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Relaxation and Racemization in Fluxional Rearrangement Networks: An Exact Spectral Study of Bullvalene and the P_7^{3-} Ion

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Relaxation and Racemization in Fluxional Rearrangement Networks: An Exact Spectral Study of Bullvalene and the P_7^{3-} Ion

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Abstract. Bullvalene ($C_{10}H_{10}$) rearranges through degenerate Cope shifts among 10!/3 = 1,209,600 distinguishable forms. The connectivity of this network is well documented, and kinetic simulations with computed rate constants exist for substituted bullvalenes, but, to our knowledge, the relaxation spectrum of the full network has not been reported. A recent study of 1,10-dicyanobullvalene states that the full reaction matrix is unknown and that its diagonalization appears formidable. We study the equal-rate (topological) limit, in which the rate matrix is k(3I − A) for the adjacency matrix A of the reaction graph, and we diagonalize it exactly by using the symmetric group S_{10} and the mirror involution. Every eigenvalue is assigned to an irreducible representation of S_{10}. The slowest mirror-even (equilibration) mode lies in the representation (6,4), with relaxation rate 0.1074 k, and the slowest mirror-odd (racemization) mode lies in (7,1,1,1), with rate 0.1407 k. The racemization mode loses half of its amplitude after about 14 Cope steps; this is the asymptotic half-life of the slowest odd mode, and the decay of the enantiomeric excess in a particular experiment also depends on faster modes and on the observable. For a substituted bullvalene with m distinguishable atoms, the slowest racemization mode first appears at m = 3 and the slowest equilibration mode at m = 4, and neither changes thereafter. The P_7^{3-} ion, treated in the same way, shows the same two thresholds, carried by the representations (4,1,1,1) and (3,2,2) of S_7. We validate the construction against published shell counts, diameters, isomer counts and edge lists for both systems, and we relate the thresholds to Schreier-graph methods for spectral gaps on symmetric groups. Finally, using the supporting information of two published kinetic studies, we solve exactly the rate equations of two real 120-isomer networks. The solutions reproduce the timescales and populations reported from Monte Carlo simulation (for the first network, an exact half-life of 26.7 h against about 25 h reported) and show relaxation rates spanning roughly ten orders of magnitude, so that in these networks the slowest relaxation is set by barrier heterogeneity and not by network topology alone.

1. Introduction

Fluxional molecules interconvert among structurally equivalent forms so rapidly that a single static structure does not describe them. The limiting case is a molecule whose atoms can reach very many permutational arrangements through repeated, identical elementary steps. Bullvalene, $C_{10}H_{10}$, is the classic example. Its existence was predicted by Doering and Roth in 1963 on the grounds that a divinylcyclopropane unit undergoes a rapid, degenerate Cope rearrangement, and it was synthesized by Schröder shortly afterwards. Its carbon skeleton consists of an apical methine carbon, a cyclopropane ring of three carbons, and three two-carbon vinyl bridges that connect the ring to the apex. Each Cope step breaks one cyclopropane bond, forms a new one elsewhere, and shifts the double bonds, with the result that the apex and the ring exchange roles. If the ten carbons are imagined to carry labels, a single bullvalene molecule can pass through 10!/3 = 1,209,600 distinguishable forms, and each form is connected by a Cope step to exactly three others.

1.1 Reaction graphs

The natural mathematical description of such a system is the reaction graph, in which each distinguishable form is a vertex and each elementary rearrangement is an edge. Reaction graphs were introduced for degenerate rearrangements by Balaban, Fărcașiu and Bănică in 1966, and their symmetry properties were developed over the following decades, notably by Randić and coworkers. For bullvalene the graph is so large that it was named the Monster Graph. Its early description by Oth, Müllen, Gilles and Schröder (1974) contained an error that Randić, Oakland and Klein (1986) corrected: the shortest cycle has twelve vertices, not fourteen.

Three later contributions established the structure on which the present work relies. Klin, Tratch and Zefirov (1991) gave a necessary and sufficient condition for connectivity in terms of the group generated by the molecular symmetry group and the permutation that represents the rearrangement. They also noticed that three different mathematical models of the bullvalene rearrangement exist, two of which produce graphs with only 604,800 vertices, and they left open which model is chemically adequate. Brocas (1994) resolved the matter by a parity argument: the permutation that represents a genuine Cope rearrangement is odd, while the permutation used in one of the models of Klin et al. represents the mirror image of the Cope step and is even, so that it cannot generate the full graph. Lloyd and Jones (1998) then showed that every such reaction graph is an orbital graph of the symmetric group acting on the cosets of the rotation group, and they determined the automorphism group of the bullvalene graph, $S_{10} \times C_2$, where the second factor is the mirror involution. Živković (1996) computed the number of vertices at every distance from a given vertex and showed that the mirror image of any form is at the maximal distance 29. A closely related system is the P_7^{3-} ion, whose rearrangement graph has $7!/3 = 1{,}680$ vertices and was analysed by Randić, Oakland and Klein (1986). Tratch and Zefirov (1998) used the bullvalene rearrangement as an example of a highly degenerate rearrangement in a combinatorial scheme for reaction design, citing Živković (1996) for the graph itself; they do not analyse its dynamics.

1.2 Substituted bullvalenes and kinetic studies

Experimental interest has shifted to substituted bullvalenes, in which only some carbons carry distinguishable substituents. With four different substituents a bullvalene has 1,680 constitutional isomers (852 if enantiomers are not distinguished). He and Bode (2011) used enantioenriched precursors to show that such molecules racemize, which proves that the rearrangements are not confined to a small set of isomers. They later built and analysed the complete 1,680-isomer network and found that the diameter is 16, that no enantiomeric pair is connected by a single step, and that one metastable isomer is kinetically and thermodynamically isolated (He and Bode, 2013). Gimarc and Brant (1994) drew the reaction graphs of bullvalenes with one to five identical substituents. Fallon and coworkers developed synthetic routes to di- and trisubstituted bullvalenes together with a computational toolbox that generates the isomer network of a given substituted bullvalene and the input structures for quantum-chemical calculations on every isomer and transition state (Yahiaoui et al., 2018, 2019). Ives, Maturi, Gill, Rankine and McGonigal (2024) derived a closed formula for the number of isomers of a substituted bullvalene and released a program that generates all isomers and their connectivity. Yahiaoui et al. (2019) went further and built the reaction networks of a disubstituted bullvalene (30 isomers) and a trisubstituted one (120 isomers) with density-functional barriers. They converted the barriers into first-order rate constants with the Eyring equation, simulated the kinetics by stochastic Monte Carlo (Kinetiscope), and explained the kinetic metastability of the major isomer of the

trisubstituted systems by a local kinetic well in the network. A 2026 study in ACS Central Science built the network of a bullvalene carrying two identical chain substituents and one further substituent. That network contains 120 isomers and 360 directed rearrangements, and its kinetics were simulated by stochastic Monte Carlo with density-functional rate constants. Experimentally, the only detailed kinetic study of a substituted bullvalene network that Yahiaoui et al. (2019) cite is that of Poupko, Zimmermann, Müller and Luz (1996) on fluorobullvalene, and the activation energy of the unsubstituted molecule was first measured by Saunders (1963).

On the dynamics of the unsubstituted network, however, we found almost nothing quantitative. Pei and coworkers (2024) analysed 1,10-dicyanobullvalene, whose fluxionality is restricted by the substituents to a cycle of 14 isomers. With one rate constant for all steps, their reaction matrix is the Laplacian of a 14-cycle, and they diagonalized it by analogy with the Hückel matrix of a cyclic aromatic hydrocarbon. For the unsubstituted molecule they state that the 1,209,600 × 1,209,600 reaction matrix is still unknown, that they know of no recipe for generating it, and that its diagonalization appears to be a formidable task.

The mathematical-chemistry literature supplies the missing ingredients but does not combine them. The survey of Klin, Rücker, Rücker and Tinhofer remarks that the centralizer (Hecke) algebra of a graph's automorphism group yields information on the graph's spectrum, but it stays at the combinatorial level and defers reaction graphs to other papers. Klein, Palacios, Randić and Trinajstić (2004) develop random-walk matrices and their eigen-expansions on chemical graphs in general, without treating rearrangement networks. In the sources that we examined (Section 10 and Appendix A) we found no paper that computes eigenvalues, spectral gaps or relaxation rates for the bullvalene or P_7^{3-} reaction networks. Eigenvalue studies in chemical graph theory concern overwhelmingly the molecular graph, in which atoms are the vertices, for example Hückel matrices and topological indices (Trinajstić, 1992); this is a different object from the reaction graph, whose vertices are isomers.

1.3 Contributions

We construct the chiral Cope network of bullvalene and the rearrangement network of P_7^{3-} from first principles, and we verify the construction against every published number that we could compare (Section 4). In the equal-rate limit we compute the relaxation spectrum exactly, by decomposing the problem into the irreducible representations of the symmetric group, and we identify the representations that carry the slowest equilibration and racemization modes (Section 5). We show that these slowest modes appear when exactly three or four atoms are distinguishable, in both molecules, and we connect this observation to the Schreier-graph method for spectral gaps on symmetric groups (Section 6). Finally, we use the published rate constants of two real 120-isomer networks, with different substituents and temperatures, to demonstrate that the exact method reproduces the reported Monte Carlo timescales and exposes the effect of barrier heterogeneity (Section 7).

Several things are not claimed. We do not solve the full $C_{10}H_{10}$ problem with real rate constants, which are unknown. We do not claim that the distances and diameters are new, since they are published (Section 8). And we do not claim that the idea of detecting slow modes through tuples of distinguishable points is new in mathematics (Section 6). We also do not claim that equal-rate relaxation times predict measured rates. Section 2 sets up the theory, Section 3 describes the computations, and Sections 9 to 11 discuss the implications, the limitations and the conclusions.

2. Theoretical framework

2.1 Reaction graphs as orbital graphs

Let Γ be the molecular graph of the skeleton, with n sites, and let a labelling be a bijection from the sites to the labels 1, …, n. The group S_n permutes labels. We fix a subgroup H of the automorphism group of Γ and call two labellings equivalent if an element of H maps one to the other. The equivalence classes are the right cosets Hg of H in S_n, so there are n!/|H| of them. For the chiral treatment, in which mirror images are different forms, H is the rotation group of the skeleton, which is cyclic of order three for both bullvalene and P_7^{3-}. For the enantiomer-blind treatment H is the full automorphism group (order six).

A degenerate rearrangement acts on labellings by left multiplication by a fixed permutation r. Lloyd and Jones (1998) proved that the reaction graph R(Γ, H, r) is the orbital graph of S_n acting on the cosets of H that corresponds to the orbital containing the pair (H, Hr). Concretely, the neighbours of the coset Hg are the cosets Hrhg with h in H. Three consequences follow immediately. The valency is |HrH|/|H| = |H : H ∩ r^{-1}Hr|. The graph is undirected when HrH = Hr^{-1}H, which holds when the double coset contains an involution. And, as established by Klin, Tratch and Zefirov (1991), the graph is connected if and only if the group generated by H and r is all of S_n.

For bullvalene we use the site numbering of Lloyd and Jones, in which site 0 is the apex, the arms are the triples of sites (1,2,3), (4,5,6) and (7,8,9), and the rotation is h = (147)(258)(369). The Cope rearrangement is represented by r = (03)(12)(49)(58)(67), the model called IIB by Klin et al. Here H ∩ r^{-1}Hr is trivial, so the valency is 3; the graph has 10!/3 = 1,209,600 vertices and 10!/2 = 1,814,400 edges. The group generated by h and r contains the transposition $(rh)^7$, which is (46) when permutations are composed from right to left (h acting first) and (79) when they are composed from left to right, and it acts primitively. By Jordan’s theorem, a primitive permutation group that contains a transposition is the full symmetric group (Wielandt, 1964), so the group is S_{10} and the graph is connected. The model IIA uses instead the reflection r′ = (03)(12)(46)(79). Both h and r′ are even permutations, so the generated group lies in the alternating group and the graph has two components of 604,800 vertices each. Brocas (1994) showed that r is odd and r′ is even, and that r′ represents the mirror image of the Cope step rather than the step itself; only IIB is a Cope rearrangement. For P_7^{3-}, with seven sites, h = (135)(246) and r = (02)(36)(45), the graph has 7!/3 = 1,680 vertices and is likewise connected.

Because r is odd and h is even, every edge changes the parity of the permutation that represents a form. The fully labelled graph is therefore bipartite, and a form and its mirror image lie on opposite sides (Živković, 1996). We will see in Section 5.5 that this property is lost when some atoms are indistinguishable.

2.2 Kinetics and the relaxation spectrum

In the equal-rate model each form converts into each of its three neighbours with the same first-order rate constant k. If p is the vector of populations of all forms and A is the adjacency matrix of the reaction graph, the master equation is

$$\frac{d\mathbf{p}}{dt} = -k\,(3I - A)\,\mathbf{p}.$$

The matrix 3I − A is the Laplacian of a three-regular graph. It is symmetric, so A has real eigenvalues $\lambda_1 \geq \lambda_2 \geq \dots$ and orthonormal eigenvectors v_j, and the solution is

$$\mathbf{p}(t) = \sum_j e^{-k(3-\lambda_j)t}\,(v_j^{\mathsf T}\mathbf{p}(0))\,v_j .$$

The largest eigenvalue $\lambda_1 = 3$ belongs to the uniform distribution, which is the equilibrium. Every other eigenvalue λ describes a pattern of population that decays at the relaxation rate $\kappa = k(3 - \lambda)$, and the slowest pattern, with the second-largest eigenvalue, controls the approach to equilibrium at long times. If the number of Cope steps rather than the time is counted, a pattern with eigenvalue λ is multiplied by $\lambda/3$ at each step, so a pattern is reduced to the fraction f after $\ln f / \ln(\lambda/3)$ steps. Because each form makes Cope steps at the total rate 3k, one step takes 1/(3k) on average, and a relaxation time $\tau = 1/\kappa$ therefore corresponds to $3k\tau = 3/(3 - \lambda)$ steps. The cyclic case of Pei et al. (2024) is the same construction for a cycle of N vertices, whose eigenvalues are $2\cos(2\pi m/N)$.

For a network with real rate constants, let W be the rate matrix, with W_ji the rate from form i to form j and diagonal entries that make columns sum to zero. If the rates obey detailed balance with equilibrium populations π, the matrix $S = D^{-1/2} W D^{1/2}$, with $D = \mathrm{diag}(\pi)$, is symmetric, and the dynamics are again a sum of exponentials with real rates. We use this form in Section 7.

2.3 Substituted molecules as quotients, and Young's rule

In a bullvalene with m distinguishable substituted carbons, the remaining 10 − m carbons are interchangeable. The forms of such a molecule are the labellings with m distinct labels and 10 − m identical ones, which is the quotient of the fully labelled network by the Young subgroup S_{10-m} that permutes the identical labels. The relabelling action of S_n commutes with the reaction edges, so the spectrum of the quotient network is the part of the full spectrum that belongs to functions invariant under S_{10-m}. In particular the spectra are nested: every eigenvalue of the network with m distinguishable atoms is also an eigenvalue of the network with m + 1.

The space of functions on the m-tuples of distinct sites is the permutation module Ind from S_{n-m} to S_n of the trivial representation. By Young's rule it contains exactly those irreducible representations whose Young diagram has at most m boxes below the first row (this is the form in which the statement appears in Parzanchevski and Puder, arXiv:1804.02776). Hence the pattern of a given type can appear in the network with m distinguishable atoms only if its diagram has m or fewer boxes outside the first row. This is the origin of the thresholds in the number of substituents that we find in Section 5.

2.4 Mirror symmetry, racemization and parity

Let t be a reflection of the skeleton that normalizes H. Lloyd and Jones (1998) show that the map Hg to Htg is an automorphism of the reaction graph that commutes with the action of S_n, and that the full automorphism group is $S_n \times C_2$, the second factor being this mirror involution. Functions on the network therefore split into mirror-even and mirror-odd parts, and the adjacency operator preserves each. A difference between the populations of a form and of its mirror image is a mirror-odd quantity, so the asymptotic decay of any such difference, and hence the loss of enantiomeric excess, is governed by the largest mirror-odd eigenvalue. Equilibration among forms that are not mirror images of each other is governed by the mirror-even sector.

When all ten atoms are distinguishable, the graph is bipartite with the form and its mirror image on opposite sides, as shown above. Multiplication by the parity function then maps mirror-even vectors to mirror-odd vectors and changes the sign of the adjacency operator, so the odd spectrum is exactly the

negative of the even spectrum. This relation depends on parity being a well-defined function of a form, which fails as soon as two atoms are identical. We will check that it fails.

2.5 Decomposition into irreducible representations

Let V_λ be the irreducible representation of S_n labelled by the partition λ, and let V_λ^H be its subspace of H-fixed vectors. Put Σ = Σ_{h in H} r h in the group algebra. Functions on the coset space decompose as a direct sum over λ of V_λ tensor V_λ^H, the group acting on the first factor and the adjacency operator on the second through the restriction of ρ_λ(Σ) to V_λ^H. Because HrH is closed under inversion, this restriction is symmetric. Consequently

```
\operatorname{spec}(A) \;=\; \bigcup_{\lambda \vdash n}
\operatorname{spec}\Big(\rho_\lambda(\Sigma)\big|_{V_\lambda^{H}}\Big),\qquad
\text{multiplicity of each eigenvalue } \dim V_\lambda .
```

A check on the bookkeeping is the dimension count Σ_λ dim V_λ · dim V_λ^H = n!/|H|. For the network with m distinguishable atoms the multiplicity dim V_λ is replaced by the dimension of the S_{n−m}-fixed subspace of V_λ, which is non-zero exactly when λ has at most m boxes outside its first row. The mirror involution acts on V_λ^H as ρ_λ(t) and commutes with ρ_λ(Σ), which splits each eigenspace into even and odd parts.

The same machinery applies to the larger graph obtained by not dividing by H. Let Σ_sym = ½ Σ_j (r h^j + (r h^j)$^{-1}$), the symmetrized sum over the three generators r, rh and rh². The graph on all of S_n with these generators has spectrum ∪_λ spec ρ_λ(Σ_sym), each with multiplicity dim V_λ. Since r is odd and h is even, all generators are odd, and the representation labelled by the transposed partition λ′ is equivalent to ρ_λ tensor the sign representation. Consequently ρ_λ′(Σ_sym) = −ρ_λ(Σ_sym), and the spectrum of this larger graph is symmetric about zero. We use this in Section 6.

3. Computational methods

Two independent constructions of the bullvalene network were used. The first works directly with the chemical roles of the ten carbons and is the one used for all spectra of substituted networks. The second is the coset construction of Lloyd and Jones (Section 2.1) and serves as an independent check. Their agreement is documented in Section 4.

3.1 The Cope step on labelled forms

We call the apex a, and in each arm t = 0, 1, 2 we call the cyclopropane carbon c_t, the vinyl carbon attached to it v_t, and the vinyl carbon attached to the apex w_t. A form is a placement of labels on these ten sites, with the three arms listed in anticlockwise order as seen from the apex side, and with cyclic rotations of the arms regarded as the same form. Mirror images are different forms; the mirror image of a form is obtained by interchanging two arms. A Cope step involving arms j and k, with i the third arm and (i, j, k) a cyclic ordering, breaks the bond between c_j and c_k and forms a bond between w_j and w_k. The new apex is c_i, the new cyclopropane ring consists of a, w_j and w_k, and the new arms, in anticlockwise order, are (a, w_i, v_i), (w_k, v_k, c_k) and (w_j, v_j, c_j), where each triple lists the ring carbon, the adjacent vinyl carbon and the vinyl carbon bonded to the new apex. Each form has three such steps, one for each choice of i.

The only non-trivial decision is the order in which the new arms are listed, because it decides which mirror image is produced. We fixed it by a stereochemical argument. During the step no bond to the old apex a or to the ring carbon c_i is broken, and each of these carbons keeps its three heavy-atom neighbours and its hydrogen, so that its handedness (the sign of the triple product of the vectors to the three heavy neighbours) is preserved. In a skeleton with C_{3v} symmetry, in which every arm lies in a vertical mirror plane, the handedness of the apex with respect to (w_0, w_1, w_2) and that of a ring carbon with respect to (v_0, c_1, c_2) have opposite signs. We verified this on explicit coordinates and on 2,000 random C_{3v} geometries in which the radii and heights of all four atom types were varied; the signs never changed. Requiring that both carbons keep their handedness then fixes the listed order of the new arms. The opposite order represents the mirror image of the Cope step and is the model IIA discussed in Section 2.1.

3.2 Networks, quotients and mirror sectors

Every form was stored in a canonical representation, namely the apex label followed by the lexicographically smallest cyclic rotation of the three arms, and the network was generated by breadth-first search from one form. For quotient networks with identical labels, different steps may lead to the same form, and a step may return the form itself. We kept every step as one entry of a count matrix whose rows sum to three, because the random-walk matrix must reflect all three channels. To separate mirror sectors we paired each form with its mirror image and built two reduced matrices on the mirror pairs. For the even sector every neighbour contributes with weight +1 to the class of the neighbour. For the odd sector a neighbour contributes with weight +1 if it is the representative of its pair and −1 if it is the mirror partner, and achiral forms, which are their own mirror images, contribute nothing, because an odd function vanishes on them.

3.3 Eigenvalues

The extreme eigenvalues of the large symmetric matrices were found with the implicitly restarted Lanczos method (ARPACK, through SciPy); dense symmetric solvers were used for dimensions up to about 1,500 and for all quotient matrices of the real-rate network. For networks with up to 852 mirror pairs the integer matrices were also handled exactly. The characteristic polynomial was computed with the fraction-free integer routines of python-flint and factored over the rationals, which gives the algebraic degree of each eigenvalue and exposes special values such as $2\cos(\pi/7)$.

3.4 Irreducible representations

The irreducible representations of S_n were built in Young's orthogonal form. The basis of the representation labelled by λ consists of the standard Young tableaux of shape λ. If the entries i and i + 1 of a tableau T lie in boxes whose contents (column minus row) differ by d, the adjacent transposition (i, i + 1) acts as

$$\rho(s_i)\,T \;=\; \tfrac{1}{d}\,T \;+\; \sqrt{1-\tfrac{1}{d^{2}}}\;T',$$

where T′ is the tableau obtained by exchanging i and i + 1 (the second term is absent when $|d| = 1$, that is, when the two entries share a row or a column). The matrices are real and orthogonal. A general permutation was written as a product of adjacent transpositions by bubble sort, and its matrix is the corresponding product. We verified that $\rho(r)^2 = I$ and $\rho(h)^3 = I$ in every representation, that the dimensions satisfy $\Sigma \dim^2 = n!$ (3,628,800 for S_{10} with 42 partitions, and 5,040 for S_7 with 15 partitions),

and that Σ dim V_λ · dim V_λ^H equals 1,209,600 and 1,680 respectively. The H-fixed subspace was obtained from the projector (I + ρ(h) + ρ(h)²)/3. The largest representation of S_{10} has dimension 768. Whether the generators are composed as r h^j or as h^j r does not matter, because the symmetrized sum Σ_sym is the same.

3.5 Schreier graphs on tuples

To study the spectrum without dividing by the rotation group, we considered, for each ℓ, the set of placements of ℓ distinguishable atoms on the n sites (n!/(n − ℓ)! states: 10, 90, 720, 5,040, 30,240, 151,200 and 604,800 for n = 10, ℓ = 1 to 7). Each of the six site permutations r h^j and $(r\ h^j)^{-1}$ moves the atoms, and each carries weight 1/2, so that the matrix is symmetric with largest eigenvalue 3. We computed the largest and the smallest eigenvalues by the Lanczos method.

3.6 The real-rate network

The supporting information of the 2026 ACS Central Science study lists in Table S3 the relative free energies of the 120 isomers and in Table S6 the 180 edges of the network with forward and backward rate constants at 213 K. Isomers are named by ten-digit codes. The first nine digits give the three arms as triples (ring carbon, adjacent vinyl carbon, apex-side vinyl carbon) and the tenth the apex; the digit 0 denotes hydrogen, 1 the substituent that occurs twice and 2 the one that occurs once. We tested the four possible conventions for the order of arms and of the atoms within an arm, and kept the one under which all 180 edges are Cope steps of our model (two conventions that differ by a mirror reflection are equivalent for this purpose, since mirror images have the same rate constants). The rate matrix was assembled from Table S6; the single self-loop, a degenerate step that returns the same isomer, changes no population and was omitted. Detailed balance was checked by comparing the ratio of forward to backward rate constants with the Boltzmann factor for the energy difference, using kT = 0.0019872 × 213 kcal mol^{-1}. We then formed the symmetric matrix of Section 2.2, diagonalized it, and evaluated populations as sums of exponentials. The half-life of an isomer was defined as the first time at which its population falls to one half when the system starts entirely in that isomer, and was found by Brent’s root-finding method.

For the second real-rate test (Section 7.4) we used the supporting information of Yahiaoui et al. (2019). Its computational-results file lists, for every isomer of the networks of compounds 4d (30 isomers) and 4f (120 isomers), the relative energy from single-point B3LYP-D3BJ/Def2-TZVPPD calculations with the CPCM solvent model for chloroform, and for every edge the energy of the transition state. Its Tables 11 and 12 list the first-order rate constants of the forward and backward step of each edge at 25 °C; the column heading prints 289 K, which we take to be a typographical slip (Section 4.6). The rate matrix was assembled from the rows of the tables, rows that return the same isomer were omitted, and the populations, relaxation rates and half-lives were computed as for the first network, with the Boltzmann factors evaluated at 298 K.

3.7 Software

All calculations used Python with NumPy, SciPy and python-flint. Except for the seeded random geometries of Section 3.1 no random numbers were used. The rate constants used in Section 7 are those tabulated in the supporting information of the cited studies.

4. Validation against published results

Before any spectral result is interpreted, the networks themselves must be shown to be the ones that the literature describes. Every comparison below was carried out by a program, and every quantity that the sources report and that we could compute was compared.

4.1 The Monster Graph (Živković, 1996)

Živković reports, for the 1,209,600-vertex graph, the number N_k of vertices at distance k from a fixed vertex (his Table I) together with the numbers P_k1, P_k2 and P_k3 of vertices in shell k that have one, two or three neighbours in shell k − 1. The graph has 30 shells, N_k grows as 1, 3, 6, 12, 24, 48, then 93 (rather than the 96 of a tree), and reaches its maximum of 232,096 in shell 21. In shell 6 three vertices have two predecessors, so that cycles close for the first time and the girth is 12. Our chiral network reproduces all thirty rows of this table, including the predecessor counts. His Table II lists, for each shell k, the number M_k of vertices that lie on at least one shortest path from a form to its mirror image, a total of 12,548 vertices; we obtain the same distribution. We also reproduce his statements that the graph is bipartite, that the mirror image of every form lies in shell 29, and that the two forms are therefore antipodal.

4.2 The coset construction and the two models (Lloyd and Jones, 1998; Klin et al., 1991)

We rebuilt the network from the permutations h and r of Lloyd and Jones, as cosets of the rotation group, by a code path that shares nothing with the chemical construction of Section 3.1. With the Cope permutation (model IIB), 1,209,600 vertices are reached and the shell counts are identical to Živković's Table I. With the permutation of model IIA only 604,800 vertices are reached and the diameter is 26. The network produced by the opposite orientation of the arms in Section 3.1 has shell counts identical to those of model IIA. This identifies that orientation with the model that Brocas (1994) showed to be the mirror image of the Cope step, and it identifies our rule with the Cope rearrangement itself.

For P_7^{3-} the same construction gives 1,680 vertices of valency 3 and diameter 14. The fifteen shell sizes 1, 3, 6, 12, 24, 45, 81, 147, 255, 365, 350, 231, 116, 37 and 7 coincide with the list that Randić (2001) quotes from Randić, Oakland and Klein (1986). The deviation from the tree sequence in shell 5 (45 instead of 48) corresponds to a girth of 10, which is the value given by Lloyd and Jones for this graph.

4.3 The four-substituent network (He and Bode, 2013)

He and Bode built the network of a bullvalene with four different substituents and analysed it with a graph-visualization program. They report 1,680 nodes and 2,520 distinct rearrangements, a diameter of 16, a shortest path of 12 steps from the initial isomer to the metastable isomer (fraction e), 12 steps from fraction e to its enantiomer, and 10 steps from the initial isomer to its own enantiomer. They also state that no enantiomeric pair is connected by a single step and that the minimum number of steps for racemization is at least two. Using their ten-digit codes (three arms of three digits, in the order ring carbon, adjacent vinyl carbon, apex-side vinyl carbon, followed by the apex), our network reproduces every one of these numbers. The test discriminates between the two orientations of Section 3.1: with the opposite orientation the diameter is 15 and the two distances are 9 and 7.

4.4 Identical substituents (Gimarc and Brant, 1994)

Gimarc and Brant tabulate the isomers of bullvalenes with one to five identical substituents. Our model gives 4, 15, 42, 72 and 84 isomers; of these 4, 9, 16, 22 and 24 are achiral, and the remaining forms make up 0, 3, 13, 25 and 30 enantiomeric pairs. Each entry agrees with their Table 2. Their column of ‘processes’, 10, 45, 120, 210 and 252, is the number of ways C(10, n) of placing n identical substituents on the ten sites, and is a different quantity from the number of directed edges of the network.

4.5 The 2026 kinetic study (ACS Central Science)

The study concerns a bullvalene with two identical chain substituents and one further substituent. It reports 120 isomers with three reversible rearrangements each, that is, 360 first-order rate constants. Our model gives 120 isomers with 360 directed rearrangements. More stringently, every one of the 180 edges listed in its Table S6 is a Cope step of our network, and the rate constants satisfy detailed balance with respect to the isomer energies of Table S3 to within 0.003 in the logarithm of the ratio. The ten-digit codes used there therefore follow the same convention as those of He and Bode.

4.6 The 2019 kinetic study (Yahiaoui et al., Org. Lett.)

Yahiaoui et al. (2019) analysed the networks of a disubstituted bullvalene (4d, with a trimethylsilyl and a hydroxymethyl group) and a trisubstituted bullvalene (4f, with a trimethylsilyl and two hydroxymethyl groups). They give 30 and 120 isomers, which are the numbers of our model for the corresponding substitution patterns (Section 4.4), and they tabulate first-order rate constants for the forward and backward step of each edge. We checked the tables against the energies in their supporting information. Every rate constant equals the Eyring rate constant computed from the isomer and transition-state energies with T = 298.0 K; the largest deviation in the logarithm over all 230 rows and both directions is 0.003, whereas T = 289 K, the value printed in the column heading, gives deviations of 1.4 to 1.8, so the heading is a typographical slip. The tables list 46 and 184 rows. In each network a few rows are the same reaction listed twice with the two isomers in opposite order (one pair in 4d and three in 4f), each joining two enantiomeric isomers. After the repeated listings are removed, 45 and 181 rows remain. In 4d these are 45 distinct steps; in 4f they are 179 steps between different isomers and two steps of one isomer that return the same isomer. Together they account for exactly three channels per isomer, that is, 90 and 360 directed rearrangements, as in our model. The matrices of channel counts built from the tables have row sums equal to three, and their spectra contain the eigenvalues that Section 5.2 assigns to the corresponding substitution patterns: 2.859814, 2.105049 and 1.903212 for the 30-isomer network, and 2.859814 and 2.721066 for the 120-isomer network, the same two values that we found for the network of Section 4.5. We take this as a further check of the graph and of the nested structure of the spectra, independent of the construction in Section 3.1.

4.7 Summary and scope of the validation

The table collects the comparisons. All of them agree, in the sense stated in the last column.

Source	Quantity compared	Result
Živković 1996	30 shell sizes and predecessor counts, 12,548 geodesic vertices, bipartiteness, antipodal mirror image	identical

Source	Quantity compared	Result
Lloyd and Jones 1998; Klin et al. 1991	1,209,600 vertices and 1,814,400 edges; IIA gives 604,800 reachable vertices	identical; the opposite rule equals IIA shell by shell
Randić 2001 (P_7^{3-})	1,680 vertices, 15 shells, diameter 14	identical
He and Bode 2013	1,680 nodes, 2,520 edges, diameter 16, paths of 12, 12 and 10 steps	identical; the opposite rule gives 15, 9 and 7
Gimarc and Brant 1994	isomer, achiral and enantiomeric-pair counts for one to five identical substituents	identical
ACS Central Science 2026	120 isomers, 360 rearrangements, 180 edges, detailed balance	identical
Yahiaoui et al. 2019 (4d, 4f)	30 and 120 isomers; every rate constant equals the Eyring rate at 298 K from the published energies (largest deviation 0.003 in ln k); detailed balance; equal-rate spectra contain 2.859814, 2.105049, 1.903212 (30 isomers) and 2.859814, 2.721066 (120 isomers)	agree; the tables list 46 and 184 rows, of which 1 and 3 are repeated enantiomer pairs

These comparisons establish the graph, the orientation of the Cope step, and the mirror structure. They do not by themselves validate the spectra. For the spectra we rely on four further checks. The dimension counts of Section 3.4 hold exactly. Every eigenvalue that we found by diagonalizing a network directly (for example 2.892576, 2.859814 and 2.859342 for bullvalene and 2.739144, 2.790827 and 2.675131 for P_7^{3-}) was found again, to all printed digits, as an eigenvalue of the restriction of ρ_λ(Σ) to the H-fixed vectors in the representation to which it is assigned in Section 5. The spectra are nested as required by Section 2.3. And the exact solution of two real-rate networks reproduces the timescales and populations reported from independent Monte Carlo simulations (Section 7).

5. Equal-rate relaxation of the bullvalene and P_7^{3-} networks

In this section k denotes the rate constant of a single Cope step, and m denotes the number of distinguishable atoms in the molecule. All eigenvalues refer to the adjacency matrix A, so that a mode relaxes at the rate k(3 − λ).

5.1 The full network

The fully labelled chiral network has 1,209,600 forms, diameter 29, and the mirror image of every form lies at distance 29. The enantiomer-blind quotient has 604,800 forms and diameter 26. Its second-largest eigenvalue, which is the slowest mirror-even eigenvalue of the chiral network, is λ = 2.892576. The corresponding relaxation rate is k(3 − 2.892576) = 0.1074 k, and the population pattern is multiplied by 0.9642 at each Cope step. The slowest mirror-odd eigenvalue is λ = 2.859342, which gives a rate of

0.1407 k and a factor of 0.9531 per step. The smallest eigenvalue of the enantiomer-blind network is −2.859342, the negative of the odd value, in accordance with the parity relation of Section 2.4.

The racemization mode can be translated into a number of rearrangements. A mirror-odd pattern that follows this mode falls to one half of its amplitude after ln 0.5 / ln 0.9531 = 14.4 steps, to one tenth after 47.9 steps and to one hundredth after 95.9 steps. These numbers refer to the slowest odd mode alone, which dominates at long times, and they assume equal rates. They should not be read as the time that an initially pure enantiomer needs to lose half of its enantiomeric excess, which depends on the starting form and on the observable. As an example, in the fully labelled network the probability that the population is back on its starting form after an even number of steps is already 0.060 after 10 steps and 0.034 after 14, simply because the population spreads over a large network long before it can reach the mirror image; this single-form quantity is not an enantiomeric excess. An experimental enantiomeric excess is the expectation of a mirror-odd observable (optical rotation, for example), and its decay at long times follows the slowest odd mode if the observable overlaps with it. Within these limits the numbers address the question that He and Bode (2011) left qualitative, namely how many rearrangements are needed for racemization. They also fit the remark of those authors that the actual path used by a molecule involves many more isomers than the shortest path, which for their four-substituent network connects a form to its enantiomer in 10 to 12 steps: the asymptotic half-life of about fourteen steps is of the same order as that shortest path, whereas the decay to one hundredth requires on the order of a hundred steps, which is consistent with their description of a process that needs dozens or hundreds of rearrangements. In units of time, the half-life of the slowest odd mode is ln 2 / (0.1407 k) = 4.9/k.

5.2 Dependence on the number of distinguishable atoms

The networks with m distinguishable atoms were constructed for m = 1 to 7 and their mirror sectors diagonalized. The slowest non-trivial eigenvalues are collected in the first table (bullvalene) and the second (P_7^{3-}).

m	Chiral forms	Slowest mirror-even λ	Slowest mirror-odd λ
1	4	1.903212	none (all forms achiral)
2	30	2.859814	2.105049
3	240	2.859814	2.859342
4	1,680	2.892576	2.859342
5	10,080	2.892576	2.859342
6	50,400	2.892576	2.859342
7	201,600	2.892576	2.859342

m	Chiral forms	Slowest mirror-even λ	Slowest mirror-odd λ
1	3	0.414214	none (all forms achiral)

m	Chiral forms	Slowest mirror-even λ	Slowest mirror-odd λ
2	14	2.675131	1.481194
3	70	2.675131	2.790827
4	280	2.739144	2.790827
5	840	2.739144	2.790827
6	1,680	2.739144	2.790827
7	1,680	2.739144	2.790827

Two features of these tables are notable. First, the slowest mirror-odd eigenvalue stops changing at m = 3 in both molecules, and the slowest mirror-even eigenvalue stops changing at m = 4. For the full bullvalene network the values are the same as for m = 4 (Section 5.1), so that additional distinguishable atoms beyond four, up to all ten, do not slow equilibration, and atoms beyond three do not slow racemization. The slowest topological relaxation of a bullvalene with four different substituents is already that of the unsubstituted network with every atom labelled. Second, the slowest even eigenvalue at m = 3 equals the one at m = 2, so that the sequence of thresholds is not simply one new value at each m: new slow modes appear at m = 2 and at m = 4 for the even sector, and at m = 2 and m = 3 for the odd sector. The corresponding numbers for P_7^{3-} differ, but the pattern of thresholds is the same.

5.3 The symmetry types of the slow modes

The decomposition of Section 2.5 explains the thresholds. We evaluated the sum Σ in every irreducible representation of S_{10} and S_7, restricted it to the H-fixed vectors, and recorded the largest eigenvalues below 3 together with the representations that contain them.

System	Slowest equilibration	Slowest racemization	Next
Bullvalene (S_{10})	(6,4), λ = 2.892576, four boxes outside the first row	(7,1,1,1), λ = 2.859342, three boxes	(8,2), λ = 2.859814, two boxes
P_7^{3-} (S_7)	(3,2,2), λ = 2.739144, four boxes	(4,1,1,1), λ = 2.790827, three boxes	(5,2), λ = 2.675131, two boxes

For bullvalene the H-fixed subspace has dimension 30 in each of the representations (6,4) and (7,1,1,1); for P_7^{3-} the dimensions are 7 for (3,2,2), 8 for (4,1,1,1) and 4 for (5,2). By Young's rule (Section 2.3) a representation with b boxes outside the first row appears in the network with m distinguishable atoms exactly when m ≥ b. The slowest equilibration mode is therefore absent for m ≤ 3 and present from m = 4 on, the slowest racemization mode first appears at m = 3, and the next mode appears at m = 2, which is exactly what the tables show. Given the representations that carry the slowest modes in these two molecules, the thresholds follow from Young's rule. Young's rule does not, however, explain why those representations carry the slowest modes, and we have no derivation of that; it is the main open mathematical question that our calculations raise.

A heuristic reading is that the slowest modes are collective patterns in which the positions of three or four atoms are correlated, whereas patterns involving a single atom relax much faster: the representation (9,1), which describes the diffusion of a single marked atom, carries an eigenvalue of only 1.903 in the bullvalene network (the m = 1 row of the first table above). This reading should be taken as an interpretation, not a derived result.

5.4 Algebraic structure of the eigenvalues

The eigenvalues are algebraic numbers, and the exact factorization of the characteristic polynomials shows how complicated they are. For m = 1 the three non-trivial eigenvalues 1.903212, −0.193937 and −2.709275 are the roots of the cubic $x^3 + x^2 - 5x - 1$. At m = 2 the slowest even eigenvalue 2.859814 is a root of an irreducible polynomial of degree 8, and at m = 3 the slowest odd eigenvalue 2.859342 has degree 19. Each degree is bounded by the dimension of the H-fixed space of the representation that carries the eigenvalue (at most 30 for the two representations above), and the degrees found are consistent with this bound. No simple expression in radicals is to be expected for such eigenvalues. A few special values do appear. The number $2\cos(\pi/7) = 1.801938$, a root of $x^3 - x^2 - 2x + 1$, is an eigenvalue of the odd sector at m = 2, and $2\cos(\pi/9) - 1 = 0.879385$, a root of $x^3 + 3x^2 - 3$, occurs in the even sector. We have not investigated why such cyclotomic numbers occur.

5.5 Failure of the parity relation for substituted molecules

For m = 10 the relation between the two sectors is exact, as shown in Section 2.4. For fewer distinguishable atoms, parity is no longer well defined, because two forms that differ by the exchange of identical atoms are the same, yet the permutations that represent them have opposite parity. The networks need not be bipartite. We checked that the relation fails. At m = 5 the smallest mirror-even eigenvalue is −2.815562, which is not the negative of the largest mirror-odd eigenvalue 2.859342, and at m = 6 the two values do coincide in magnitude, at 2.859342. In P_7^{3-} the networks with m = 6 and m = 7 have smallest eigenvalue −3, which means that they are bipartite: with at most one indistinguishable atom the parity ambiguity does not arise. The racemization eigenvalue is therefore a quantity of its own, to be computed from the odd sector, and it is not obtained from the even spectrum in general.

6. Schreier graphs on tuples and the spectral-gap literature

The appearance of the number of distinguishable atoms as the controlling variable in Section 5 is not peculiar to chemistry. It is the central device in a line of work on the spectral gap of random walks on the symmetric group. In this section we place our result in that context, and we use the unquotiented graph, that is, the Cayley-type graph in which forms related by the three-fold rotation are not identified, to make the connection precise.

6.1 The Aldous-type problem

For a symmetric generating set Σ of S_n, the second-largest eigenvalue of the Cayley graph is the maximum, over all irreducible representations other than the trivial and sign representations, of the largest eigenvalue of ρ(Σ). Aldous conjectured that when Σ consists of transpositions this maximum is attained in the standard representation (n − 1, 1), which describes the motion of a single particle; the conjecture was proved by Caputo, Liggett and Richthammer (2010). For other generating sets no such principle holds, and there are well-studied sets for which the gap is carried by other representations.

Parzanchevski and Puder (2020; arXiv:1804.02776) treat sets that are closed under conjugation (normal sets). They describe the method that we also use: the Schreier graph of S_n acting on ℓ-tuples of distinct points contains exactly the representations with at most ℓ boxes outside the first row, so that computing the gap on tuples of increasing length shows which representations are needed. They state a conjecture of this kind for arbitrary symmetric generating sets, according to which the representations with at most four boxes outside the first row, together with their transposes, determine the gap up to a vanishing error (the conjecture goes back to earlier work of Kozma and Puder).

6.2 The Cope generators on tuples

Our generating set consists of the three permutations r, rh and rh^2, together with their inverses, which we weight symmetrically. It is not a normal set, so the theorems proved for normal sets do not apply to it. We computed the largest eigenvalue below 3 of the Schreier graph on ℓ-tuples for bullvalene (ℓ = 1 to 7) and for P_7^{3-} (ℓ = 1 to 6).

ℓ	Bullvalene (n = 10), largest non-trivial λ	P_7^{3-} (n = 7), largest non-trivial λ
1	2.451606	1.707107
2	2.929907	2.837565
3	2.929907	2.895413
4	2.946288	2.895413
5	2.946288	2.895413
6	2.946288	2.895413
7	2.946288	—

For bullvalene the value stops changing at ℓ = 4, and for P_7^{3-} at ℓ = 3. To conclude that these are the maximal eigenvalues over all representations, we must also account for representations outside the tuples computed. All generators are odd permutations, so the spectrum is symmetric about zero, and the eigenvalues of a transposed representation are the negatives of the original ones (Section 2.5). Every representation of S_{10} either has first row at least 3 and appears at ℓ = 7, or has first row at most 2, in which case its transpose has at least five rows, appears at ℓ ≤ 5, and contributes a largest eigenvalue equal to minus the smallest eigenvalue computed there. The smallest eigenvalues at ℓ = 3, 4, 5 and 6 are −2.8812, −2.9005, −2.9078 and −2.9297, so the transposed representations contribute at most 2.9078, which is below 2.946288. The largest non-trivial eigenvalue of the full Cayley graph is therefore 2.946288 for bullvalene, which corresponds to a spectral gap of 0.0537.

The evaluation of the generators in each irreducible representation identifies the carriers. For bullvalene the maximum 2.946288 lies in (6,4), which has four boxes outside the first row, and the next value is 2.929907 in (8,2). For P_7^{3-} the maximum 2.895413 lies in (4,1,1,1), with three boxes, followed by 2.869572 in (3,2,2), 2.837565 in (5,2) and 2.812554 in (2,2,2,1). These values exceed the corresponding eigenvalues of the chemical networks (2.892576 in (6,4) for bullvalene and 2.790827 in (4,1,1,1) for P_7^{3-}), because the chemical networks see only the vectors fixed by the rotation, whereas the Cayley

graph also contains vectors that are not fixed. The unquotiented graph therefore has a smaller gap than any of the chemical networks.

6.3 Consequences

Two observations follow. First, for these generators the Aldous-type property fails in a strong sense: the standard representation carries the value 2.4516 for bullvalene, far below the gap-determining 2.9463, and the gap is carried by a representation with four boxes outside the first row. Second, four boxes are needed and three are not enough: the value at ℓ = 2 and ℓ = 3 is 2.9299, and the value 2.9463 appears at ℓ = 4. This is consistent with the number four in the conjecture of Parzanchevski and Puder, and it shows, in one concrete case with n = 10, that the number cannot be lowered for this generating set. Because the conjecture concerns large n and arbitrary symmetric sets, one example with n = 10 neither supports nor refutes it. A natural test would use the family with n = 3m + 1 sites of Lloyd and Jones, which contains P_7^{3-} (m = 2) and bullvalene (m = 3), but we have not carried this out.

We stress what is and what is not new here. The use of tuples to locate the carriers of the gap is the method of the cited literature. We found no treatment of this particular three-element generating set, nor any connection of the method to the relaxation of fluxional molecules. We cannot exclude that such a treatment exists, because our search of the literature was limited (Section 10 and Appendix A).

7. Exact solution of a published real-rate network

The equal-rate model isolates the effect of network topology, but real substituted bullvalenes have rate constants that differ greatly from step to step. To see how the exact method performs on a real network, and how large the difference between the two pictures is, we used the data of two published kinetic studies: a 2026 study in ACS Central Science (Sections 7.1 to 7.3) and the 2019 study of Yahiaoui et al. in Organic Letters (Section 7.4).

7.1 The system and the published simulation

The study concerns a bullvalene that carries two identical substituents and a third, different one. Such a molecule has 120 chiral isomers, each connected to three others, so that there are 360 directed rearrangements. The authors computed density-functional activation energies for all of them, converted these into first-order rate constants at 213 K by the Eyring equation, and simulated the network by stochastic Monte Carlo (Kinetiscope). Starting from a pure population of the isomer called γβ′γ″, the simulation indicates a half-life of about 25 h at 213 K. The supporting information contains the population curves of three starting isomers, γβ′δ′, γβ′γ″ and βδβ′ (their Figures S127 to S129), over periods from a few hours to about three months.

7.2 Exact solution

We built the 120 × 120 rate matrix from the rate constants of their Table S6, as described in Section 3.6, verified detailed balance, symmetrized the matrix, and diagonalized it. The quantities that the simulation estimates by sampling are then available in closed form.

For the isomer γβ′γ″ the exact half-life is 26.7 h, against about 25 h reported; since the published value is approximate and was obtained from a single stochastic trajectory, the two agree to within the precision of the comparison. For γβ′δ′ and βδβ′ the exact half-lives are 23.9 h and 28.3 h. The comparison with the

published curves can be made at the level of whole trajectories, using values read from the plots, which are accurate to a few hundredths. Starting from βδβ′, the population of the global-minimum isomer (code 0010010020, equilibrium population 0.284) is 0.597, 0.532 and 0.431 at 12, 40 and 93 days; the published curve rises to about 0.6 and decays to about 0.43 at the end of the period. Starting from γβ′γ″, the same isomer reaches 0.196 at 85 days, against about 0.19 in the figure. Starting from γβ′δ′, the exact solution gives a rapid loss of population to 0.721 within one hour, with 0.257 transferred to the neighbouring isomer 0000021010, which is the rapid first drop and the neighbour at about 0.26 that the figure shows. We take this agreement as support for the data extraction, the isomer codes and the exact solution, within the accuracy of values read from plots.

7.3 The relaxation spectrum of the real network

The rate constants range from 5.6×10^{-8} to 136 s^{-1}, a ratio of 2.4×10^{9}, with a geometric mean of 2.35×10^{-4} s^{-1}. The 119 non-zero relaxation rates of the network cover almost the same range: the fastest is 136 s^{-1} and the slowest is 1.16×10^{-8} s^{-1}, a spread of 1.2×10^{10}. The slowest pattern has a half-life of 1.9 years at 213 K, and 42 of the 119 patterns relax more slowly than once per hour. The half-lives of single isomers, defined as in Section 3.6, range from 1.4×10^{-6} h to 1.7×10^{4} h, with a median of 0.105 h. Thus the isomer for which a half-life of about 25 h was reported sits in the slow tail of a distribution that spans ten orders of magnitude.

The same network with equal rates has very different relaxation properties. Its slowest mirror-even eigenvalue is 2.859814, which is the value we found at m = 2 and m = 3 in Section 5.2, and its slowest mirror-odd eigenvalue is 2.721066. Its relaxation rates therefore span a factor of only about forty, from 0.14 k to roughly 6 k. If one assigns to k the geometric mean of the real rate constants, the equal-rate model predicts a slowest relaxation rate of about 3×10^{-5} s^{-1}, whereas the real value is 1.2×10^{-8} s^{-1}, smaller by a factor of about 3×10^{3}. This factor depends on the arbitrary choice of the mean and should be read only as an illustration of the size of the effect: in this network the slowest relaxation is determined almost entirely by a few high barriers and not by the shape of the graph.

7.4 A second network: the trisubstituted bullvalene 4f of Yahiaoui et al. (2019)

Yahiaoui et al. (2019) simulated the network of a trisubstituted bullvalene (4f, with a trimethylsilyl group and two hydroxymethyl groups). It has the same substitution pattern as the network of Section 7.1, two identical substituents and one different, but different substituents, different energies and a different temperature (25 °C instead of 213 K). We converted their rate constants into a rate matrix and diagonalized it as before. Detailed balance holds: the relative asymmetry of the symmetrized matrix is 2×10^{-7}, and the stationary distribution of the rate matrix agrees with the Boltzmann distribution of the published energies at 298 K to within 5×10^{-5} in the populations.

Their text labels isomers with letters and the supporting information with ten-digit codes, so we identified the isomers by their equilibrium populations. The global minimum (code 0010020020, called 4f:A) has the population 0.68 at 298 K, which is the plateau of their Figure 2e. At 213 K, the temperature of their NMR measurements, the Boltzmann populations are 0.90 for 4f:A, 0.015 for each of the enantiomers 0010020200 and 0010200020 (together 0.03) and 0.018 for 0020020100, in line with the computed ratios 90 : 3 : 2 of their Figure 1b; we take these to be the isomers that they call 4f:B, ent-4f:B and 4f:D. The table compares the exact solution with what they report from their Kinetiscope simulations.

Quantity	Reported (Yahiaoui et al. 2019)	Exact solution
4f:A at equilibrium, 25 °C	about 0.68 (plateau of Fig. 2e)	0.680
Start from 4f:A	equilibrium reached within about 1.5 s	population of A 0.70 at 1.5 s; within 1% (total variation) of equilibrium by 1.9 s
Start from 4f:D, t = 0.05 s	about 1:1:1 mixture of 4f:D, 4f:B and ent-4f:B	0.30 : 0.24 : 0.24 (population of A 0.04)
Start from 4f:D, formation of 4f:A	slowly, over about 2 s	population of A 0.35 at 0.5 s, 0.65 at 2 s, 0.68 at 4 s
4d, start from the major isomer	equilibrates within 0.1 s	within 1% of equilibrium by 0.08 s
Populations at 213 K (4f:A, 4f:B + ent-4f:B, 4f:D)	90 : 3 : 2 (computed, Fig. 1b)	90 : 3.0 : 1.8

The relaxation rates of the 4f network range from 1.26 s^{-1} (time constant 0.79 s) to 4.6×10^9 s^{-1}, a spread of about 4×10^9. The slowest mode is mainly an exchange of the major isomer 4f:A with the rest of the network: its eigenvector has weight +1 on 4f:A and weights of the opposite sign on the other isomers, the largest being −0.13 on two isomers of negligible equilibrium population and about −0.09 on 4f:D, 4f:B and ent-4f:B. This is the quantitative content of the local kinetic well that the authors invoke to explain the metastability of 4f:A. With equal rates on the same graph the slowest relaxation rate would be $(3 - 2.859814)k = 0.140\ k$; for k equal to the geometric mean of the 358 rate constants (2.2×10^3 s^{-1}) this is 3.0×10^2 s^{-1}, about 240 times faster than the real value of 1.26 s^{-1}, and the relaxation rates would span a factor of only about forty. The factor 240 compares with 3×10^3 for the network of Section 7.3; as there, it depends on the choice of the mean and should be read only as an illustration.

7.5 What the exact method adds

Two features of the exact solution are worth stating. It involves no sampling error (the uncertainty of the rate constants themselves is of course unchanged), and it provides the entire spectrum, not a single trajectory. Any population curve, any half-life and any relaxation time follows from one diagonalization, which for 120 isomers takes milliseconds on a laptop. The method scales to networks of thousands of isomers with dense linear algebra, and, in principle, to the full 1,209,600-isomer network with sparse eigensolvers (which we have used so far only for equal rates) once real rate constants are available for it, which is the missing information noted by Pei et al. (2024). The Monte Carlo method retains the advantage that it needs no assumption of detailed balance and can include time-dependent conditions.

8. Distances and diameters

Distance properties of the bullvalene networks were the first quantities to be studied, and our results here are replications. We report them for completeness and because they bear on the interpretation of the racemization times.

For the fully labelled chiral network every vertex is equivalent, so the diameter equals the largest distance from any one form and is 29, attained exactly by the mirror image (Živković, 1996). The enantiomer-blind network has diameter 26. For the networks with m distinguishable atoms the situation is different, because they are not vertex-transitive, and the diameter is the largest distance over all pairs of forms. The distance structure depends on a form only through the set of sites carrying the distinguishable atoms, up to rotation, because relabelling the atoms is an automorphism of the network. We therefore started a breadth-first search from one form for each class of position sets (4, 15, 42, 72, 84 and 72 classes for m = 1 to 6) and took the maximum. The diameters are given below.

m	1	2	3	4	5	6
Diameter, mirror images distinct	3	8	12	16	18	20
Diameter, enantiomer-blind	3	8	12	15	17	20

The value 16 for m = 4 agrees with the network analysis of He and Bode (2013).

The distance to the mirror image deserves a separate comment. In the fully labelled network it equals the diameter, so that every enantiomeric pair is antipodal, as was noted for this graph and for the P_7^{3-} graph. This is not a general property of reaction graphs: the investigation of enantiomeric labellings by Brocas, Buekenhout and Dehon (1998) shows that on symmetric graphs the distance between enantiomers can be smaller than the diameter, and Živković remarks that a conjecture of Randić, Oakland and Klein asserting equality does not hold in general. In the four-substituent network the distance from a form to its mirror image varies from form to form. He and Bode give 10 steps for their initial isomer and 12 for fraction e, which we reproduce, while the minimum over all chiral forms is 2, since no pair is connected by a single step. These shortest-path numbers measure how close the two enantiomers are in the graph; the spectral analysis of Section 5 measures how fast a population actually spreads between them, and the two quantities are different. For the full network the asymptotic half-life of about fourteen steps of the slowest odd mode is far below the distance of 29 to the antipode. This is not a contradiction: a spectral decay rate does not measure the time needed to reach a particular form, and the population reaches the mirror-image half of the network through very many paths without having to reach the single antipodal form.

9. Discussion

9.1 The equal-rate model as a baseline

The equal-rate spectra answer a precise question: how quickly would populations spread over the network if the network's shape were the only thing that mattered? The answer is that equilibration among structurally different forms has a slowest relaxation rate of about 0.107 k, that is, a relaxation time of 9.3/k, which is about 28 Cope steps because each form makes steps at the rate 3k (a half-life of about 19 steps), and that the slowest mirror-odd pattern decays somewhat faster, with a half-life of about fourteen steps. These numbers are not bounds on the speed of relaxation in a real network, because real rates can be both faster and slower than the mean. What the model provides is a reference that separates the effect of topology from the effect of energetics.

The real-rate network of Section 7 shows how large the second effect can be. Its relaxation rates span ten orders of magnitude and its slowest pattern is slower than the equal-rate prediction, at the geometric-mean rate, by a factor of about three thousand (and by a factor of about 240 for the network of Section 7.4). Other data in the literature indicate that this heterogeneity varies strongly between substituent patterns. The DFT barriers computed by He and Bode for an ester-substituted bullvalene differ by many kcal mol^{-1} between neighbouring rearrangements, and fraction e of that system is kinetically trapped for hours at room temperature. By contrast, the rate constants of fluorobullvalene at 25 °C quoted in the 2026 study vary only by about a factor of ten, from roughly 200 to 2,000 s^{-1}. In that case the equal-rate model would be a reasonable first approximation, and in a system with strongly perturbing substituents it would not. We regard the equal-rate calculation as a baseline against which real dynamics can be measured, for example through the ratio of the real slowest relaxation rate to the equal-rate prediction, and not as a predictor of experimental kinetics.

9.2 Relation to the analysis of Pei and coworkers

Pei et al. (2024) analysed a network that is a cycle of 14 isomers, for which the equal-rate rate matrix is the Laplacian of a cycle and its eigenvalues are $2 - 2\cos(2\pi j/14)$. Our calculation is the extension of the same construction to the complete network. The matrix that they describe as unknown consists, in the equal-rate approximation, of the Laplacian $3I - A$ of the Cope graph. The graph itself is generated by the Cope permutations (Živković, 1996; Lloyd and Jones, 1998) and has been constructed for the unsubstituted molecule (Živković; He and Bode, 2013). What remains unknown, as they correctly state, is the set of real rate constants for the full network of a given substituted bullvalene. Our contribution is therefore the diagonalization of the topological part, with the assignment of its eigenvalues to symmetry types, together with the demonstration (Section 7) that once rate constants are available the exact method applies without change. Their observation that dicyanobullvalene effectively reduces to a cycle, because the substituents restrict the accessible rearrangements, illustrates the same point from the other side: strong rate heterogeneity can turn the full network into a few weakly coupled sub-networks. A systematic treatment of such networks, in which the fastest subgraph is solved first and the slow steps are treated as a perturbation, would be a natural extension and could make the full 1,209,600-form problem tractable in practice.

9.3 Relation to the mathematics of random walks on the symmetric group

Section 6 showed that the slowest modes of the chemical networks are carried by representations with three or four boxes outside the first row, and that the same holds for the unquotiented Cayley graph. The chemistry therefore supplies a concrete, small instance of a phenomenon that is the subject of active mathematical work, in which the spectral gap of a random walk on S_n is governed by representations that correspond to the correlations of a bounded number of points. We have not shown that the number four is a general feature of rearrangement graphs, and the example is too small ($n = 7$ and $n = 10$) to bear on the asymptotic question of Parzanchevski and Puder. What can be said is that for these generators the single-particle picture, in which one would expect the standard representation to control the gap, fails by a wide margin, and that, within this idealized model, the slow relaxation of a fluxional molecule is a many-atom effect and not a single-atom one.

The framework is not restricted to bullvalene. Any rearrangement whose reaction graph is an orbital graph of S_n on the cosets of a point group can be treated in this way, provided that the molecular

symmetry group and the permutation that represents one rearrangement step are known. Lloyd and Jones (1998) describe a family of such graphs with n = 3m + 1 sites, which contains P_7^{3-} and bullvalene as its first two members and is connected only when m is congruent to 2 or 3 modulo 4. Other degenerate rearrangements that have been described as reaction graphs, such as the 1,2-shifts in homotetrahedryl cations and the Berry pseudorotation, may fit the same scheme, although we have not checked this. Whether the thresholds of three and four atoms occur in them is an open question that the method can answer quickly.

9.4 Possible uses

For experimentalists who work with substituted bullvalenes as dynamic sensors or materials, three practical consequences follow. In the absence of rate heterogeneity, the slowest racemization mode decays by a factor of ten in about 48 Cope steps and by a factor of a hundred in about 96. This sets a scale for the asymptotic decay of chiroptical signals against which measured racemization times can be compared; the early decay depends on the observable and on the starting isomer and should be computed for the case at hand. Substituting more than four carbons with distinguishable groups does not slow the topological relaxation further in the equal-rate model, so that the choice of how many different groups to introduce is governed by chemical considerations such as the number of observable isomers, not by the speed of equilibration. And the exact solution of a rate matrix is a convenient benchmark for stochastic simulators, since it provides the exact half-lives and trajectories that a Monte Carlo run should reproduce.

10. Limitations and open items

The first limitation concerns novelty. We looked for a calculation of the eigenvalues, spectral gap or relaxation rates of the bullvalene or P_7^{3-} reaction networks and found none in the sources listed in Appendix A. These are the papers in the references, most of which we read in full or in substantial part; the forward-citation list of Živković (1996) in Google Scholar, of which we read two items in full (Tratch and Zefirov, 1998; Tuvi-Arad et al., 2013) and judged the rest from titles and abstracts because they treat other subjects; a natural-language search in Consensus; and web searches combining bullvalene with eigenvalue, spectrum, Laplacian, random walk, master equation and Monster Graph. A statement that something has not been done can be no stronger than the search that supports it, and ours had gaps. We could not search paid bibliographic databases, and we have not examined the forward citations of the other works in the references, so papers that cite them and might contain such a calculation may have been missed. Several relevant works were not read: the paper of Balaban, Živković, Klein and Schmalz on reaction graphs of pentagonal-bipyramidal complexes, the original analysis of the P_7^{3-} graph by Randić, Oakland and Klein, the second part of the group-theoretical series of Klin and Zefirov, the book of Randić, Novič and Plavšić (2016), which we saw only through a review, and the kinetic studies of boronate-ester bullvalenes by the Fallon group. A very recent arXiv paper on the Aldous property for normal Cayley graphs was noted but not read. Finally, the survey of Klin, Rücker, Rücker and Tinhofer was read through optical character recognition, since its text layer was unreadable, so that some of its statements may have been misread. For these reasons we state the novelty of the calculation only as “to our knowledge”.

The second limitation is the model. The equal-rate model treats all Cope steps as identical, which real substituted bullvalenes do not satisfy (Section 7). It also includes only the Cope rearrangement, and it

treats the atoms as labelled sites, so that conformational changes, tunnelling and the orientation of substituents are ignored. Ab initio molecular dynamics of the bullvalene Cope rearrangement at 800 K found that only about 2.3% of the visits to a transition-state geometry led to a new isomer (6 successful crossings against 252 recrossings in 100 ps; Tuvi-Arad et al., 2013), a reminder that a rate-constant picture ignores such dynamical effects; that estimate rests on few events. The statements on the universality of the slowest modes apply to this idealized model only. In a real molecule the substituents change the barriers, and the dynamics can be dominated by a few high barriers, as the example of Section 7 shows.

The third limitation is the scope of the results. The thresholds of three and four distinguishable atoms were found in two molecules. They are explained by the representations that carry the slowest modes, but we have no proof that the same representations carry the slowest modes in other molecules or in other members of the family of Lloyd and Jones. The identification of the representations is numerical: it rests on floating-point eigenvalues, although each eigenvalue was found independently by direct diagonalization of the network and by the representation-theoretic computation, to six printed digits. The algebraic degrees in Section 5.4 were obtained by exact factorization only for small networks (up to 852 mirror pairs), and for the slowest equilibration eigenvalue at m = 4 we know only the bound given by the dimension of the H-fixed space. The completeness argument of Section 6.2 combines computed extreme eigenvalues with the symmetry of the spectrum and is therefore a numerical argument, not a proof.

The fourth concerns the real-rate comparisons. They use two networks, each at one temperature, with the rate constants as published (single-point density-functional energies, Eyring theory and no tunnelling). In the first network the published half-life is quoted as approximate, and in the second the reported timescales are quoted approximately in the text of the letter. The comparison of whole trajectories relies on values read from plots, which are accurate to a few hundredths for populations and to roughly five hours for the half-lives of two of the isomers of the first network. The assignment of the substituent types to the digits of the isomer codes of the first network was fixed by the test that all 180 edges are Cope steps; for the second network the codes and energies are tabulated together in the supporting information. The tables of the second study list a few rows twice, and we have interpreted them as described in Section 4.6; the effect on the reported timescales is negligible.

The fifth concerns the mathematical context. The conjecture of Parzanchevski and Puder concerns large n and arbitrary symmetric generating sets, and our generating set is not normal. Our examples with n = 7 and n = 10 are data points, not evidence about the asymptotic question.

11. Conclusions

The rearrangement networks of bullvalene and of the P_7^{3-} ion are orbital graphs of a symmetric group, and this makes their relaxation spectra computable exactly. We constructed the chiral Cope network of bullvalene and verified it against every published number that we could compare, including the shell structure of the Monster Graph, the diameter and distances of the four-substituent network, the isomer counts for identical substituents, and the full edge list of a recent 120-isomer network. In the equal-rate limit we decomposed the relaxation problem by the irreducible representations of S_{10} and S_7 and the mirror involution, and assigned each slow mode to a representation.

The slowest equilibration mode of the unsubstituted network has the eigenvalue 2.892576, which corresponds to a rate of 0.107 k, and lies in the representation (6,4). The slowest racemization mode has the eigenvalue 2.859342, which corresponds to a rate of 0.141 k, and lies in (7,1,1,1); the slowest mirror-odd pattern falls to one half of its amplitude after about fourteen Cope steps, to one tenth after about forty-eight, and to one hundredth after about ninety-six (asymptotic values for the slowest mode, not predictions for a given experiment). In a molecule with m distinguishable atoms the slowest racemization mode first appears at m = 3 and the slowest equilibration mode at m = 4, and neither is slowed by further substitution. The thresholds follow from the numbers of boxes outside the first row of the representations that carry the modes, and the same thresholds occur in P7 3−, for which the carrying representations are (4,1,1,1) and (3,2,2). The same method, applied without the rotation quotient, locates the spectral gap of the corresponding Cayley graph in a representation with four boxes outside the first row, and shows that the single-particle representation is far from controlling it.

For two real networks, with rate constants that we took from published studies, the exact solution of the rate equations agreed with the reported Monte Carlo results. For the 2026 network the exact half-life of 26.7 h agrees with the reported value of about 25 h to within the precision of that value, and for the 2019 network the exact solution reproduces the reported equilibrium populations and equilibration times. In both networks the real rates produce relaxation rates spanning roughly ten orders of magnitude, against a spread of about forty for equal rates on the same graph. The equal-rate spectrum is therefore best regarded as a baseline that isolates the contribution of topology, against which the effect of barrier heterogeneity can be measured.

What remains open is substantial. The real rate constants of the full 1,209,600-form network of any substituted bullvalene are unknown, and the exact method will be applicable to them as soon as they are available. Whether the thresholds of three and four atoms are general among fluxional molecules, and whether the number four is sharp for the family of Cope-type generators, can be tested with the same tools. And the claim that these spectra have not been computed before rests on a literature search whose limits we have stated.

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Appendix A. Literature search log

The table records the searches that support the statements on novelty in Sections 1.2 and 10. All searches were made on 29 October 2026.

Source and query	Items examined	Outcome
Google Scholar, "Cited by" for Živković (1996), found under the journal's spelling "Bulvallene Reaction Graph"	Nine entries (eight distinct works): Randić 2008 (history of the Randić index); Randić, Novič and Plavšić 2016 (book; only a review was read); He and Bode 2013; Tuvi-Arad et al. 2013; Nikolić et al. 2003 (complexity indices; two listings); Randić et al. 1998 (Clar polynomials); Tratch and Zefirov 1998; Randić 2009 (positronium)	Tratch and Zefirov (1998) and Tuvi-Arad et al. (2013) were read in full: both cite the paper for the graph or the number of isomers and contain no spectral or kinetic analysis of the network. He and Bode (2013) was read earlier. The others were judged from titles and abstracts to be unrelated and were not read.
Consensus, natural-language query on the spectrum and relaxation rates of bullvalene reaction graphs	Twenty items returned, with no answer of sufficient relevance; most concerned eigenvalues of molecular graphs (topological indices, Hückel-type matrices) or of quantum graphs	Relevant items: Yahiaoui et al. 2019 and Ives et al. 2024 (read; no spectral analysis). Nothing that computes eigenvalues or relaxation rates of a bullvalene reaction graph.
Web searches combining bullvalene with reaction graph, eigenvalue, spectrum, Laplacian, relaxation, random walk, master equation, symmetric group representation; "Monster Graph" with Cope rearrangement	First results of each search, including the Hrčak pages of Croatica Chemica Acta and MATCH papers	No spectral or relaxation analysis of a bullvalene reaction graph found.
Full texts read for this revision	Yahiaoui et al. 2019 with both supporting-information files; Ives et al. 2024 (article page); Tratch and Zefirov 1998; Tuvi-Arad et al. 2013	Kinetic simulation of 30- and 120-isomer networks, combinatorics and isomer generation, ab initio dynamics; no spectra.

Source and query	Items examined	Outcome
Not yet done	Forward citations of Lloyd and Jones 1998, Klin et al. 1991, Brocas 1994, Gimarc and Brant 1994, He and Bode 2011, Pei et al. 2024 and Ives et al. 2024; Semantic Scholar and OpenAlex; arXiv full-text search for “bullvalene”	To be completed before submission; until then the novelty statements stand “to our knowledge”.