# A Topological Rubber Glove obtained from a Synthetic Single-stranded DNA Molecule

**Erica Flapan*[a] and Nadrian C. Seeman[b]**

[a] *Department of Mathematics, Pomona College, Claremont, CA 91711, USA*
[b] *Department of Chemistry, New York University, New York, NY 10003, USA*

A 'figure-of-eight' knot synthesized from single-stranded DNA is shown to have the properties of a topological rubber glove.

The concept of chirality is far more complex than might appear at first glance. In general, if a compound has no conformation with an improper axis of symmetry we conclude that the compound is chiral. However, if a molecule is completely flexible it may be possible to deform it to its mirror image, yet impossible to deform if to a position which can be rotated to its mirror image. Mislow[1] has given examples of disubstituted biphenyls that are achiral, yet have no chemically accessible symmetry presentation. Walba[2,3] raised the question of whether such a phenomenon can occur if we replace chemical accessibility by topological accessibility. In particular, Walba has defined a 'topological rubber glove' as any structure whose molecular graph could be deformed to its mirror image, but could not be deformed to a symmetry presentation, and asked whether such structures could exist. Flapan[4] has shown that there do exist both knots and graphs that possess this property (Fig. 1). We say that a structure is 'topologically achiral' if its graph can be deformed to its mirror image, and 'rigidly achiral' if its graph can be deformed to a conformation that can then be rotated to its mirror image. Thus, a topological rubber glove is a structure that is topologically achiral but not rigidly achiral.

It was unknown whether a molecular structure with this property could be obtained through controlled synthesis. In this note we demonstrate that a 'figure-of-eight' knot synthesized from a DNA single strand[5] is, in fact, a topological rubber glove. We see that the synthetic DNA figure-of-eight is topologically achiral as follows. The DNA figure-of-eight knot has been made in a variety of sizes, ranging in length from 66 to 104 nucleotide subunits.[6] Fig. 2 illustrates the molecular structure of two individual nucleotides. As a first step to deforming this molecular graph to its mirror image, we deform the sugars so that they are planar, like the purine and pyrimidine bases. This step eliminates the chiral nature of each nucleotide. We are entitled to do this because the chirality of the sugars comes from their geometry, rather than their topology. In this way, the sugars and purine and pyrimidine bases are each their own mirror image. It is well known that a piece of rope in the form of a figure-of-eight knot can be deformed to its mirror image.[7] Thus we can deform the molecular graph so that all of the crossings of the backbone figure-of-eight knot will be reversed. However, in so doing, the purine and pyrimidine bases may be moved to a new position on the knot, relative to its sites of crossing. To return them to their original positions, we simply reptate (*i.e.* slither) the structure along itself until each one is back to where it began, tilting it as necessary to obtain the proper angle relative to the mirror plane. In this way, we have deformed our molecular graph to its mirror image. This molecule has been analysed as a knot both under non-

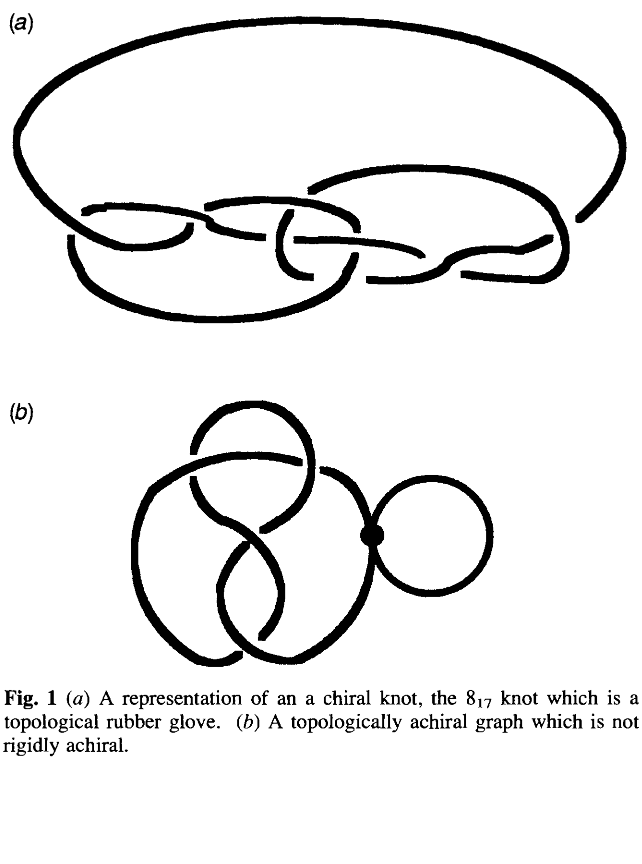


**Fig. 1** (*a*) A representation of an a chiral knot, the $8_{17}$ knot which is a topological rubber glove. (*b*) A topologically achiral graph which is not rigidly achiral.

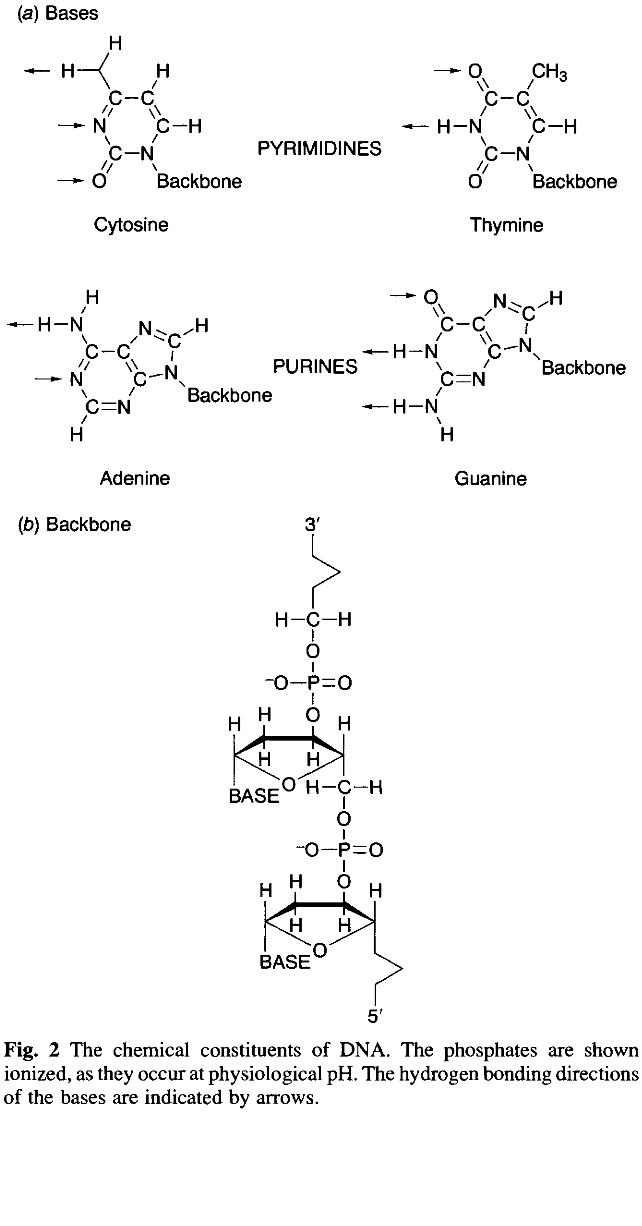


**Fig. 2** The chemical constituents of DNA. The phosphates are shown ionized, as they occur at physiological pH. The hydrogen bonding directions of the bases are indicated by arrows.

denaturing conditions that preserve its Watson–Crick hydrogen-bonded base pairing,[8] and under denaturing conditions that eliminate these interactions.[5,6] It behaves as a figure-of-eight knot in both environments. Hence we are entitled to ignore the hydrogen bonding between the base pairs in this analysis.[9]

Now, we wish to show that the synthetic DNA figure-of-eight is not rigidly achiral. Suppose that we could deform its graph to a position which could be rotated to its mirror image. In particular, such a rotation would take the backbone figure-of-eight knot to its mirror image. Fig. 3 illustrates a deformation of the figure-of-eight to a symmetry presentation with an $S_4$ axis (*i.e.* a rotation by 90° followed by a reflection takes this presentation to itself). However, it is shown in ref. 4 that no presentation of the figure-of-eight knot has a symmetry which is a rotation through an angle different from 90° followed by a reflection. So if the synthetic DNA figure-of-eight is rigidly achiral then its graph must have a presentation with an $S_4$ axis. This improper rotation must take each purine to a purine and each pyrimidine to a pyrimidine; and, after performing this rotation four times, every point on the molecular graph must return to its original position. However, the purine and pyrimidine bases do not occur in a sequence which repeats itself exactly four times. So the molecular graph of the DNA figure-of-eight cannot have such an improper rotation. Hence it cannot be rigidly achiral. We have thus shown that the single-strand synthetic DNA figure-of-eight knot is a topological rubber glove.

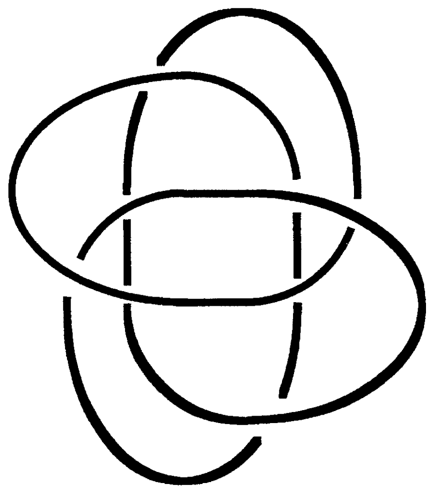

**Fig. 3** A figure-of-eight knot. This is a symmetry presentation for the figure-of-eight knot with an $S_4$ axis. Thus, a rotation by 90° followed by a reflection takes this presentation to itself.

This work has been supported by NIH grant GM-29554 and ONR grant N00014-89-J-3078 (to N. C. S). We wish to thank Kurt Mislow for making the authors aware of each other's work.

*Received, 1st August 1995; Com. 5/05132K*

## References

1 K. Mislow, *Science*, 1954, **120**, 232.
2 D. Walba, *Stereochemical Topology*, in *Chemical Applications of Topology and Graph Theory*, ed. R. B. King, Elsevier, Amsterdam, 1983, pp. 17–32.
3 D. Walba, *Tetrahedron*, 1985, **41**, 3161.
4 E. Flapan, *Pac. J. Math.*, 1987, **129**, 57.
5 S. M. Du and N. C. Seeman, *J. Am. Chem. Soc.*, 1992, **114**, 9652.
6 H. Wang, S. M. Du and N. C. Seeman, *J. Biomol. Str. Dyns.*, 1993, **10**, 853.
7 E. Flapan, *Discrete Appl. Math.*, 1988, **19**, 157.
8 S. M. Du, H. Wang, Y.-C. Tse-Dinh and N. C. Seeman, *Biochemistry*, 1995, **34**, 673.
9 For further discussion of the exclusion of hydrogen bonds from molecular graphs, see: C. Liang and K. Mislow, *J. Am. Chem. Soc.*, 1995, **117**, 4201.