A Tale of Two Topologies: Woodward–Hoffmann Rules At Your Fingertips!

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A simple procedure for determining whether a pericyclic reaction is thermally allowed is described. The focus is on the potential aromaticity of the transition state of the process, which is inferred from the topological features of the interacting orbitals and the number of electrons involved.

Introduction

A major breakthrough in our understanding of an important class of chemical transformations known as pericyclic reactions was achieved in the mid-sixties. The mysterious manner in which some thermal processes occur readily, while apparently related ones do not, the way the preferences are reversed when the reactions are tried under photochemical conditions, and most importantly, how some stereochemical features are faithfully followed were all sorted out by Robert Woodward and Roald Hoffmann. The validity and predictive power of Woodward-Hoffmann (W–H) rules were repeatedly demonstrated by subsequent work. Not surprisingly, the understanding and application of W–H rules now forms a core component in the organic chemistry curriculum.

Usually, W–H rules are taught following the original derivations, which emphasise the role of symmetry in orbital correlation diagrams. The procedure is quite involved and often appears nebulous for teachers and students alike. It is also not obvious why the symmetry rules are so rigidly obeyed in reactions of unsymmetrical derivatives used as illustrations.

Several alternative descriptions have been proposed over the years. While the original W–H approach is quite comprehensive and also aesthetically attractive, simpler strategies may be more appropriate

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for undergraduates. I have found over the years that a programme for the understanding and application of W–H rules, based on the approach of Dewar and Zimmerman, is the the easiest.

W–H Rules in a Nutshell

We define W–H rules simply as, *reactions wherever possible proceed through aromatic transition states.*

Aromaticity in the ground state of cyclic systems is a familiar concept. But how does one infer the aromatic nature of transition states of pericyclic reactions? One can do so by identifying the geometric relationship of the interacting orbitals and the number of electrons involved.

The orbital topology in cyclic systems can be classified as two categories, viz., Hückel and Möbius. Hückel systems are aromatic with $4n + 2$ electrons, while Möbius aromaticity requires $4n$ electrons (n is an integer). Let us see how the classification is done and also examine the basis of the simple electron counting principle.

Orbital Topologies

Consider a cyclic array of *s* orbitals. It is obvious that each orbital can have an energetically favourable in-phase overlap with its immediate neighbours. This is also true if the interacting orbitals are $p(\pi)$ orbitals. Side-on overlap is possible in this case. This type of orbital topology which resembles a smooth ribbon is termed a Hückel system (*Figure* 1a).

Figure 1. Cycle of orbitals with (a) Hückel and (b) Möbius topologies.

(a)

(b)
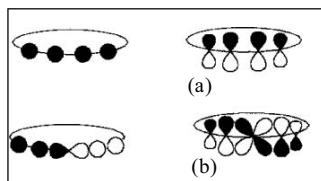
If a *p* orbital is introduced in the cycle of *s* orbitals, in-phase interaction throughout the ring is no longer possible. A $d(\pi)$ orbital in a cyclic array of $p(\pi)$ orbitals also has the same disruptive effect (*Figure* 1b). The node (change of orbital phase) within the additional orbital necessarily makes a pair of adjacent orbitals somewhere in the cycle have out-of-phase overlap. It is no longer possible for every orbital to have favourable overlap with each of its

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Box 1. How to make Hückel and Möbius Strips, Catenanes and Knots

Hückel pericycle: Bring the ends of a 1" X 12" paper strip together and glue the ends. The pericycle will have two surfaces (inner and outer) and no nodes (dislocations). Cut the ring around the middle to get two identical pericycles with no nodes.

Möbius pericycle: Bring the ends of a 1" X 12" paper strip together. Hold firmly one end by the left hand and the other by the right. Give the right hand end a 180° twist and glue the ends. We now have a Möbius pericycle with 1 node. Möbius pericycle has only one surface. Check this by drawing a line around the middle of the strip. The line will cover the entire surface of the strip. Carefully cut the strip around the middle. A large pericycle with two nodes will result.

Catenanes: Bring the ends of a 1" X 18" paper strip together. Hold firmly one end by the left hand and the other by the right . Give the right end two successive 180° twists and glue the ends. The pericycle will have 2 nodes. Carefully cut around the middle. Two pericycles which are interlocked and have two nodes will result.

Knots: Bring the ends of a 1" X 18" paper strip together. Hold firmly one end of the strip by the left hand and the other by the right. Give the right end three successive 180° twists and glue the ends. The pericycle will have 3 nodes. Cut along the middle carefully. A single pericycle with a knot (6 nodes!) will result.

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neighbours. A twist has been introduced in the ribbon of orbitals. This topology is classified as a Möbius system (see *Box* 1 for procedures to make models of twisted ribbon topologies).

A more general definition can be proposed. Hückel systems correspond to a cyclic array of orbitals with zero or an even number of nodes along the ring. Möbius systems, on the other hand, are characterised by an odd number of nodes around the cycle.

The orbital topology determines the pattern of molecular orbital (MO) energies that result from mutual interaction. The MO energies in Hückel systems can be derived using simple calculations. The results can also be understood qualitatively since they follow a simple, regular pattern. For each ring of N orbitals, there is a highly stabilised MO, followed by pairs of higher energy orbitals, all

Figure 2. *MO energy patterns for Hückel and Möbius ring systems. The energy of an MO can be derived from the points at which the polygons touch the enclosing circles. Points below the centre are bonding, those above are antibonding and those along the centre are non-bonding. For example, the π orbitals of square cyclobutadiene (a Hückel system) form a highly stabilised bonding MO, two non-bonding MOs and a highly destabilised antibonding MO.*
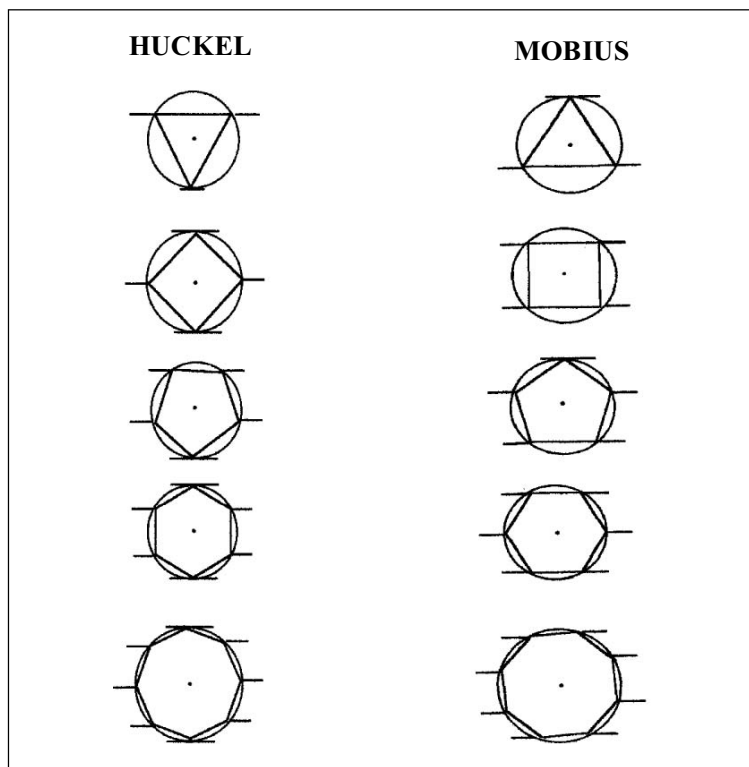
adding up to N molecular orbitals (*Figure* 2). This is because it is possible to form a molecular orbital which has in-phase overlap around the circuit, i.e., with zero nodes along the interaction cycle. This unique combination is more stable than its counterpart in an acyclic arrangement. Increasingly higher energy combinations can be derived by introducing out-of-phase combinations or nodes. These orbitals with non-zero nodes come in pairs, with equal energy.

The MO energy pattern of a Möbius system is quite different. Due to the intrinsic nodal pattern, it is not possible to construct a combination with zero nodes. The unique stabilised orbital found in Hückel systems is therefore not present in a Möbius ring. Instead one finds pairs of MOs with increasing energy (*Figure* 2).

In order to have maximum stability, the bonding orbitals should be filled and there should be a closed shell configuration. In a Hückel system, these conditions can be met only if there are 2, 6, 10, ...

electrons. Hence, Hückel systems with $4n + 2$ electrons (where n is an integer) are aromatic. In the case of Möbius systems, with doubly degenerate bonding orbitals, closed shell configurations are possible only with $4n$ electrons. As an interesting corollary, Hückel systems with $4n$ electrons and Möbius systems with $4n + 2$ electrons would have open shells. These are not aromatic. They are quite destabilised and hence termed antiaromatic.

There are numerous examples of molecules and ions which are Hückel aromatic systems. Benzene, cyclopropenium cation, and cyclopentadienyl anion are some of the most famous examples. But Möbius aromatic molecules are quite rare. Severe geometric constraints would be involved in the construction of twisted molecular rings.

Interestingly, both Hückel and Möbius topologies are repeatedly encountered in transition state structures of pericyclic reactions. Therefore, by determining the topology and the number of electrons involved, one can readily discern whether the system is aromatic or not. The reaction is *allowed* if the transition state is aromatic and *forbidden* otherwise. Let us consider a few specific cases.

Applications

For applying the topological approach, we have to consider the nature of the idealised transition state (TS) of the pericyclic process of interest. The orbitals associated with the bonds being formed, broken and rearranged are monitored. The number of nodes in the cycle of interacting orbitals at the TS geometry is determined. This immediately reveals whether the TS is a Hückel or a Möbius system. After taking into account the number of electrons involved in the process, the prediction of aromaticity (or the lack of it) is straightforward.

All reactions within the purview of W–H are reversible. The transition state analysed is common for both the forward and reverse reactions. The preferred direction of the reaction will be controlled

In order to have maximum stability, the bonding orbitals should be filled and there should be a closed shell configuration.

by thermodynamic factors. It must also be borne in mind that the predictions refer to thermal reactions. There is a reversal on going to photochemical processes since MO occupancies are altered in the excited states. For detailed predictions of the feasibility of photochemical reactions, the traditional correlation diagram approach is more powerful.

The application of the above principles will now be illustrated with important areas where W–H is useful.
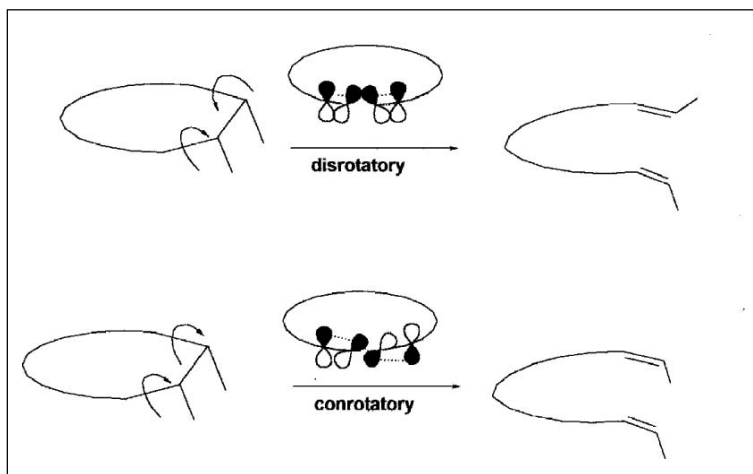
Electrocyclic Reactions

In an electrocyclic process, a chain of π orbitals is closed to form a ring by forming a new σ bond between the ends. Equivalently, one can visualise the reverse process of a σ bond connecting a π framework in a ring being opened up to form a chain of π orbitals. There are two ways the reaction can occur. In the *disrotatory* mode, the σ bond is broken by twisting the ends in opposite directions (*Figure* 3). Alternatively, the end groups can both be twisted in the same direction, leading to the *conrotatory* mode. The mode of the reaction determines the stereochemistry of the products.

The orbitals to be considered are the *p* orbitals of the π unit and the hybrid orbitals of the σ bond being broken or formed. The latter are shown as pure *p* orbitals for the sake of simplicity. The orbital topology differs for the two modes of electrocyclic reactions. In the TS of the disrotatory path, it is possible to arrange all the interacting orbitals in a cycle without any nodes (*Figure* 3). So this process is governed by Hückel topology. In contrast, the idealised transition state for the conrotatory process involves a twist at the σ bond being broken. In the cycle of orbitals, the phase changes at this point leading to one node (*Figure* 3). Hence the TS corresponds to a Möbius system.

A direct consequence of the above classification is that electrocyclic reactions involving 6 electrons would occur via the disrotatory path, while the conrotatory mode should be preferred in systems with 4

electrons. Ring opening of cyclobutenes involves reorganising 4 electrons. Hence, only the conrotatory path is thermally allowed. In the case of 1,3-cyclohexadiene, the disrotatory path is the allowed pathway. These results and the associated stereochemistry are shown in *Figure* 4.
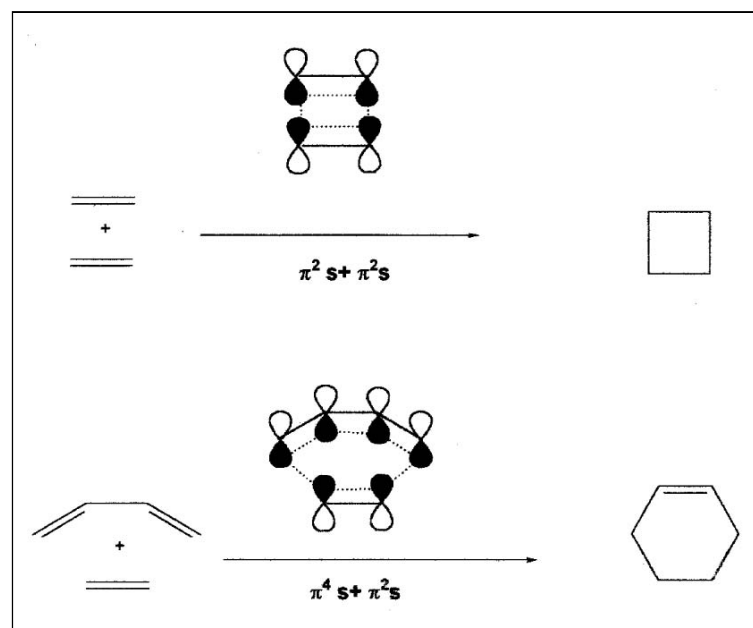
Cycloaddition Reactions

Formation of cyclobutane from two ethylene molecules is a simple example of a cycloaddition reaction. Two π bonds are converted to two new σ bonds resulting in the cyclic product. The well known Diels–Alder reaction involves the addition of an olefin to a diene. In
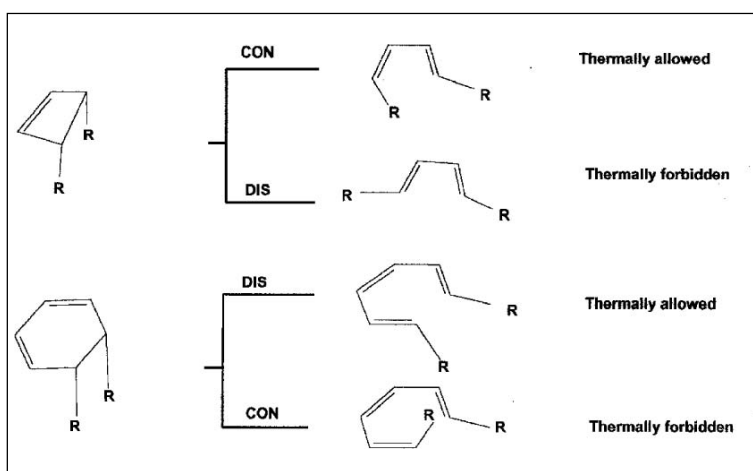
Figure 4. W–H predictions for typical electrocyclic reactions.

this process, three π bonds are reconstructed to form two σ bonds and a rearranged π bond. More complex examples involving multiple components, combinations of σ and π bonds, heteroatoms, cyclic reactants, etc., are all known. Here we shall focus on cycloadditions between two simple conjugated systems.

The mechanism following the *concerted* pathway, i.e., with a transition state characterised by partial bond formation and breaking, is of interest since it leads to well-defined stereochemistry in the products. Hence, the idealised TS to be considered is a cyclic structure. The simplest of these is obtained by bringing the reactant π orbitals face to face. This mode is known as the *suprafacial* approach with respect to each of the reactants. In this case, the interacting orbitals can all have favorable overlap with immediate neighbours (*Figure* 5). Hence the topology is obviously that of a Hückel system. An aromatic TS is obtained with 6 electrons, but not with 4. Hence, $\pi^2 s + \pi^2 s$ cycloaddition (indicating the type of bond, number of electrons and mode of approach for each component) is a thermally forbidden process. But Diels–Alder reaction ($\pi^4 s + \pi^2 s$) involving an aromatic TS is allowed. Möbius type transition states are encountered if one of the reactants is brought in an *antarafacial* manner.

Figure 5. Schematic representation of two cycloaddition reactions. The topology of the interacting orbitals at the idealised transition state is shown in the middle.

$\pi^2 s + \pi^2 s$

$\pi^4 s + \pi^2 s$

Hence, π^2s + π^2a would be an allowed thermal reaction. However, this places severe geometric constraints on the TS structure. An antarafacial approach is more likely in systems containing large rings.

Sigmatropic Reactions

In several systems, it is possible to rearrange a σ bond to a new location across a π periphery. Such reactions are called sigmatropic shifts. For example, [1,3]- and [1,5]-shifts are shown in *Figure* 6. The migrating group can be hydrogen or a more complex unit. The well known Cope and Claisen rearrangements correspond to [3,3]-shifts. A remarkable example of a molecule undergoing multiple [3,3]-shifts is discussed in *Box* 2.

In the simplest stereochemical possibility, the migrating group, say hydrogen, is smoothly transferred across the π framework in a suprafacial manner. In the idealised transition state, the orbital on the migrating hydrogen and the *p* orbitals of the π unit form a Hückel framework (*Figure* 6). Counting the electrons in the migrating σ bond and those in the π part, it is clear that [1,3]-hydride shift is
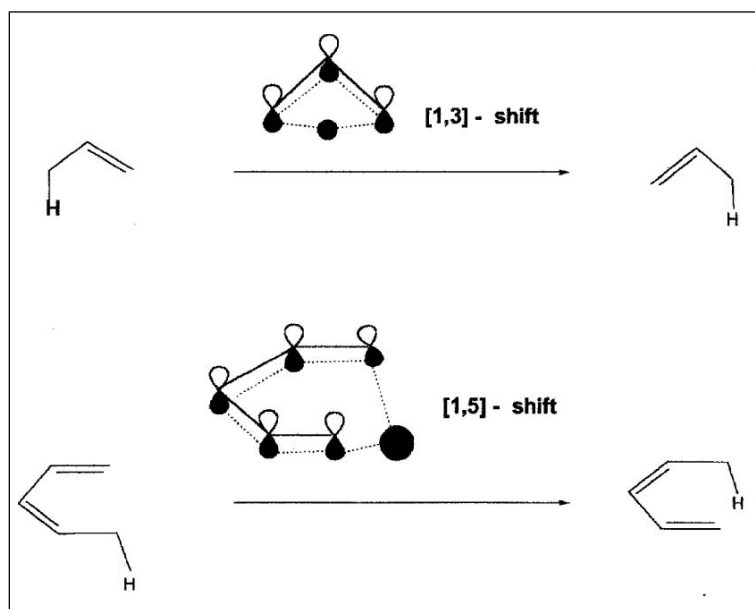

Figure 6. Typical sigmatropic shifts are shown. The topology of the interacting orbitals at the transition state is shown in the middle.

Box 2. Fluxional Molecules

The low activation energy associated with [3,3]-shifts has enabled the design of structures where, in the extreme case, bond reorganization can lead to any number of equivalent structures.

Bullvalene provides an ideal illustration. Bullvalene has a three-fold axis of symmetry. Each of the cyclopropane bonds is part of a 1,5-hexadiene unit capable of undergoing Cope rearrangement. With each [3,3]-shift, the atomic and bond positions change, but the structure is regenerated! In bullvalene the shifts take place rapidly even at moderate temperatures making all the 10 carbon atoms equivalent.

This can be readily shown by labeling the atoms. Note that there are four non-equivalent positions, a, b, c and d in a static structure of bullvalene. Choose four adjacent atoms 1, 2, 3 and 4 in each of the above positions. After one [3,3]-shift, atoms change types. By migrating bond I, atom 1 changes to a type 'd' position, 2 to 'c' and so on. A different scrambling occurs by moving bond II or III. It can be shown that each of the four positions could become any of the non-equal positions. Thus bullvalene around 100ºC can be viewed as ten points in a three-dimensional surface! Bullvalene is a perfect example of a *fluxional* molecule, one capable of giving rise to any number of equivalent structures by bond reorganization. In the present case, the possibilities are 10!/3 = 1.2 million.

Side view   View along the 3-fold axis

Bullvalene

The migrating σ bond is indicated on the arrow
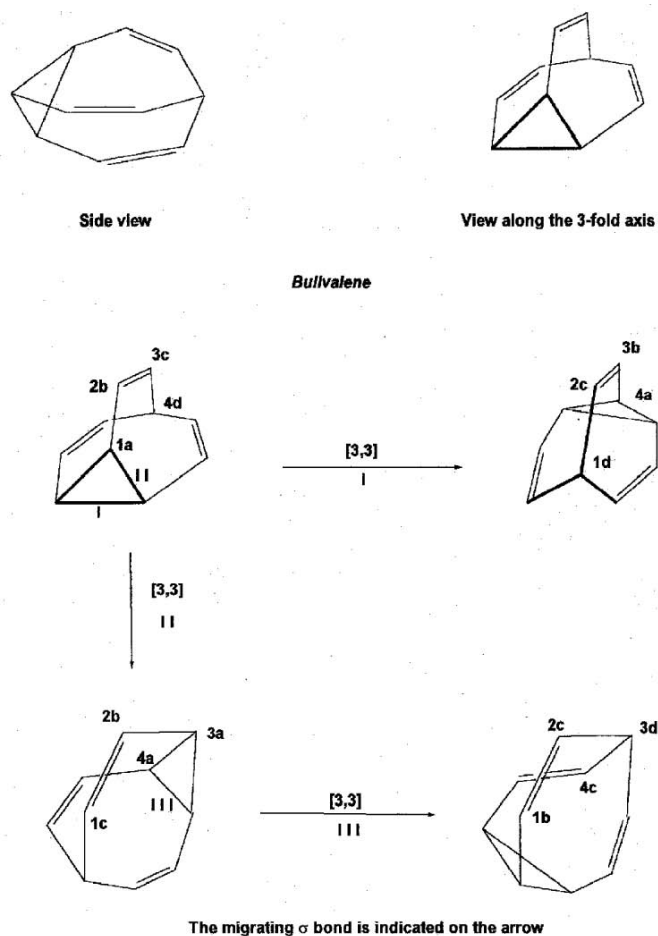
thermally forbidden while [1,5]-shift is allowed. Since 6 electrons are involved in the rearrangement, [3,3]-shifts are also allowed.

Sigmatropic reactions with Möbius transition states can be visualised in two cases. The migrating group which initially forms the σ bond with one face of the π unit ends up forming the bond at the opposite face. Alternatively, the migrating group undergoes an inversion during the rearrangement. In either case, a combination of antarafacial and suprafacial stereochemistry is involved. In the idealised TS, one node is present in the orbital cycle. With this stereochemistry, [1,3]-shifts are allowed, but not [1,5]-shifts.

Conclusions

A simple procedure was outlined for determining whether a pericyclic process is likely to be facile under thermal conditions. The analysis does not require detailed knowledge of MO theory and symmetry arguments. It can be applied even for complex substrates. The emphasis is on topology, rather than on symmetry. It enables one to appreciate why W–H rules hold good even in highly unsymmetrical systems.

Suggested Reading

◆ **R B Woodward and R Hoffmann.** *The conservation of orbital symmetry.* **Verlag Chemie. Weinheim, 1970.**
◆ **A P Marchand and R E Lehr.** *Pericyclic reactions.* **Academic Press. New York, 1977.**
◆ **T Gilchrist and R E Storr,** *Organic reactions and orbital symmetry.* **Cambridge University Press, 1979.**
◆ **N S Isaacs,** *Physical Organic Chemistry.* **Longman, 1987.**
◆ **T H Lowry and K S Richardson.** *Mechanism and theory in Organic Chemistry.* **Harper Collins. New York, 1987.**

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It feels like I am posing with the Bourbaki group, where every member is a Zel'dovich