

All the Ways To Have Substituted Nanothreads

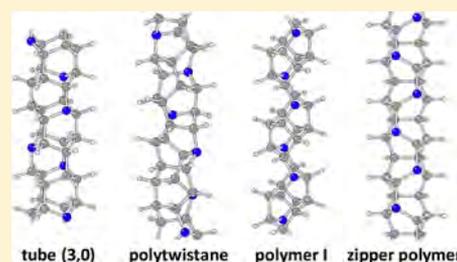
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Supporting Information

ABSTRACT: We describe a general, symmetry-conditioned way of enumerating isomers of saturated singly substituted one-dimensional nanothreads of the $(\text{CH})_5\text{E}$ and $(\text{CH})_5\text{CR}$ type, where E is a heteroatom and R is a substituent. Four nanothreads — so-called tube (3,0), polytwistane, the zipper polymer, and polymer I, are treated in detail. The methodology, combining symmetry arguments and computer-based enumeration, is generally applicable to isomerism problems in polymers.



1. INTRODUCTION

In 2014, for the first time in the over 100 years that benzene has been compressed,¹ material well-ordered in two dimensions was recovered, the benzene nanothreads.² These solids contain hexagonal arrays of largely saturated one-dimensional polymers of predominant composition CH, each polymer ~ 6.5 Å in diameter (van der Waals radius included). They are thought, based on the evidence so far, to lack thread-to-thread registry along the chain axis. Narrow Raman spectral features are observed for nanothreads, however, suggesting that individual threads have a significant degree of order along their length.^{2,3} Moreover, order over several nanometers is observed by transmission electron microscopy.⁴

Isomerism makes chemistry useful and interesting ... and also makes life complicated for chemists. Several nanothread structures were suggested prior to the experimental synthesis.^{5–7} Of course, being suggested by theoreticians, these nanothreads were quite regular. The linkage isomerism possibilities in one-dimensional fully saturated benzene polymerization grow very rapidly with system size. Limiting oneself to a certain topological repeat unit (the distinction between crystallographic and topological repeats will be defined below), Xu, Lammert, and Crespi enumerated 50 isomeric saturated nanothreads.⁸ Chen et al. derived a roadmap for polymerization, defining the simpler isomeric possibilities for polymers having one or two double bonds remaining on each $(\text{CH})_6$ ring, i.e., on the way from a stack of benzenes to a completely saturated nanothread.⁹

Attempts to derivatize the nanothreads are underway, and the polymerization of heterosubstituted aromatics such as pyridine has also led to some ordered polymers, likely also nanothreads.¹⁰ We have therefore undertaken a systematic study of the isomeric possibilities, either of $(\text{CH})_5\text{E}$ (e.g., pyridine) or of $(\text{CH})_5(\text{CR})$, where R is a substituent. The latter case has also been theoretically studied, for a selection of

isomers and substituents, in a recent paper by J. Silveira and A. Muniz.¹¹

Here we present a systematic exploration of the isomeric possibilities of four substituted nanothreads, in the process laying out a symmetry-conditioned permutational analysis that can be applied to any of the other threads, and to potential greater degrees of substitution and, more generally, to isomerism problems in other polymers.

2. RESULTS

2.1. The Nanothreads Studied and Our Approach.

Figure 1 shows the four nanothreads that we will consider.

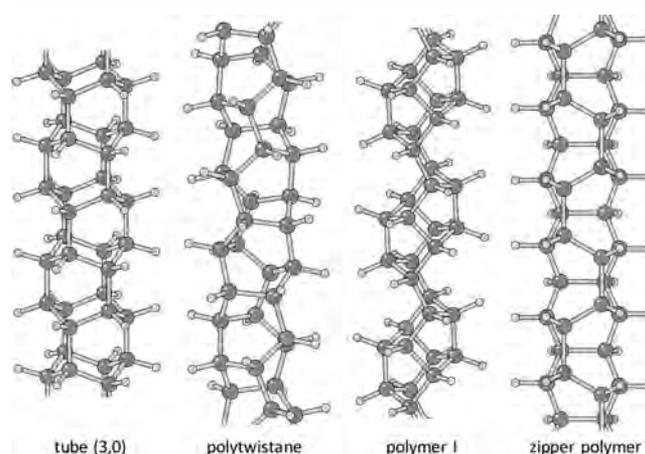


Figure 1. Structures of four benzene nanothreads.

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Each thread is made up solely of sp^3 C–H units. The most stable of these (not by much energy) is polytwistane, originally suggested by D. Trauner,⁷ a structure with remarkable symmetries. It forms a helix of irrational pitch, which, with little distortion, can be “rationalized” to a unit cell containing 12 benzenes. Perpendicular to the helix axis run two distinct 2-fold axes – such axes will play a role in our analysis.

Polytwistane also allows us to distinguish between a topological and a crystallographic unit cell. If we keep the pitch irrational, the crystallographic (one-dimensional) unit cell is infinite; but the topological unit cell is one $(CH)_6$, for the connection pattern or linkage to the next one along the chain of each $(CH)_6$ ring is the same. Underlying this single-benzene chemical repeat unit is a smaller two-carbon-atom cell whose screw translations reconstitute the entire thread. In the so-called polymer I⁶ the topological and crystallographic unit cells both contain two benzene units ($Z_{\text{topo}} = Z_{\text{cryst}} = 2$).

Since nanothreads based on pyridine constitute so far the only substituted system that is experimentally accessible,¹⁰ we focus on polymers of this molecule. Substitution of one CH per ring by N (or in the case of functionalization by CR) naturally introduces further possibilities for isomerism. We now introduce a symmetry-based methodology for dealing with the complex isomerism facing us.

2.2. Easy Isomerism: The Zipper Polymer. This nanothread is named after the geometrically seemingly facile process of zipping up a polymer formed by Diels–Alder reactions of a stack of benzenes.² Its structure is shown in Figure 2; see the SI for the structural relations of the four

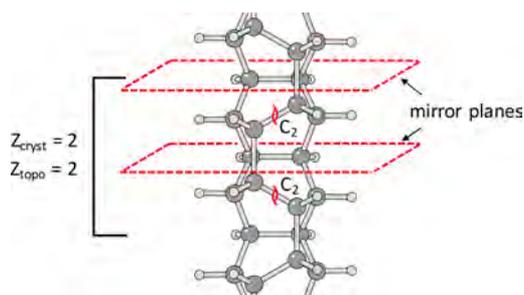


Figure 2. Structure of the zipper polymer.

nanothreads in Figure 1 to a stack of benzene molecules. The zipper polymer has the same number (Z) of six-membered rings in the topological unit cell, as it does in the primitive crystallographic repeat unit, i.e., $Z_{\text{topo}} = Z_{\text{cryst}} = 2$. Note the mirror planes and 2-fold axes of the polymer, which we will use. There is also a glide plane, which is not marked. The zipper polymer tends to curve if no periodic boundary condition is imposed. We study only the isomerism in an uncurved polymer.

To begin the enumeration, we number the ring positions clockwise, looking down along the thread axis (Figure 3). The second ring is numbered with blue numbers bearing primes. One can see three strands in the zipper polymer, $-6-1-1'-6'-$, $-3-2-3'-2'-$, and $-4-5-4'-5'-$.

With the numbering notation, one can assign an identifier to each thread, based on substitution positions. For example, if one isomer of a pyridine thread has a nitrogen at position 1 of the first ring and at position 2' of the second ring, and if the third ring repeats the first and so on, its identifier is 12'. One can, of course, use a redundant sequence 12'–12'–12'... as the identifier for this structure; but given the crystallographic unit

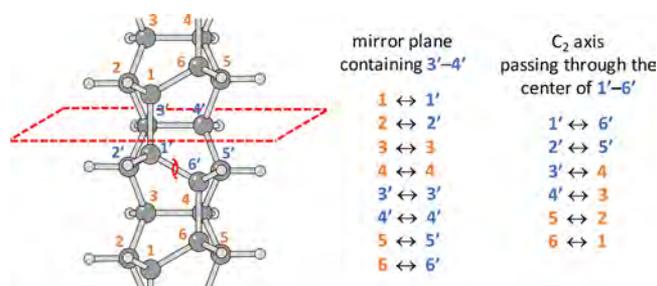


Figure 3. Ring position numbering and two sets of correspondences associated with two symmetry operations in the zipper polymer.

cell $Z_{\text{cryst}} = 2$ for this thread, 12' is the minimal unique identifier. Nevertheless, by writing out the redundant sequence, one can clearly see that $12' = 12'-12'-12' = 1-2'1-2'1-2' = 2'1$. The only difference between 12' and 2'1 is which ring, the unprimed or the primed, is chosen as the first ring. However, at this point we cannot say $2'1 = 21'$, because we have not established the correspondences of the unprimed and primed numbers.

Of course, nitrogen-substituted threads can have $Z_{\text{cryst}} > 2$, up to infinity. A simple example is 12'13', in which the nitrogen position in the fourth ring is not the same as in the second ring (if they were the same, the thread would be 12'12' = 12'). We limit ourselves to pyridine threads with $Z_{\text{cryst}} = 2$; the identifiers for these structures have only two digits.

Following a combinatorial scheme for two independent numbers, the first one ranging from 1 to 6 and the second from 1' to 6', one can easily list all structures with $Z_{\text{cryst}} \leq 2$ ($6 \times 6 = 36$ in total). Since there are symmetry elements in the parent thread structure, one can be sure that there are duplicates among these 36 structures. Two symmetry operations of the one-dimensional polymer are, as noted, mirror planes and 2-fold axes in addition to the translation. These symmetry operations interrelate atoms where substitution of CH by N or CR might take place, and we use them to eliminate duplicates. We have already used the translational symmetry to derive $12' = 2'1$. Next, we derive the correspondences induced by the mirror planes and 2-fold axes.

As shown in Figure 3, the mirror plane containing 3'–4' relates 1 to 1', 2 to 2', 5 to 5', and 6 to 6' but has no effect on 3, 4, 3', and 4'. The other mirror plane containing 3–4 yields the same set of correspondences. Similarly, the C₂ axis passing through the center of bond 1'–6' transforms 1' to 6', 2' to 5', 3 to 4', and so on. The two-headed arrow in Figure 3 indicates these inter-relationships and generates two sets of correspondences or mapping rules, one associated with the mirror plane and the other with the 2-fold axes.

An example will make the process clear. Consider the question whether 21' is the same or different from 12'. Yes, one can physically look at a model of the substituted polymer, but one can also apply the correspondences. Applying the mapping rules associated with the mirror plane, one easily finds $12' = 21'$. One can also apply the set of correspondences associated with a C₂ axis to 12', to obtain $12' = 5'6$. Note, and this is important, that since both mirror reflection and 2-fold rotation reverse the thread direction, the sequence of the numbers in the identifier should also be reversed after the identifier is subjected to the mapping rules. Therefore, applying the mirror to 12', one obtains 21', not 1'2 as would be if the sequence were not reversed (see Figure 4). Manipulating a model helps here. However, for this particular structure with $Z_{\text{cryst}} = 2$, 1'2 can be

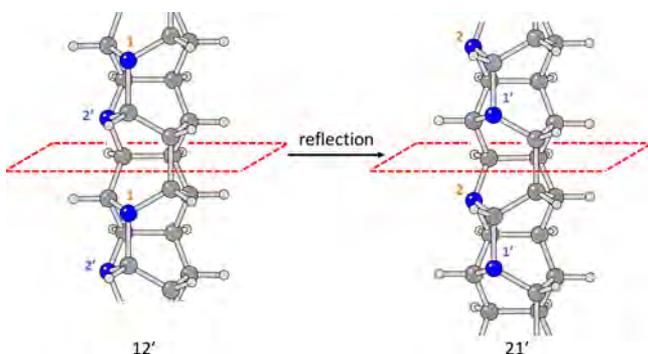


Figure 4. Mirror reflection transforms isomer $12'$ to $21'$ of the nitrogen-substituted zipper polymer.

transformed to $21'$ by translation, so that this is not a good example to illustrate the reversal of sequence upon mirror operation or C_2 rotation. A better example will be provided below for polytwistane.

Next consider the case of $26'$ (Figure 5). Using the C_2 axis mapping rules and remembering the switch in the direction of the polymer, this is identical to $1'5'$. Applying the mirror plane mapping rules, we reach $5'1'$. Then translation then takes $5'1'$ to $15'$.

Having established the two sets of correspondences, we apply them to the 36 combinatorial possibilities for $Z_{\text{cryst}} = 2$, so as to eliminate duplicates. A general strategy of transforming the identifiers is to make the first digit unprimed and as small as possible. Figure 6 lists the 36 identifiers, with the 17 distinct ones in red, and those can be transformed to the distinct ones in black. Among the distinct isomers, those with neighboring N atoms, i.e., N–N bonds, are indicated by * in Figure 6. The reason for the identification is that in our forthcoming consideration of the energetics of those polymers (with neighboring N atoms) emerge as being of high energy.

Some transformations of the identifiers in Figure 4 utilize only one set of correspondences. For instance, $21' = 12'$ makes use of just the mirror plane and the C_2 rotation, respectively, while $65' = 2'1'$ arises from the application of the mapping rules associated with the C_2 axis. Many other transformations involve both sets of correspondences, as illustrated in Figure 5 for $26' = 1'5' = 5'1'$.

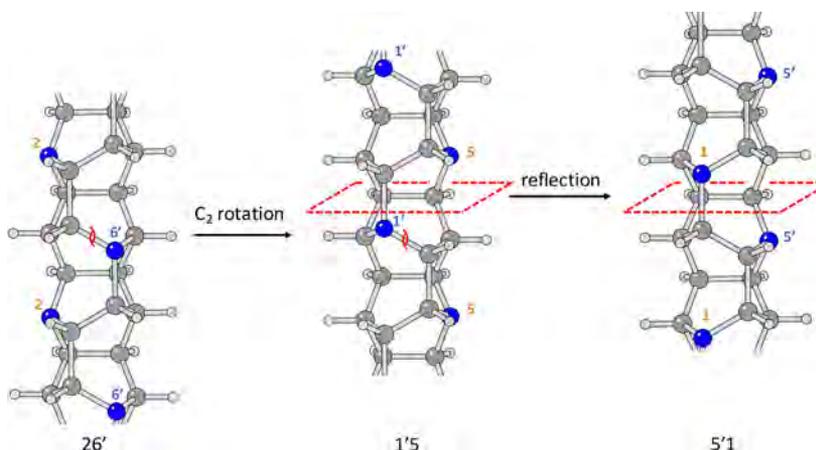


Figure 5. C_2 rotation plus mirror reflection transforms $26'$ to $1'5'$ and $5'1'$.

$11'$ (*)	$21'=12'$	$31'$
$12'$	$22'$	$32'$ (*)
$13'$	$23'$ (*)	$33'$
$14'$	$24'$	$34'$
$15'$	$25'$	$35'=2'4'=4'2'=24'$
$16'$	$26'=1'5'=5'1'=15'$	$36'=1'4'=4'1'=14'$
$41'$	$51'=15'$	$61'=16'$
$42'$	$52'=25'$	$62'=26'$
$43'$	$53'=42=2'4=42'$	$63'=41=1'4=41'$
$44'=33'$	$54'=32=2'3=32'$	$64'=31=1'3=31'$
$45'=2'3'=3'2=23'$	$55'=2'2=22'$	$65'=2'1=12'$
$46'=1'3'=3'1=13'$	$56'=1'2=21'$	$66'=1'1=11'$

Figure 6. Isomer list for $Z_{\text{cryst}} = 2$ pyridine threads of the zipper polymer with explicit illustration of the process of using correspondences to identify identical isomers. The starred isomers contain adjacent N atoms.

One aspect of our process might cause confusion; some transformations yield two unprimed or two primed numbers, such as the first equation in $35' = 2'4' = 4'2' = 24'$ (Figure 7). In this case, $2'4'$ means that the second ring has two nitrogens at positions $2'$ and $4'$ and no nitrogens in the first ring. How is that possible?

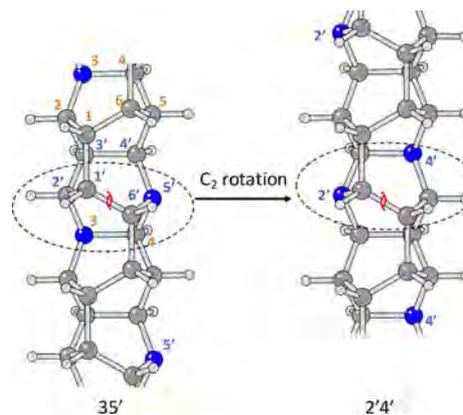


Figure 7. C_2 rotation transforms $35'$ to $2'4'$. The latter has the two nitrogens in the same ring.

That two nitrogens appear in the same ring is possible because there is an inherent ambiguity, a choice, in subdividing a completed thread into successive six-membered rings. Take

the 35' polymer as an example (Figure 7). One way we have used to choose rings is such that the orange unprimed and the blue primed numbers indicate different rings. In the other way, the rings contain mixed unprimed and primed numbers, e.g., 1'2'345'6' as indicated by the oval dash in the left structure of Figure 7. Let us call the two ways Choice-1 and Choice-2. Of course, a different choice of rings results in different numbering. However, upon a mirror reflection or C_2 rotation that reverses the thread direction, the Choice-2 rings of the original thread become the Choice-1 rings of the new thread. It is obvious in Figure 7 that the nitrogens that belong to different rings in the original thread are now in the same ring of the transformed thread.

We note that additional symmetry operations could be used to introduce further correspondences, but we have found them redundant. Probably the minimal set of symmetries needed for the purpose, given a linear translational (or frieze) group, is derivable; this remains a possible topic for future work.

Again, it is obvious that the isomer set we have derived is the simplest one, for Z_{cryst} after substitution maintained at 2. As we noted, if one allows the second, third, etc. polymer unit to be substituted in a different way from the first one, then the number of isomeric possibilities increases rapidly. Also, every chiral isomer will of course have an enantiomer. The absence or presence of a mirror plane in any isomer is easy to spot.

2.3. Harder: Polytwistane Isomers. Polytwistane is a 1D helical structure of irrational pitch, i.e., $Z_{\text{cryst}} = \text{infinite}$. It takes very little distortion per atom to make a rational pitch polymer out of it, with $Z_{\text{cryst}} = 12$ (Figure 8). In either case $Z_{\text{topo}} = 1$. The structure has a screw axis along the thread axis, and perpendicular to it two different C_2 axes pass through the center of every C–C bond and intersect with the screw axis. Note that these C_2 axes are of two distinct types, one passing through centers of two C–C bonds, and the other passing through the center of one C–C bond and the center of a ring on the opposite side. We use C_2 and C_2' to denote the two types in Figure 8. These symmetry operations will be used in the enumeration to eliminate duplicate structures.

An interesting structural feature of polytwistane is that all six-membered rings (6mrs) are in twist-boat conformation — hence the name. One easily recognizes a few twist boats in Figure 8, but many of them are less clear. We will show this in detail below. We note here that simply from the fact that all rings are twist boats, i.e., they are all the same, one can acclimate to the idea that polytwistane has $Z_{\text{topo}} = 1$.

Following the same procedure of enumerating isomers, we start by numbering the rings. In Figure 9 top left, different colors indicate different rings; three 6mrs are numbered. Looking down the thread axis from the top, ring atoms of all 6mrs are numbered 1 through 6, clockwise. In the second 6mr (blue), the atoms are numbered with primes and in such a way that atom 1' is connected to atom 6 of the first ring. There are also 2'–3 and 4'–5 connections. The third ring is numbered in a similar fashion but with double primed numbers. We obtain three intertwined CH strands running along the axial direction: $-1-6-1'-6'-1''-6''-$, $-2-3-2'-3'-2''-3''-$, and $-4-5-4'-5'-4''-5''-$. Polytwistane is a triple helix in this sense. Obviously, atoms with the same number, primed or unprimed, have the same connection pattern, which clearly shows that all 6mrs are topologically equivalent (i.e., $Z_{\text{topo}} = 1$).

For the $Z_{\text{cryst}} = 12$ polytwistane approximant any nitrogen-substituted threads with $Z_{\text{topo}} = 1, 2, 3, 4, 6,$ or 12 will be commensurate. The number of isomers grows very quickly with

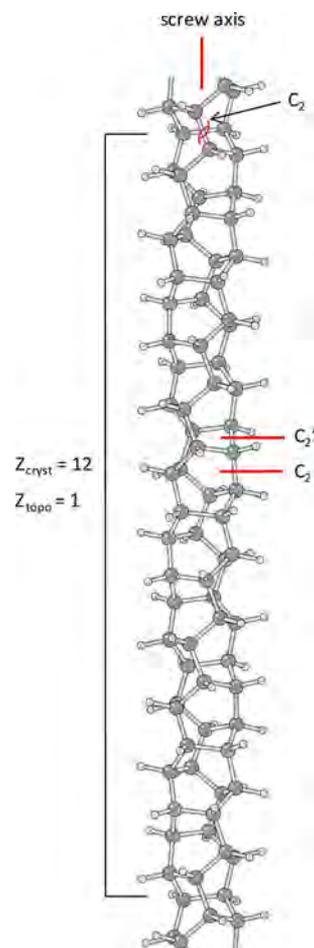


Figure 8. Structure of polytwistane. Symmetry elements of this structure include a screw axis and C_2 axes passing through the center of every C–C bond and intersecting the screw axis. Three C_2 axes are shown; only two are distinct, others being generated by helical symmetry operations. Building a physical model of this structure is instructive and aesthetically rewarding.

increasing Z_{topo} . We enumerate here only $Z_{\text{topo}} \leq 3$; some $Z_{\text{topo}} = 4$ isomers are given in the SI.

Next we derive the mapping rules used to eliminate duplicate structures. The four structures in Figure 9 are the same structure viewed from different directions. Let us focus on the top left one, which shows the twist-boat conformation most clearly for the first ring (dashed oval with orange numbering). A counterclockwise (looking down from top) rotation of about 30° leads to the top-middle structure, in which the twist-boat conformation is clearest for the second ring (with blue numbering). A translation upward along the axial direction of the top middle structure takes it back to the top left structure. What we just described is a screw symmetry operation — rotation plus translation — that transforms the first ring to the second. A set of correspondences (set 1 in Figure 9) is thus derived for this symmetry operation, which simply says that the unprimed ring is equivalent to the primed ring. Repeating this screw operation will relate the first ring to the third ring and so on, so that the unprimed, primed, and double primed numbers are equivalent. This is extremely useful in looking for duplicates, because one can freely add or drop primes for an identifier, as long as one does so consistently for all numbers in an identifier.

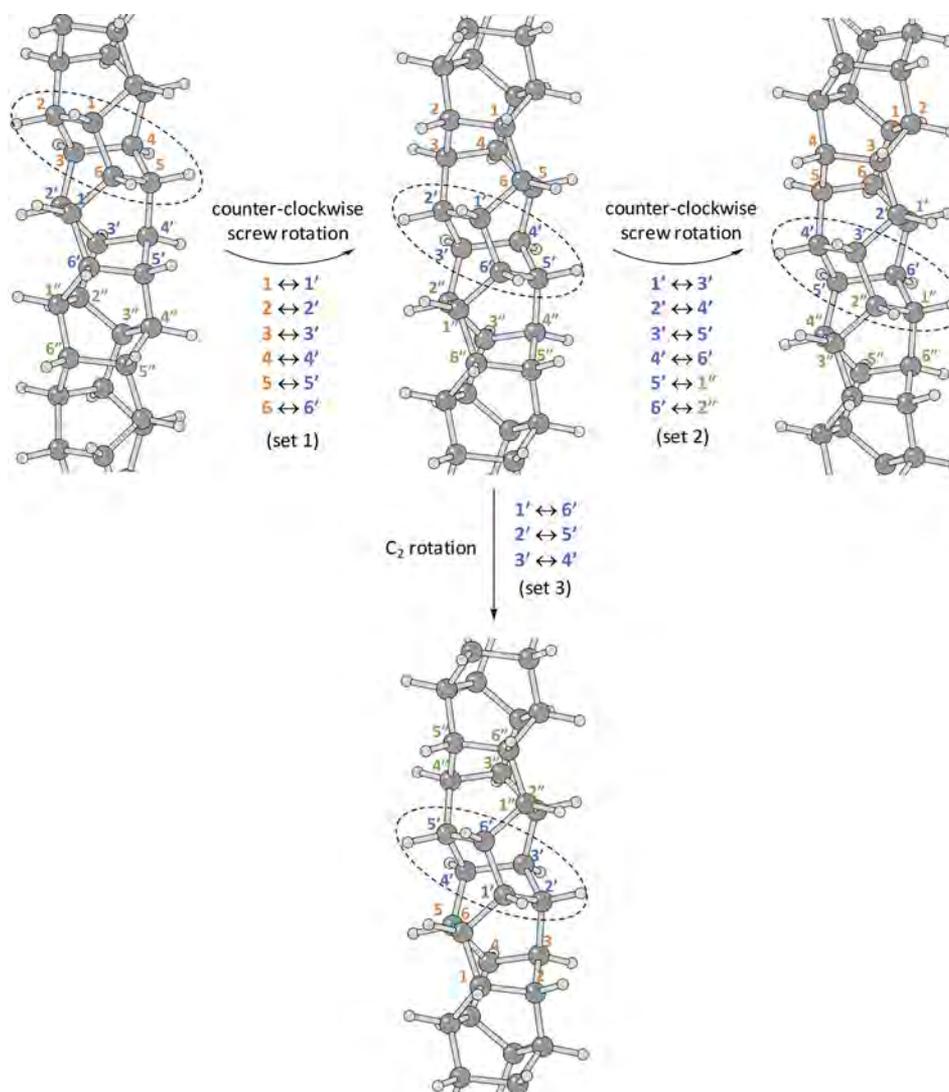


Figure 9. Ring position numbering and mapping rules in polytwistane. Three sets of correspondences were derived corresponding to three symmetry operations — two screw rotations with different screw angles and a C_2 rotation. Note that the C_2 rotation reverses the thread direction.

Starting from the top-middle structure, if one does the screw operation with a different screw angle, about 130° counter-clockwise, one reaches the top-right structure, in which the clearest twist-boat ring (dashed oval) comprises four atoms from the second ring and two from the third ring. Mapping rules for this screw rotation are given as set 2 in Figure 9, which simply relates odd numbers to odd numbers and even numbers to even numbers. Although we only list six pairs of relations in set 2, when they are coupled with set 1 one can derive that all odd numbers are equivalent, as are all even numbers.

It has been shown that all carbons in polytwistane are equivalent,⁷ which means that the sets of odd and even numbers must also be equivalent. One gets this relation from C_2 operations. The bottom structure in Figure 9 is produced by a 180° rotation about the C_2 axis passing through the centers of bonds $1'-6'$ and $3'-4'$ of the middle (blue) 6mr. The set of correspondences derived from the C_2 rotation (set 3) indeed shows that odd-number positions are equivalent to even-number positions.

Important in applying the correspondences arising from the C_2 axes is to realize that the polymer is flipped up/down by

these operations, so one must take care to reverse the sequence of numbers in the identifiers.

In summary, the three sets of mapping rules ensure that, for a given position in a given ring, every other position in the same ring is equivalent (sets 2 and 3), and this equivalency propagates to adjacent rings throughout the entire structure (set 1). The three sets of correspondences demonstrate that every position is equivalent and, as we found, are sufficient to eliminate duplicates. However, again, we do not formally prove that this group of three sets is minimal.

Figure 10 lists the identifiers for pyridine polymers of polytwistane with $Z_{\text{topo}} \leq 3$, with distinct ones in red. The star symbol denotes isomers with N–N bonds. Lists for some $Z_{\text{topo}} = 4$ are given in the SI. For $Z_{\text{topo}} = 1$ there is only one distinct structure, since every position is equivalent. For $Z_{\text{topo}} = 2$ there are 7 distinct isomers, with two whose identifiers start with 2 ($23'$ and $25'$). Since every position is equivalent, one should be able to transform any identifier so that it starts with 1. That is true, but when we do such transformations for $23'$ and $25'$, we obtain $23' = 3'2 = 1'6'$ and $25' = 5'2 = 1'4'$ (the first equation uses translation, and the second equation uses set 2 in Figure 9), in which the two nitrogens are in the same ring. This

$Z_{\text{topo}}=1$		
1	2=3=4=5=6=1	
$Z_{\text{topo}}=2$		
11'=1	21'=1'2=12'	31'=1'3=13'
12'	22'=5'5=3'3=1'1=1	32'=2'3=23'
13'	23' (*)	33'=1'1=1
14'	24'=3'5=1'3=13'	34'=12'
15'	25'	35'=13'
16' (*)	26'=1'5=15'	36'=14'
41'=1'4=14'	51'=1'5=15'	61'=1'6=16'
42'=2'4=24'	52'=2'5=25'	62'=5'1=15'
43'=3'4=34'	53'=3'5=35'	63'=4'1=14'
44'=3'3=1	54'=4'5=45'	64'=3'1=13'
45'=23'	55'=33'=1	65'=2'1=12'
46'=1'3=13'	56'=1'2=12'	66'=1'1=1
$Z_{\text{topo}}=3$		
11'1''=1	12'1''=11'2''	13'1''=11'3''
11'2''	12'2''=55'6''=11'2''	13'2'' (*)
11'3''	12'3''	13'3''
11'4''	12'4''	13'4''=34'6''=12'4''
11'5''	12'5''	13'5''
11'6'' (*)	12'6'' (*)	13'6'' (*)
14'1''=11'4''	15'1''=11'5''	16'1''=11'6''
14'2''	15'2''	16'2''
14'3''=36'5''=21'4''=14'2''	15'3''	16'3''
14'4''=36'6''=11'4''	15'4'' (*)	16'4''=31'6''=16'3''
14'5''	15'5''	16'5''=21'6''=16'2''
14'6''=13'6''	15'6''=12'6''	16'6''=11'6''
21X=1X2		
221=122	231=123	241=124
222=1	232 (*)	242=535=313=133
223 (*)	233=445=223	243=435=213=132
224=355=133	234=345=123	244=335=113
225	235	245=235
226=155	236=145	246=135
251=125	26X=Y15=15Y	331=133
252	31X=1X3	332=233
253 (*)	32X=2X3	333=1
254=325=253		334=112
255=225		335=113
256=125		336=114
341=134	351=135	36X=Y14=14Y
342=534=312=123	352=235	4XM=NY3=3NY
343=334	353=131	5XM=NY2=2NY
345=234	354=132	6XM=NY1=1NY
346=134	355=133	
	356=134	

Figure 10. Isomer list for $Z_{\text{topo}} \leq 3$ pyridine threads of polytwistane. Distinct isomers are in red. X and M are defined in the text. The starred isomers contain adjacent N atoms.

phenomenon arises due to the multiple partitions into rings, similar to the case of the zipper polymer.

For $Z_{\text{topo}} = 3$, there are 27 distinct isomers. Several interesting points can be made. First, traveling down and up along the axis are different. Take 12'3'' and 3'2''1 as an example. The former is a sequence of 123 down the thread; the latter is the same sequence traveling up the thread. They are not the same, as $3'2''1 = 13'2'' \neq 12'3''$. Second, as mentioned before, a C_2 operation reverses the thread direction, so that the identifier should also be reversed. Take the example $13'4'' = 34'6'' = 12'4''$. The first equation makes use of the correspondences of set 3, and the second equation makes use of the correspondences of set 2. Note that the C_2 rotation reverses the sequence, so that $13'4'' = 34'6''$, not $64'3''$. $34'6''$ and $64'3''$ are not the same; they would be, only if there were mirror planes perpendicular to the thread axis.

During the enumeration, we noticed that the primes and double-primes used to differentiate rings can be dropped if we carefully avoid transforming two nitrogens into one ring by correspondences of set 2. Dropping the primes and double-primes simplifies the identifiers, but one should keep in mind that each number in, for instance, 223 indicates a nitrogen position in a different ring.

In the enumeration and subsequent examination of duplicates in Figure 10, we first examined the isomers 1XM one by one. However, one can also examine a batch of isomers at the same time. For example, using the C_2 correspondences, one gets $36X = Y14 = 14Y$, where $X + Y = 7$. One immediately finds that all 36X are duplicates of 14Y, which are already examined. Similarly, $4XM = NY3 = 3NY$, where $X + Y = 7$ and $M + N = 7$.

Once again, we have identified the isomers with adjacent N atoms, likely disfavored in energy, with a starred entry in Figure 10.

2.4. Polymer I. Polymer I has $Z_{\text{topo}} = 2$ and $Z_{\text{cryst}} = 2$. There is one vertical mirror plane and two distinct C_2 axes in this structure. Figure 11 shows two views of the polymer and the symmetry operations in it.

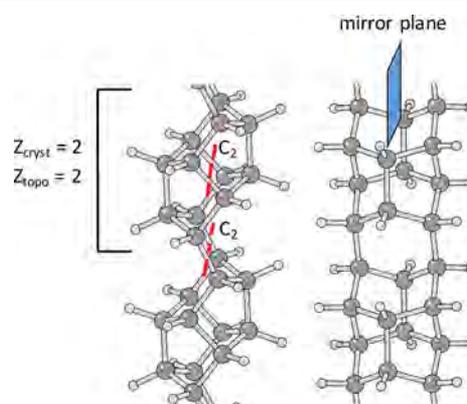


Figure 11. Symmetry elements in polymer I.

Polymer I differs from the other two polymers discussed above in that there are two choices of six-membered rings, and the rings from the two choices have different topology. Specifically, as shown in Figure 12, one choice results in rings with a 4–2 connection, i.e., four bonds going up and two going down, or vice versa (previously called “class II”⁸). The other choice gives rings with a 3–3 connection (class III”⁸).

We derived the correspondences based on the symmetry elements and enumerated isomers, as we did above for two

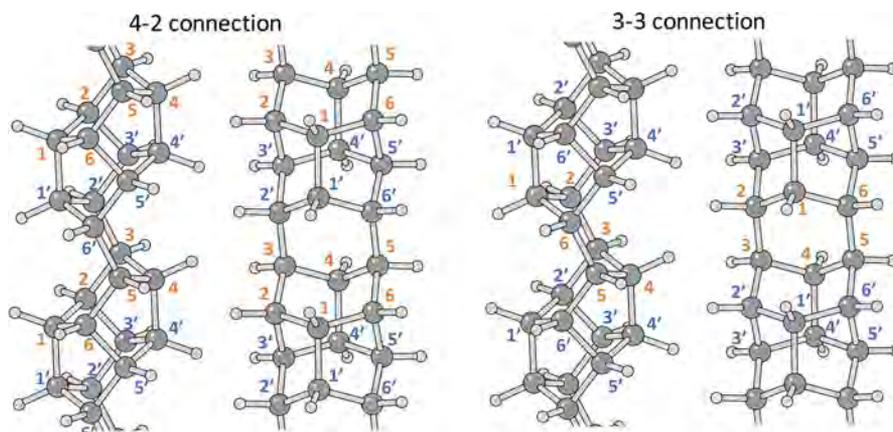


Figure 12. Two choices of rings and the respective numbering in polymer I.

other polymers, but here for both choices of rings. Then we derived the correspondences between the numberings of the two ring choices and used them to eliminate duplicates that are distinct within their given ring choice. This is less complicated than it reads. We list in Figure 13 the distinct isomers. Details of the enumeration are given in the SI. In total there are 14 distinct isomers for pyridine threads of polymer I type, given $Z_{\text{cryst}} = 2$.

4-2 connection		
11' (*)	21'	31'
12'	22'	32' (*)
13'	23' (*)	36'
14'	25'	41'
	26'	
3-3 connection		
13'	23' (*)	
14'	24'	
	25'	

Figure 13. Distinct isomers for $Z_{\text{topo}} \leq 2$ pyridine threads of polymer I. Starred isomers contain adjacent nitrogen atoms.

2.5. A Scheme for Computer-Based Isomer Enumeration, Illustrated for Tube (3,0). The previous examples illustrate how polymer symmetry can aid isomer enumeration. It is also clear, though this was not said explicitly, that for higher Z , this is a job for a computer. In this section we show how such a program operates for the case of tube (3,0) isomers. We first follow a procedure similar to that we used in previous cases to identify the symmetry elements in tube (3,0) and the sets of correspondences associated with the symmetry operations. Then we implement such symmetry operations into a computer program, letting it run through all identifiers, eliminating duplicates for any given Z_{topo} .

2.5.1. Symmetry Elements and Notations. Tube (3,0) has an achiral structure with $Z_{\text{topo}} = 1$ and $Z_{\text{cryst}} = 2$. It has a 3-fold axis of rotation (C_3) along the thread axis (which is also the screw axis), three vertical reflection planes (σ_v), horizontal reflection planes (σ_h), and 2-fold axes of rotation (C_2) perpendicular to the thread axis (Figure 14). Not all of the symmetry elements are needed to derive the minimum sets of correspondences that are sufficient for eliminating duplicate structures. Here we choose the 60° screw rotation (counter-

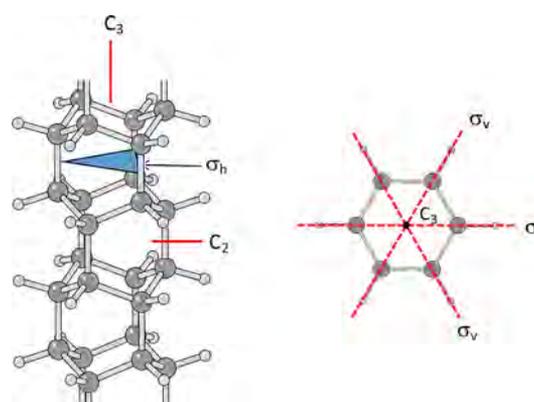


Figure 14. Two views of the tube (3,0) structure and the symmetry operations in it and the numbering of atoms in tube (3,0).

clockwise), C_2 and σ_v . The sets of correspondences associated with the three symmetry operations are shown in Figure 15.

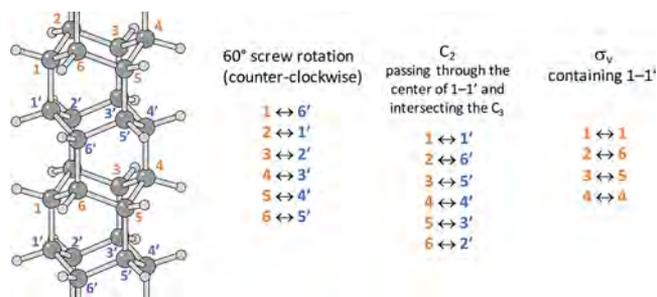


Figure 15. Numbering of atoms in tube (3,0) and sets of correspondences.

As shown in Figure 15, we number the ring positions clockwise, looking down the thread. The position 1 of the first ring (orange numbers) is so chosen such that the atom at this position bonds “down” to position 1' of the second ring (blue numbers). The colloquial descriptors “bonding down” and “bonding up” refer to the direction of bonds when the thread is placed vertically. Note the different bonding directions of positions 1 and 1'.

2.5.2. Implementation into a Computer Program. Each pyridine thread structure is assigned an identifier with the number indicating the N positions. The identifier is treated as an array in the program; a symmetry operation is implemented

as a numerical operation on each of the digits in the array, resulting in a new array. The general flow or algorithm of the program is as follows (exemplified by $Z = 4$ threads):

1. *List All Isomeric Possibilities Including Their Mirror Images.* The isomeric possibilities for $Z = 4$ threads are simply the combinatorial possibilities for four numbers, each running through 1–6, i.e., 1111, 1112, ..., 6666. Note that we drop the primes for the numbers, keeping in mind that the second place is not the same as the first place (e.g., position 1 in the second ring is not the same as position 1 in the first ring). We make use of the sets of correspondences for σ_v in Figure 15 to generate the mirror images. The identifier is stored as an array, for example, $A = [1\ 2\ 3\ 4]$.

2. *Apply the Screw and C_2 Rotations to Both the Original Structures and Their Mirror Images.* The goal here is to search all identifiers that correspond to the same structure. See the SI for how one can guarantee that one finds all equivalent identifiers.

We call a 60° rotation (counterclockwise) an α operation. Using the correspondences in Figure 15, applying operation α once to the identifier 1234, one gets $\alpha A = [6\ 1\ 2\ 3]$. Applying α twice to A , one gets $\alpha^2 A = [5\ 6\ 1\ 2]$, and three times $\alpha^3 A = [4\ 5\ 6\ 1]$. It is easy to see that applying operation α n times to an array results in a new array with n subtracted from each element, i.e., $\alpha^n A = A - n$; if the resulting number in the new array is ≤ 0 , then 6 is added to that number to produce a positive number. Figure 16 illustrates the α operation. Note

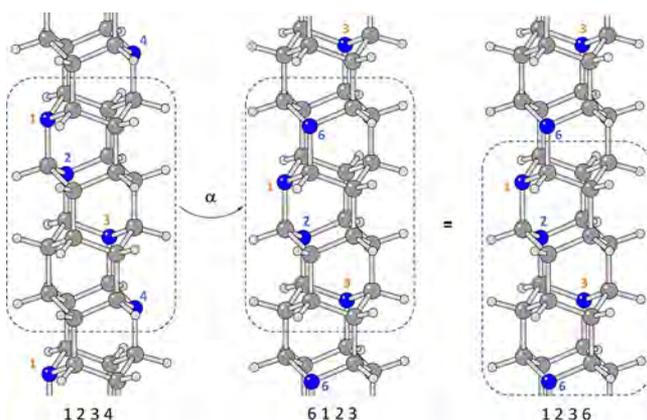


Figure 16. Illustration of symmetry operation α (60° counterclockwise rotation) on a structure with an identifier 1234 and a shift along the thread axis after rotation. $\alpha [1\ 2\ 3\ 4] = [6\ 1\ 2\ 3] = [1\ 2\ 3\ 6]$.

that the α operation changes the orange-numbered ring to blue-numbered ring and vice versa. A shift of the unit cell is necessary in order for the first number of the identifier to be associated with the orange-numbered ring.

We call a C_2 rotation a β operation. This operation turns the topological unit cell upside down, thus reversing the order of the rings and the bonding directions of C/N atoms. The correspondences for C_2 in Figure 15 show that, except for $1 \leftrightarrow 1$, the two numbers on both sides of each arrow add up to 8. For instance, as shown in Figure 17, applying β to $[1\ 3\ 1\ 4]$, one gets $\beta [1\ 3\ 1\ 4] = [4\ 1\ 5\ 1]$.

3. *Choose the Smallest Identifier (Here Viewing It as a Number) To Represent the Distinct Structure.* In step 2, for each identifier we have generated all equivalent identifiers that correspond to the same structure. In this step, we pick the smallest identifier to represent the distinct structure and

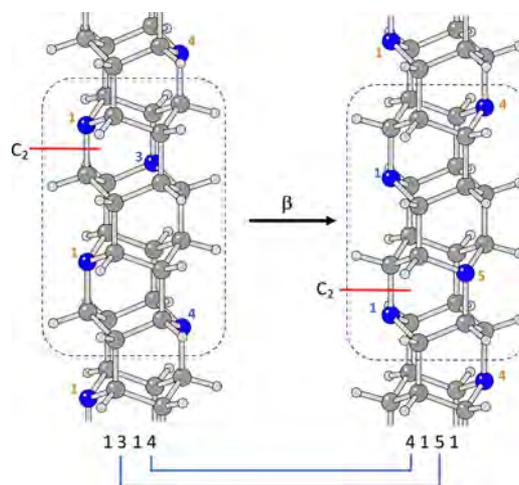


Figure 17. Illustration of symmetry operation β (C_2 rotation). $\beta [1\ 3\ 1\ 4] = [4\ 1\ 5\ 1]$. The lines at the bottom show that, except 1, the two corresponding numbers in the old and new array add up to 8. Also notice the reversal of the order of the digits.

remove all other equivalent identifiers to obtain a final result. Note that a structure and its mirror image are treated as the same, even though they may have opposite chirality (e.g., 12 = 16; and we only print out 12). We also convert supercells to fundamental unit cells, e.g., 121212 = 1212 = 12.

4. *Optimization of the Code.* One can use a similar algorithmic structure for enumerations of isomers in any thread type, being aware that different symmetries in different threads give rise to different numerical operations on the identifier array. Additional optimization of the code may be obtained by imposing constraints derived from thread-specific symmetry considerations or chemical intuition. For example, in listing the isomeric possibilities in step 1, one only needs to list those with identifiers starting with 1, since all isomers with identifiers starting with 2–6 can be transformed to identifiers starting with 1 by screw operations and/or C_2 operations discussed above. In other words, we do not have to list all 1111 to 6666 candidates but only 1111 to 1666. This constraint reduces the computation cost to 1/6 of the original.

Here is another example of optimization of the code. In step one, we list all possible identifiers and store the list in computer memory. In step 2, we search for equivalent identifiers for 1111, 1112, ..., 1666 in an ascending order (see the SI for how to find all equivalent identifiers without missing one). Since identifier 1111 has the smallest number, its equivalent identifiers must have numbers greater than 1111. Now we delete those identifiers that are equivalent to but greater than 1111 from the list, so that we do not need to examine symmetry operations for those identifiers again. One realizes that there is no equivalent identifier to 1111 in the range of 1111–1666. This optimization allows us to do symmetry operations only on identifiers with relatively small numbers instead of all of them and will cut down the computational cost to approximately $\frac{1}{2 \times Z_{\text{topo}}}$. After those optimizations, it only takes under a second for a modest laptop computer to find the topologically distinct isomers for $Z_{\text{topo}} = 4$. The case $Z_{\text{topo}} = 6$ takes 20 times longer, which underlines the importance of optimizations as the thread repeat unit increases.

There might be more efficient implementations of the algorithmic process suggested. The idea here is to show how

one can use the computer to assist in the enumeration, especially for large topological unit cells. Our code (Matlab) can enumerate any even $Z_{\text{topo}} = 4, 6, \dots$ for pyridine threads of tube (3,0) type; the code is given in the SI. We list in Figure 18

$Z_{\text{topo}}=2$		
11 (*)		
12		
13		
14		
$Z_{\text{topo}}=4$		
1112 (*)	1213	1251
1113 (*)	1214	1253
1114 (*)	1215	1254
1122 (*)	1216	1261
1123 (*)	1231	1263
1124 (*)	1234	1264
1125 (*)	1235	1314
1126 (*)	1241	1315
1133 (*)	1243	1331
1134 (*)	1244	1335
1135 (*)	1245	1364
1144 (*)		

Figure 18. Distinct isomers for $Z_{\text{topo}} = 2$ and 4 pyridine threads of tube (3,0), 38 in total. Starred isomers contain adjacent nitrogen atoms.

the topologically distinct structures for tube (3,0) pyridine threads with $Z_{\text{topo}} = 2$ and 4; the ones with neighboring N atoms are designated by *. The isomers for $Z_{\text{topo}} = 6$ are listed in the SI.

3. CONCLUSION

There are many possible benzene nanothreads, one-dimensional fully saturated polymers of composition $(\text{CH})_6$. If one substitutes for a hydrogen or replaces a heteroatom E for CH, as in $(\text{CH})_5\text{CR}$ or $(\text{CH})_5\text{E}$, the number of isomeric possibilities grows further. We provide a methodology for exhaustively enumerating the isomeric possibilities, using sets of atom correspondences or mapping rules that follow from translational or point-group symmetries.

At first sight, it might seem that we have in fact introduced two methods. In fact they are the same, both making use of the polymer symmetries. The difference is only that the second method (shown explicitly for tube (3,0)) is explicitly adapted for the enumerating capabilities of a computer program.

That we get 1, 7, 27 distinct isomers for $(\text{CH})_5\text{E}$ in a polytwistane thread with $Z_{\text{topo}} = 1, 2, 3$, respectively, is not as important as the fact that we have a symmetry-based algorithmic procedure for generating these and eliminating duplicates. The methodology is widely applicable to other polymers as well. We will next proceed to put an energy metric on the various isomers, to search for regularities in the isomer stability of pyridine nanothreads.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.7b00911.

Structural relations of the four nanothreads in Figure 1 to a stack of benzene molecules; isomer list of some pyridine threads based on polytwistane, for $Z_{\text{topo}} = 4$;

enumeration of isomers based on the polymer I structure; method for finding all equivalent identifiers for a given identifier; code for enumerating pyridine threads of tube(3,0) type; $Z_{\text{topo}} = 6$ pyridine nanothreads isomers of tube (3,0) type (PDF)
Structures of enumerated threads (ZIP)

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Notes

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■ REFERENCES

- (1) Bridgman, P. W. Change of Phase under Pressure. I. the Phase Diagram of Eleven Substances with Especial Reference to the Melting Curve. *Phys. Rev.* **1914**, 3 (3), 153–203.
- (2) Fitzgibbons, T. C.; Guthrie, M.; Xu, E.; Crespi, V. H.; Davidowski, S. K.; Cody, G. D.; Alem, N.; Badding, J. V. Benzene-Derived Carbon Nanothreads. *Nat. Mater.* **2015**, 14 (1), 43–47.
- (3) Li, X.; Baldini, M.; Wang, T.; Chen, B.; Xu, E.-S.; Vermilyea, B.; Crespi, V. H.; Hoffmann, R.; Molaison, J. J.; Tulk, C. A.; Guthrie, M.; Sinogeikin, S.; Badding, J. V. Mechanochemical Synthesis of Carbon Nanowire Single Crystals. *J. Am. Chem. Soc.* **2017**, 139 (45), 16343–16349.
- (4) Juhl, S. J.; Li, X.; Crespi, V. H.; Badding, J. V.; Alem, N. Carbon Nanothreads Probed by High-Resolution Transmission Electron Microscopy. Submitted.
- (5) Stojkovic, D.; Zhang, P.; Crespi, V. H. Smallest Nanotube: Breaking the Symmetry of sp^3 Bonds in Tubular Geometries. *Phys. Rev. Lett.* **2001**, 87, 125502.
- (6) Wen, X.-D.; Hoffmann, R.; Ashcroft, N. W. Benzene under High Pressure: A Story of Molecular Crystals Transforming to Saturated Networks, with a Possible Intermediate Metallic Phase. *J. Am. Chem. Soc.* **2011**, 133, 9023.
- (7) (a) Olbrich, M.; Mayer, P.; Trauner, D. A step toward polytwistane: synthesis and characterization of C2-symmetric tritwistane. *Org. Biomol. Chem.* **2014**, 12, 108. (b) Barua, S. R.; Quanz, H.; Olbrich, M.; Schreiner, P. R.; Trauner, D.; Allen, W. D. Polytwistane. *Chem. - Eur. J.* **2014**, 20 (6), 1638–1645.
- (8) Xu, E.; Lammert, P. E.; Crespi, V. H. Systematic Enumeration of sp^3 Nanothreads. *Nano Lett.* **2015**, 15 (8), 5124–5130.
- (9) Chen, B.; Hoffmann, R.; Ashcroft, N. W.; Badding, J.; Xu, E.; Crespi, V. Linearly Polymerized Benzene Arrays As Intermediates, Tracing Pathways to Carbon Nanothreads. *J. Am. Chem. Soc.* **2015**, 137 (45), 14373–14386.
- (10) Li, X.; Wang, T.; Duan, P.; Baldini, M.; Huang, H.-T.; Chen, B.; Juhl, S.; Koeplinger, D.; Crespi, V. H.; Schmidt-Rohr, K.; Hoffmann, R.; Alem, N.; Guthrie, M.; Badding, J. V. Carbon Nitride Nanowire Crystals Derived from Pyridine. To be submitted.

(11) Silveira, J. F. R. V.; Muniz, A. R. Functionalized Diamond Nanothreads from Benzene Derivatives. *Phys. Chem. Chem. Phys.* **2017**, *19*, 7132–7137.

(12) Contreras, M. L.; Avila, D.; Alvarez, J.; Rozas, R. Exploring the Structural and Electronic Properties of Nitrogen-containing Exohydrogenated Carbon Nanotubes: A Quantum Chemistry Study. *Struct. Chem.* **2010**, *21*, 573–581.

(13) Contreras, M. L.; Villarroel, I.; Rozas, R. How Structural Parameters Affect the Reactivity of Saturated and Non-Saturated Nitrogen-Doped Single-Walled Carbon Nanotubes of Different Chiralities: A Density Functional Theory Approach. *Struct. Chem.* **2015**, *26*, 761–771.

(14) Contreras, M. L.; Villarroel, I.; Rozas, R. Hydrogen Physisorption Energies for Bumpy, Saturated, Nitrogen-Doped Single-Walled Carbon Nanotubes. *Struct. Chem.* **2016**, *27*, 1479–1490.

■ NOTE ADDED IN PROOF

We direct the reader also to several papers on nitrogen-containing saturated threads. Please see refs [12](#), [13](#), and [14](#).