species. In *From Chemical Topology to Three-Dimensional Geometry*; Balaban, A. T., Ed.; Plenum Press: New York, 1997; pp 297–341.
- (113) King, R. B. Some aspects of the symmetry and topology of possible carbon allotrope structures. *J. Math. Chem.* **1998**, *23*, 197–227.
- (114) Klein, D. J. Topo-Graphs, Embeddings, and Molecular Structure. In *Chemical Topology*; Bonchev, D.; Rouvray, D. H., Eds.; Gordon & Breach: Amsterdam, 1999; pp 39–83.
- (115) Ivanciuc, O.; Bytautas, L.; Klein, D. J. Mean-field resonating-valence-bond theory for unpaired π -electrons in benzenoid carbon species. *J. Chem. Phys.* **2002**, *116*, 4735–4748.
- (116) Ivanciuc, O.; Klein, D. J.; Bytautas, L. Unpaired π -spin density in defected graphite. *Carbon* **2002**, *40*, 2063–2083.
- (117) Klein, D. J. Quasilocal Defects in Regular Planar Networks: Categorization for Molecular Cones. *Int. J. Quantum Chem.* **2003**, *95*, 600–616.
- (118) Babić, D.; Došlić, T.; Klein, D. J.; Misra, A. Kekuléoid Addition Patterns for Fullerenes and Some Lower Homologues. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2003–2010.
- (119) Clark, M.; Cramer, R. D.; van Opdenbosch, N., III Validation of the General Purpose Tripos 5.2 Force Field. *J. Comput. Chem.* **1989**, *10*, 982–1012.
- (120) Halgren, T. A. Merck molecular force field I. Basis, form, scope, parametrization, and performance of MMFF94. *J. Comput. Chem.* **1996**, *17*, 490–519.
- (121) Halgren, T. A. Merck molecular force field II. MMFF94 van der Waals and electrostatic parameters for intermolecular interactions. *J. Comput. Chem.* **1996**, *17*, 520–552.
- (122) Halgren, T. A. Merck molecular force field III. Molecular geometries and vibrational frequencies for MMFF94. *J. Comput. Chem.* **1996**, *17*, 553–586.
- (123) Halgren, T. A.; Nachbar, R. B. Merck molecular force field IV. Conformational energies and geometries for MMFF94. *J. Comput. Chem.* **1996**, *17*, 587–615.
- (124) Halgren, T. A. Merck molecular force field V. Extension of MMFF94 using experimental data, additional computational data, and empirical rules. *J. Comput. Chem.* **1996**, *17*, 616–641.
- (125) Rappé, A. K.; Casewit, C. J. *Molecular Mechanics across Chemistry*; University Science Books: Sausalito, CA, U.S.A., 1997.
- (126) Clark, M.; Cramer, R. D.; Van Opdenbosch, N., III Validation of the General Purpose Tripos 5.2 Force Field. *J. Comput. Chem.* **1989**, *10*, 982–1012.
- (127) Spartan'04 for Windows, Wavefunction, Inc., 18401 Von Karman Ave., #370, Irvine, CA 92612 U.S.A.
- (128) SigmaPlot 2000 for Windows, SPSS Inc., 233 South Wacker Drive, Chicago, IL 60606-6307 U.S.A.
- (129) Walba, D. M. *Stereochemical Topology in Chemical Application of Topology and Graph Theory*; King, R. B., Ed.; Elsevier: Amsterdam, 1983; pp 17–32.
- (130) Dodziuk, H. *Modern Cnformational Analysis, Elucidating Novel Exciting Molecular Structures*; VCH: New York, 1995.
- (131) Cerf, C. Atlas of Oriented Knots and Links. *Topology Atlas Invited Contribution 3*, 1998; pp 1–32 (<http://at.yorku.ca/ta/i/c/31.htm>).
- (132) Piel, L. *Ideas of Quantum Chemistry (in Polish)*; PWN: Warsaw, 2004.
- (133) Jiang, B.; Lin, X.-S.; Wan, S.; Wu, Y.-Q. Achirality of knots and links. *Topol. Applications* **2002**, *119*, 185–208.
- (134) Ramadevi, P.; Govindarajan, T. R.; Kaul, R. K. *Mod. Phys. Lett.* **1994**, A93205–3218.
- (135) Cerf, C. private information.