

The Reaction Cell of the Sulfur Pair: Co-synthesis on a Single Chrysene Unit, a Disulfide Bridge, and Two Forced Asymmetries

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Abstract

The corpus establishes, by inspection, that exactly two of the twenty structures require a heteroatom with no source within the carrier, and places them under a hypothesis about the medium which it states and declines to establish [Sch26e]. This paper supplies the object in which those two structures are formed, and replaces that hypothesis with one about the carrier. The object is one unit of the stack carrying two ether-linked tethers to adenosine, its arms leaving toward opposite faces. Its skeleton admits exactly one non-trivial symmetry, an involution realised as a point inversion, and the unit carries no datum breaking it: a symmetric object is asked to make two structures that the symmetry does not exchange. Four results are finite. Over the site types the atom map supplies, the unit admits exactly three pairings, of which one is excluded outright and two survive the skeleton — and the pairing adopted here is the more expensive of those two on every measure the skeleton can state, a concession recorded before the argument that overturns it. A disulfide bridge cannot close between two sites exchanged by an inversion, the two substituents being antipodal about its centre: a bridge would require a site within 1.02 Å of that centre, which no peripheral vertex of a fused four-ring aromatic is. The bound is independent of bond length and of any model. The mixed pairing is the unique pairing whose sulfur sites are not so exchanged, and hence the unique pairing the unit can bridge. And the fracture of that pairing treats three of four symmetry orbits equivariantly and fails on exactly one, so that the whole of the skeletal symmetry breaking is a choice between two edges.

Two asymmetries are forced rather than assumed. The external electron demand is affine in the oxidation level of the remnant and vanishes at one value only: a redox-self-sufficient cell yields one benzylic remnant at the aldehyde level and one at the alcohol level, although the two are exchanged by the symmetry as graphs. This is the account's most directly testable consequence and a single product analysis decides it. And the choice of bridge site is the choice that resolves the edge orbit: the unit ceases to be symmetric where the disulfide binds and shows it where the skeleton breaks. Whether these are one choice is open.

The selection rests on two hypotheses — that sulfur arrives as a disulfide and that neither sulfur afterwards migrates — and the premise of co-synthesis on one unit is this paper's own. The bridge closes only on a dearomatised intermediate, and what that distortion may do to the exclusion is bounded but not closed. No energy is computed and no barrier estimated; the numbered statements read *excluded*, *admissible*, or *forced under the premises named*.

Keywords: Chrysene Formalism; reaction cell; co-synthesis; sulfur pair; disulfide bridge; 1,2-dithiolane; graph automorphism; point inversion; symmetry breaking; fracture strip; oxidation balance; exogenous decoration; forced asymmetry.

1 Introduction

1.1 The problem

The corpus establishes that exactly two of the twenty structures require a heteroatom with no source within the carrier, and it establishes it *by inspection*. It then places those two structures

at complementary slots under a hypothesis — that one delivery serving two structures is preferred to two deliveries that must coincide — which it states, uses once, and declines to establish. That hypothesis is an argument about a medium and not about a carrier, and it is the only unsupported premise carrying a headline result of that paper. The paper says as much, and asks for an independent ground for it or a demonstration that the

placement it forces is unavailable.

Two questions survive. In what object are the two structures formed? And does anything about that object, rather than about the medium, distinguish the pairing the corpus adopts from the pairings it does not?

This paper takes the first and answers the second. It does not establish the corpus's hypothesis. It replaces it.

1.2 The object

The object is one unit of the stack: a 6, 12-disubstituted chrysene carrying two ether-linked tethers, each running through a phosphodiester to the C2 position of an adenosine, the two arms leaving the skeleton toward opposite faces. It is called the reaction cell, after the usage of the corpus, and Remark 2.3 records that no cluster of this paper is called a cell.

Three features make it the right object for the question. Both sulfur-bearing structures are formed on it, so their co-location is a property of the carrier rather than a coincidence of delivery. Its skeleton admits exactly one non-trivial symmetry, so a symmetry-breaking argument has a definite thing to break. And it carries no datum breaking that symmetry, so whatever breaks it must be produced by the transformation and is therefore available for study.

1.3 The objective

To supply the cell; to enumerate exhaustively the pairings it admits; to determine whether anything distinguishes one of them; and — the part the corpus's own experience [Sch26e, Sch26g] recommends — to state precisely what the distinction rests on, so that a reader may see how much of the account would survive its failure.

The last is answered at Section 11 and the answer is not comfortable: two hypotheses carry the principal result between them, where the corpus's rested on one. What has changed is that both concern the carrier and what is delivered to it rather than the preference of an event, and that what follows from them follows without further assumption.

1.4 What is established

Subject to the premises of Table 1 — of which the premise of co-synthesis, that the two sulfur residues are formed on one unit, is this paper's own and is new — the following is established.

1. **The carrier has exactly one symmetry, and the cell does not break it.** Theorem 4.5: $\text{Aut}(X) \cong \mathbb{Z}/2$, generated by the involution σ , which is fixed-point-free on vertices and fixes one edge. Proposition 4.17: every datum of the cell is σ -symmetric, no base point being assigned.
2. **The pairings are three, and two survive the skeleton.** Theorem 5.5: over the two site types the atom map supplies,

the cell admits exactly three pairings; the pairing placing both sulfurs internally is excluded on two independent grounds. Proposition 5.6 identifies the two mixed pairings as one object under σ .

3. **The pairing this paper adopts is the more expensive.** Proposition 5.9 and Corollary 5.10: six carbon–carbon bonds severed against four, the unit divided rather than left entire, and a preparatory removal that the competing pairing does not require. The concession is stated before the argument that overturns it.
4. **The bridge requires the sites to leave the aromatic plane.** Proposition 8.16: a trigonal carbon's exocyclic direction is fixed by its ring, and sulfurs on two such carbons stand $4.78 \text{ \AA}$ apart against $2.05 \text{ \AA}$ for the bond that must join them. Ring C is dearomatised in the closing, and the ledger carries the move.
5. **No disulfide bridge closes between σ -related sites.** Theorem 8.13: two substituents at sites exchanged by an inversion are antipodal about its centre, so their separation is twice the distance of either from that centre; a bridge would require a site within $1.02 \text{ \AA}$ of the centre, which no peripheral vertex of a fused four-ring aromatic is. The inequality is strict independently of the carbon–sulfur bond length and survives any deformation preserving the inversion. Corollary 8.15: the mixed pairing is the unique pairing whose sulfur sites are not so exchanged, and hence the unique pairing the cell can bridge.
6. **The asymmetry is confined to one orbit.** Theorem 6.10: σ acts with four orbits on the seven edges meeting the strip, the fate map is equivariant on three, and it fails on exactly one orbit of two. The whole of the cell's skeletal symmetry breaking is a choice between two edges.
7. **The electron demand vanishes at one remnant level, and there only.** Theorem 7.9: the external demand is $v(k) = 2k - 2$ in the number k of remnant components at the aldehyde level. Corollary 7.11: a redox-self-sufficient cell has $k = 1$, so its two σ -equivalent remnants cannot be equivalent in oxidation state.
8. **The transformation is ordered, and the order locates the break.** Theorem 9.4: the first three stages are totally ordered by valence and by what must exist before what. Theorem 9.9: the choice of bridge site is the choice that resolves the orbit of item 5. The cell ceases to be symmetric at the bridge and shows it at the fracture.
9. **The contact is an output, not a premise.** Proposition 10.4 and Corollary 10.5: the released sulfurs stand at $3.80 \text{ \AA}$, within the range of a sulfur–hydrogen–sulfur contact, because they arrived bonded and the cleavage lets them recede no further. Lemma 10.7 records that the angular condition is not determined here.

1.5 What is not claimed

Section 3, twelve clauses, stated before the constructions they guard. Three deserve mention here. No chemical species is identified in any numbered statement. The selection rests on Hypothesis 8.19 and Hypothesis 8.20 together, and not on the carrier alone. And the atom map was abstracted from the series of Appendix A, which is therefore its source and not its evidence.

1.6 Precedence

Where this paper and its predecessors overlap they do not carry the same weight, and the order is by subject. The corpus is authoritative on the carrier, the registry, the letter assignment and the structures themselves; the cage literature on conformation and margins, and Hypothesis 4.8 is to be imported from it if it is established there. This paper is primary on the reaction cell, on the enumeration of pairings, and on the bridge. Where it corrects the corpus, the corrections are collected in Appendix C and are not argued in the body.

1.7 What is deferred

The placement of the two structures at codons, the relation between reading frames, and the initiation site are not addressed here. They are the subject of the companion paper, and nothing in the present one presupposes any of them. A reader who declines the companion loses no statement below.

1.8 Organization

Section 2 fixes the register and declares the scope, which excludes external simulation and is what makes the form of the results what it is. Section 3 refuses twelve readings. Section 4 is the cell and Section 5 the enumeration; these two fix the object and the question. Section 6 counts the fracture and Section 7 the electrons; these two are bookkeeping and are independent of the conformation. Section 8 is the argument. Section 9 orders the transformation and locates the symmetry breaking within it, and Section 10 states what the transformation leaves. Section 11 restates the refusals, indexes the open problems and sets the targets. Appendix A is the atom map and its provenance, Appendix B the verification, Appendix C the corrections owed to the corpus, and Appendix D the record of what was withdrawn in the course of this work.

2 Conventions and the register

2.1 Status

Definition 2.1 (Status labels). Every numbered statement carries exactly one label.

[A] Purely finite. Proved without reference to any axiom of the corpus and without any chemical premise. Every such statement in this paper is a computation over a graph on eighteen vertices or over a set of at most sixty-four elements, and each is discharged in Appendix B.

[D] Derived under hypotheses named at the point of use.

[C] Imported. Stated and not reproved; the source is named.

[E] A molecular reading. Enters no proof.

Scholia carry no label and enter no proof. The formal content of this paper is unchanged if every scholium is deleted.

Remark 2.2 (Where the chemistry is). [A] Three premises are chemical: the atom map of Appendix A, from which the retained sets and the site types are read; Hypothesis 4.8, on the conformation of the unit in the cage; and Hypothesis 8.19, on the species in which sulfur is delivered. All three are marked at the point of statement and are collected at Table 1. Beyond them the chemistry of this paper is confined to Appendix A and to scholia, and Section 3 (i) records what is lost by deleting both.

2.2 Nomenclature

Remark 2.3 (The word cell). [A] The corpus declines to use the word *cell* for a cluster or for a vessel, and that refusal is respected here: no cluster of this paper is called a cell. The object of Section 4 is called the *reaction cell*, after the usage already established in the corpus for the chrysene–adenosine reaction cell [Sch26d], and denotes one unit of the stack together with its two tethers and the conformation of Hypothesis 4.8. Where a unit alone is meant, *unit* is written.

The vocabulary of this paper is otherwise that of the corpus, with four terms added. A *site type* is the manner in which a sulfur enters a structure, terminal at a vertex or internal in an edge (Definition 5.2). A *pairing* is an unordered pair of structures each carrying one site, subject to the disjointness of Definition 5.2. The *strip* of a pairing is the union of the ring vertices its two structures retain (Definition 5.8). A *bridge* is the configuration in which the two sulfurs of a pairing are bonded to one another and each to its site (Definition 8.6).

A *structure* is always the object of the corpus and never a chemical species; where a species is meant, Appendix A is cited.

2.3 Imported objects

Stated and not reproved here: the vessel graph and its locant registry [Sch26e]; the cluster, the frame group and the bijection between clusters and classes; the tether word and the residual count; the letter assignment; the exhibited integrated product; and the cage literature on margins and stereochemical selection. Each is cited where used.

2.4 The hypothesis register

Scholium 2.4 (The conformation is used less than it appears). Hypothesis 4.8 asserts that the unique graph automorphism of Theorem 4.5 is realised spatially as a point inversion. It is tempting to suppose that every σ -covariant statement of this paper depends on it. They do not. Section 6 and Section 7 use σ only as an automorphism of a graph, and their theorems — the edge trichotomy, the orbit theorem, the affine electron demand — stand whatever the conformation. The hypothesis is required at exactly three places: that the two nucleosides face oppositely, that two substituents at σ -related sites are antipodal, and that the thioether sulfur is displaced from the plane.

This matters for what a failure would cost, and the conclusion of Section 11 is stated against this register rather than against the impression.

2.5 Scope

Remark 2.5 (No external simulation). [A] No statement of this paper is obtained from an electronic-structure calculation, a force field, or a geometry optimisation. What this forbids: any claim that a route, a pairing or a conformation is favourable; any barrier, rate or interaction energy; and any product geometry not fixed by valence, by symmetry, or by a rigid model declared as such. What it permits: exhaustive enumeration over finite sets; exact consequences of an involution; bookkeeping of atoms and of electrons; and rigid-geometry figures, which are reported as model values and never as structure.

Accordingly the numbered statements of this paper read *excluded*, *admissible*, or *forced under the premises named*. The word *favoured* occurs in no numbered statement, and any occurrence in a scholium is a reading in the sense of Definition 2.1.

Remark 2.6 (Verification). [A] Every quantitative claim of this paper is carried by a block of the script of Appendix B,

and the block is named in the proof of the statement that makes the claim. The blocks are of two kinds and Appendix B marks each. A *computed* block derives its output from the vessel graph or from the rigid model; a *tabulated* block performs arithmetic over data entered by hand in the script itself. A tabulated block is checkable by a reader but is not self-checking: it formats an assertion, and an error in the assertion survives it. The distinction is drawn because a claim of this paper did not survive review for want of it, and Appendix D records which. Where a figure comes from the literature it is labelled [C] and is not emitted.

Remark 2.7 (Corrections). [A] Claims made and withdrawn in the course of this work are recorded in Appendix D rather than absorbed, together with how each was found. Corrections owed to the corpus are separately recorded in Appendix C.

3 Traps and non-implications

The twelve refusals below are placed before the constructions they guard, as the corpus places its own. Each names a reading the body invites and does not support, and each names the section that invites it.

Proposition 3.1 (Non-implications). [A] *None of the following is asserted anywhere in this paper.*

- (i) ***That any chemical species is identified.*** *The objects of Sections 4 to 10 are subgraphs of X with decorations, together with the sites and pairings of Section 5. Their reading as residues is Appendix A and enters no numbered statement. A reader who deletes Appendix A loses the interpretation and no result.*
- (ii) ***That the reaction cell is the integrated product of the corpus.*** *The two differ at the second arm, which there anchors a bilayer and here runs to a second nucleoside, and at the position of the linkage on the base. The object of Section 4 is stated as its own; what the corpus owes on this point is Appendix C.*
- (iii) ***That bookkeeping is feasibility.*** *Section 6 counts bonds and Section 7 counts electrons. Together they establish that the transformation is not excluded on those grounds. Neither bears on whether it occurs.*
- (iv) ***That anything is favourable.*** *By Remark 2.5 no energy is computed and no barrier estimated. Where the body excludes a route it excludes it exactly; where it admits one it admits it and no more.*

hypothesis	stated at	used at
the atom map, as imported	Appendix A	Sections 5–10
co-synthesis on one unit	Appendix A	Prop A.2, and thence Sections 5–10
centrosymmetric conformation	Hypothesis 4.8	Corollary 4.16, Theorem 8.13, Proposition 10.4
disulfide delivery	Hypothesis 8.19	Section 8, Section 9
no migration of sulfur	Hypothesis 8.20	Section 8 only

Table 1: The four premises of this paper. Two are imported or stated about the carrier; two — disulfide delivery and no migration — carry the selection of Section 8 between them. No other hypothesis is used and no axiom is added to the corpus [Sch26c].

- (v) **That admissibility is evidence.** Two pairings survive Section 5, and on every measure that section can state — bonds severed, fragmentation, preparatory removal — the pairing this paper does not adopt is the cheaper. Scholium 5.11 says so where a reader will first want it said.
- (vi) **That the selection is an argument of the carrier alone.** Theorem 8.13 is exact and concerns an inversion; but it excludes the competing pairing only if the two sulfurs arrive bonded to one another, which is Hypothesis 8.19, and only if neither afterwards moves to another site, which is Hypothesis 8.20. Those two hypotheses carry the selection between them and neither is established here.
- (vii) **That one sulfur atom serves two structures.** The cell demands two sulfur atoms, one terminal and one internal. Under Hypothesis 8.19 one event supplies both. The corpus’s phrase, that one delivery serves both, is to be read in that sense and in no other.
- (viii) **That the stages of Section 9 are a chronology.** They are a precedence among events within a single reaction cell, established by valence and by what must exist before what. No assignment, no code and no priority of one mapping over another follows, and the refusal of the corpus on that point stands unweakened.
- (ix) **That the atom map is derived.** It is abstracted from the series of Appendix A, which is therefore its source and not its evidence. A referee who treats the series as confirmation of the map has read the dependency backwards.

Two further clauses attach to the sulfur pair specifically. The coordinated formation of the two residues on one unit is touched on in the corpus and is worked here; the arrangement is new, and the retained set of the second residue is not the corpus’s. And the premise of co-synthesis is not derived from anything: it is what this paper explores. What Proposition A.2 establishes is only that, granted the premise, the amended set

follows rather than being chosen — which answers the charge of circularity against Section 8 and answers nothing else. This is the weakest joint in the account and it is named rather than buried.

- (x) **That the rigid planar model computes structure.** It fixes bond lengths and angles by construction. Its figures are reported so that inequalities may be checked, and the two places where a conclusion rests on one — Theorem 8.13 and Proposition 10.4 — are stated so that the conclusion survives any deformation preserving the inversion. Lemma 10.7 records where the model determines nothing at all.
- (xi) **That the symmetry breaking is explained.** Section 6 locates it on one orbit and Section 9 identifies the choice that resolves it. Neither says what makes the choice, and whether the same choice fixes the remnant parameter is open.
- (xii) **That the source of the α -nitrogen bears on the corpus’s exogenous proposition.** The α -nitrogen attaches at a tether carbon, which is not a vertex of X, and is therefore not a decoration of any structure. What does bear on that proposition is the side-chain nitrogen, and Appendix C records what follows.

Scholium 3.2 (The three that matter most). Clauses ((v)), ((vi)) and ((ix)) are the ones a reader is most likely to over-read, and they are of one family: each states a place where the account is weaker than its presentation might suggest. Clause ((v)) states what Section 5 concedes. The paper adopts the more expensive of two pairings and says so before arguing for it. Clause ((vi)) states what the argument rests on. Two un-established hypotheses carry the paper’s principal result between them. That they concern the species delivered and the fixity of a site, rather than the preference of an event, is an improvement in the location of the premises and not in their status; and the second was added in review, the first form of this section having asserted that one hypothesis

sufficed.

Clause ((ix)) states the direction of the dependency. The atom map was extracted from the series and the series is therefore not independent evidence for it. The corpus records the same clause for its own hypotheses, and it is repeated here because this paper's map is the object from which every retained set, every site and every cut list below is read.

4 The cell

This section fixes the object. Everything that follows is a statement about it, and the two properties on which the paper turns are established here: that the graph of the carrier admits exactly one non-trivial symmetry, and that the cell, unlike the marked vessel of the corpus, carries no datum breaking it.

That second property is the paper's premise and its difficulty together. A symmetric object is asked to make two different things, and Section 6 locates where the symmetry must give way while Section 8 says what selects the outcome. Neither is possible unless the symmetry is intact here.

4.1 Non-implications

Proposition 4.1 (Non-implications of this section). [A] *None of the following is asserted below.*

- (i) *That the cell of this paper is the integrated product of the corpus. The two differ at the second arm, which there anchors a bilayer and here runs to a second nucleoside. The object below is stated as its own and no statement of the corpus is revised by it beyond the corrections of Appendix C.*
- (ii) *That the symmetry of Theorem 4.5 is a symmetry of the cell in solution. It is an automorphism of a graph, and its realisation as a spatial inversion is Hypothesis 4.8, stated separately and separately falsifiable.*
- (iii) *That the absence of a symmetry-breaking datum is an argument that none exists. It is a statement about what this paper assumes, and Proposition 4.17 records the contrast with the corpus rather than resolving it.*
- (iv) *That any residue, codon or reading is in view. Section 4 has no sulfur, no nitrogen and no assignment in it. The atom map enters at Section 5 and the medium at Section 8.*
- (v) *That the linkage geometry of Proposition 4.14 is derived. It is read from the specification and is imported.*

4.2 The vessel graph

Definition 4.2 (Vessel graph). [C] *X is the graph of the chrysene skeleton [Sch26e]: eighteen vertices carrying the locant registry of the corpus [Sch26f], twenty-one edges, and cycle rank four, consisting of an eighteen-cycle together with the three chords C4aC12a, C4bC10b and C6aC10a. Its four hexagonal subgraphs are written A, B, C, D in the order of the corpus.*

Lemma 4.3 (Degrees). [A] *X has six vertices of degree three, namely the six chord endpoints C4a, C4b, C6a, C10a, C10b, C12a, and twelve of degree two. A vertex of degree three carries no hydrogen and admits an exocyclic substituent only after one of its edges is removed; a vertex of degree two admits one without removal.*

Proof. The degree sequence; V16r. □

Scholium 4.4. Lemma 4.3 is stated in this section, rather than where it is first needed, because Section 5 and Section 8 both use it and a forward reference between them would obscure that it is a property of the carrier and of nothing else.

4.3 The symmetry is unique

Theorem 4.5 (The automorphism group). [A] $\text{Aut}(X) \cong \mathbb{Z}/2$. *Its non-trivial element is the involution σ exchanging $A \leftrightarrow D$ and $B \leftrightarrow C$; explicitly*

$$\sigma : 1 \leftrightarrow 7, \quad 2 \leftrightarrow 8, \quad 3 \leftrightarrow 9, \quad 4 \leftrightarrow 10, \quad 4a \leftrightarrow 10a, \quad 4b \leftrightarrow 10b, \quad 5 \leftrightarrow 11, \quad 6 \leftrightarrow 12, \quad 6a \leftrightarrow 12a, \quad 6b \leftrightarrow 12b$$

Proof. Exhaustive search over the isomorphisms of X with itself; V16s. □

Corollary 4.6 (Orbit structure). [A] *σ has no fixed vertex; its nine vertex orbits all have size two. It has exactly one fixed edge, C4b–C10b.*

Proof. V16r. □

Scholium 4.7. Theorem 4.5 is the reason σ may be used throughout without justification at each use. It is not an involution selected for convenience from several available: the skeleton admits exactly one non-trivial symmetry, and every σ -covariant statement of this paper is therefore a statement about the only symmetry the carrier has. The uniqueness also fixes what a symmetry-breaking argument

must break, which is what Section 6 measures.

4.4 The realisation

Hypothesis 4.8 (Centrosymmetric conformation). [D] In the cage, the 6, 12-disubstituted unit adopts the centrosymmetric conformation: the skeleton is planar and σ is realised as the point inversion $x \mapsto 2z - x$, where z is the midpoint of the edge $C4b - C10b$. The two arms leave the plane toward opposite faces.

Remark 4.9 (Status). [A] Hypothesis 4.8 is stated as a hypothesis here and is to be re-labelled [C] if the cage literature of the corpus [Sch26d, Sch26a] establishes it. Its falsifier is a conformation placing both arms on one face, and it is entered in the register of Section 11. The alternative, in which the two arms are related by a rotation about the stacking axis rather than by an inversion, leaves both on the same face and is what the hypothesis excludes.

Proposition 4.10 (The centre lies on the fixed edge). [D] Under Hypothesis 4.8 the inversion centre z is the midpoint of the unique σ -fixed edge, at $0.70 \text{ \AA}$ from each of $C4b$ and $C10b$ in the rigid planar model, and at $1.85 \text{ \AA}$ from $C4a$ and $C10a$ and $2.52 \text{ \AA}$ from $C6a$ and $C12a$.

Proof. The fixed edge is Corollary 4.6; a point inversion has one fixed point, which must therefore be the midpoint of that edge. The distances are the rigid planar model; V16r. $\square$

Scholium 4.11. Proposition 4.10 is used twice and in two different ways. In Section 6 it identifies the σ -fixed edge as the one the sulfur insertion consumes, so that the cell's insertion occurs exactly at its own centre of symmetry. In Section 8 it supplies the point about which two substituents at σ -related sites are antipodal, which is the whole of the exclusion argument there. The two uses are independent and neither requires the other.

4.5 The arms and the tethers

Definition 4.12 (The arms). [C] The cell carries arms at $C6$ and $C12$. These form one σ -orbit by Theorem 4.5.

Definition 4.13 (The tether). [C] Each arm is the ether-linked chain

$C6-O-CH_2CH_2-O-P(=O)(OH)-O-CH_2CH_2-O-C2(\text{adenosine}),$

and the same at $C12$. Both linkages to the aromatic core and both linkages to the nucleoside are ether linkages [Sch25, Sch26b].

Proposition 4.14 (The linkage leaves the pairing faces free). [C] *The tether meets the nucleoside at $C2$ of adenine, which lies on the edge opposite the Watson–Crick face. The positions $N1$, the exocyclic amino group at $C6$, and $N7$ are therefore unobstructed, and a tethered adenosine of the cell presents a complete pairing edge.*

Remark 4.15 (A correction). [A] The corpus [Sch26e, Sch25] places the remnant on adenine at the 6-position. The linkage is at $C2$, and the correction is recorded in Appendix C. It is not cosmetic: a linkage at the 6-position would obstruct the Watson–Crick face, and the registers of the corpus, being pairing states of the tethered adenine against a coding base, would have no evident definition.

Corollary 4.16 (Both nucleosides face outward). [D] Under Hypothesis 4.8 the two arms leave toward opposite faces, so that the two adenosines of the cell present their pairing edges on opposite sides of the skeleton.

4.6 The cell is unmarked

Proposition 4.17 (No datum breaks the symmetry). [D] *The cell of Definition 4.12 and Definition 4.13 is σ -symmetric in every datum it carries: the skeleton by Theorem 4.5, the arms by Definition 4.12, the tethers by their being identical, and the conformation by Hypothesis 4.8. No base point is assigned.*

Scholium 4.18 (The contrast with the marked vessel). The corpus marks its vessel with two arms and a base point, and records that the marking selects one representative of the σ -orbit: there, the asymmetry is given. Here it is not. Both arms run to a nucleoside, no base point is assigned, and the cell enters Section 5 with its symmetry entire.

This is the paper's premise and the source of its difficulty. A σ -symmetric object is asked to produce two structures that are not exchanged by σ , and something must therefore break. Section 6 shows that the break is confined to a single edge orbit and Section 7 that a second break is forced in the remnant; whether these are one choice is left open there. What this section establishes is only that neither break is assumed in advance.

Open problem 4.19 (The origin of the base point). [D] In the corpus the base point is a datum of the marked vessel. In the cell it is the vertex at which the terminal sulfur is attached, and which vertex that is depends on the bridge site of Section 8. Determine whether the base point of the corpus is recoverable as a consequence of the cell rather than as a marking.

4.7 Falsification register for this section

statement	what would refute it
Lemma 4.3, Theorem 4.5, Corollary 4.6	a recomputation disagreeing with V16r, V16s
Hypothesis 4.8	a cage conformation placing both arms on one face
Proposition 4.14	a linkage at a position obstructing N1, the C6 amino group or N7
Proposition 4.17	a datum of the cell, not listed above, that σ does not preserve

5 The pairings

Section 4 fixed the cell: one unit of the stack, two ether tethers to adenosine, the two arms leaving toward opposite faces, and the inversion σ . This section asks what the cell can make. The question is posed on the skeleton alone, so that the answer is finite and so that the sections which follow can be seen to add to it.

The section establishes three things. The cell admits exactly two pairings up to σ ; the two mixed pairings are one object and not two; and the pairing this paper does *not* adopt is the cheaper of the two by every measure stated here. The third is recorded deliberately, and Section 8 is the section that answers it.

5.1 Non-implications

Proposition 5.1 (Non-implications of this section). [A] *None of the following is asserted below.*

- (i) *That admissibility is evidence. Two pairings survive this section and the section offers no ground for preferring either. Proposition 5.9 places the competing pairing ahead of the adopted one on the only measures available here.*
- (ii) *That the enumeration is over chemical species. It is over site types — a thiol at a vertex, a thioether in an edge — taken from the atom map of Appendix A, and its reading as a pair of residues enters no numbered statement.*
- (iii) *That a pairing not listed is impossible. The enumeration is exhaustive for the two site types the atom map*

supplies. A third site type would enlarge it, and Open problem 5.12 records what that would require.

- (iv) *That the two mixed pairings are alternatives between which something must choose here. Proposition 5.6 identifies them, and what distinguishes their two realisations is the choice recorded in Section 6.*
- (v) *That the cell makes one pair at a time. Nothing below bears on how many units of the stack are engaged, and no count of products is claimed.*

5.2 Site types

Definition 5.2 (Site type). [D] The atom map supplies two ways for sulfur to enter a structure. A *terminal site* is a vertex of X carrying an exocyclic sulfur, which becomes a thiol. An *internal site* is an edge of X into which a sulfur is inserted, which becomes a thioether. A *pairing* is an unordered pair of structures, each carrying exactly one site, whose retained vertex sets are disjoint and which demand no edge of X twice.

Lemma 5.3 (The sites the cell offers). [D] *Under the atom map, the terminal sites are C5 and C11, and the internal site is the edge C4b–C10b. The terminal sites form a σ -orbit and the internal site is σ -fixed; it is the unique σ -fixed edge of X.*

Proof. The site assignments are read from the atom map; that {C5, C11} is a σ -orbit and C4b–C10b the unique fixed edge is a finite check, V16m, V16p, and V17f. $\square$

Scholium 5.4. Lemma 5.3 already contains the shape of the section's answer. Two terminal sites exchanged by σ , and one internal site fixed by it, permit exactly two kinds of pairing: both sulfurs terminal, or one terminal and one internal. Both internal is not available, there being only one internal site. That the three cases reduce to these is the content of Theorem 5.5, and it is a statement about the orbit structure of σ rather than about chemistry.

5.3 The enumeration

Theorem 5.5 (Exhaustive enumeration of pairings). [D] *Over the site types of Definition 5.2, the cell admits exactly three pairings, of which one is excluded and two are*

admissible on the skeleton:

both internal	Met + Met	excluded
one of each	Cys + Met	admissible
both terminal	Cys + Cys	admissible

The exclusion has two independent grounds: the retained sets meet at C4b and C10b, and both structures demand the single internal site.

Proof. Exhaustive over unordered pairs of sites, with the disjointness and single-demand conditions of Definition 5.2 tested on each; V16a, V16p. $\square$

Proposition 5.6 (The two mixed pairings are one object). [D] *The pairing placing the thiol at C5 and the thioether toward C12, and the pairing placing the thiol at C11 and the thioether toward C6, are exchanged by σ . They are one pairing described under the two available frames, and no statement of this paper distinguishes them.*

Proof. σ carries each site of the one to the corresponding site of the other; V16p. $\square$

Scholium 5.7. Proposition 5.6 is the reason the enumeration of Theorem 5.5 reports three cases and not five. It is also where the cell's symmetry is still intact: at this stage the two realisations are indistinguishable, and what makes them distinguishable is the single edge orbit of Section 6. A reader who wishes to see where the cell ceases to be symmetric should read this proposition against that theorem.

5.4 The cost of each admissible pairing

Definition 5.8 (Strip and its edges). [D] For a pairing P write $W(P)$ for the union of the ring vertices its two structures retain, $E_{\text{int}}(W)$ for the edges of X induced on W , and ∂W for the edges with exactly one end in W .

Proposition 5.9 (Cost on the skeleton). [D] *For the two admissible pairings,*

	W	$ E_{\text{int}}(W) $	$ \partial W $	
Cys + Cys	{C5, C11}	0	4	one component, 16 vertices
Cys + Met	{C5, C11, C10b, C4b}	3	4	two components, 7 + 7

The competing pairing severs four carbon–carbon bonds and leaves the unit in one piece; the adopted pairing severs six and divides it.

Proof. Induced and boundary edge counts, and connected components after deletion of W ; V16q, V17c, V17g. $\square$

Corollary 5.10 (Valence). [D] *Both sites of the competing pairing have degree two in X and admit a substituent without prior removal of an edge. The adopted pairing requires the removal of C10a–C10b before its internal site can be occupied.*

Proof. The degree sequence of X ; V16a, and Lemma 8.3. $\square$

Scholium 5.11 (The concession, and why it is made here). Proposition 5.9 and Corollary 5.10 place the competing pairing ahead of the adopted one on every measure this section can state: fewer bonds severed, no fragmentation of the unit, and no preparatory removal. A section that withheld this would be describing a search whose outcome had already been assumed.

It is stated here, before Section 6 and Section 7, because those sections do not change it. Section 6 counts the fracture of the adopted pairing and Section 7 balances its electrons, and neither is a comparison. The comparison is made once, in Section 8, and it is made on a ground that none of the measures above anticipates: not how much is severed, but whether the two sulfurs can reach one another. A reader who grants this section its concession has lost nothing that Section 8 requires.

Open problem 5.12 (A third site type). [D] The enumeration is exhaustive over the two site types the atom map supplies. A sulfur inserted at a vertex removed entire, or a structure carrying two sulfurs, would enlarge it. Determine whether the series admits either, and if so re-run Theorem 5.5.

5.5 Falsification register for this section

statement	what would refute it
Lemma 5.3	a second σ -fixed edge, or a terminal site outside the orbit {C5, C11}
Theorem 5.5	a fourth pairing over the stated site types, or an admissible Met + Met
Proposition 5.6	a numbered statement of this paper distinguishing the two mixed realisations
Proposition 5.9	a recomputation disagreeing with V16q

6 The fracture strip

Section 3 fixed the two retained sets. This section states what the pair does to the vessel graph: which edges it destroys, which it keeps, and where its asymmetry sits. Every statement is a finite computation over a graph on eighteen vertices.

6.1 Non-implications

Proposition 6.1 (Non-implications of this section). [A] *None of the following is asserted below.*

- (i) *That the edge operations occur in the order in which they are listed. The fates of Theorem 6.7 are a partition of the edge set and carry no sequence; the staging is Section 6 and is stated there as a hypothesis.*
- (ii) *That the fracture is energetically favourable. This section is bookkeeping over a graph. Whether the transformation is accessible is Section 7 and is not settled here.*
- (iii) *That the pair is selected. Proposition 6.13 records that a second pairing survives this section's constraints; what excludes it is Section 6.*
- (iv) *That the symmetry breaking of Theorem 6.10 is explained. The theorem locates it on a single orbit and does not say what chooses between the two members.*
- (v) *That any chemical species is identified. The objects below are subgraphs of X with decorations, in the sense of the corpus.*

6.2 The strip

Throughout, X is the vessel graph: eighteen vertices, twenty-one edges, cycle rank four, with rings A, B, C, D and the involution σ exchanging $A \leftrightarrow D$ and $B \leftrightarrow C$.

Definition 6.2 (The strip). [D] Let $R_{\text{Cys}} = \{C5\}$ and $R_{\text{Met}} = \{C11, C10b, C4b\}$ be the ring vertices retained by the two residues of the cell. The *strip* of the pair is $W = R_{\text{Cys}} \sqcup R_{\text{Met}}$.

Proposition 6.3 (The strip is symmetric although neither residue is). [A] R_{Cys} and R_{Met} are disjoint, $\sigma(W) = W$, and $\sigma(R_{\text{Cys}}) \neq R_{\text{Cys}}$.

Proof. A finite check on the four vertices; V17f. $\square$

Scholium 6.4. Proposition 6.3 is the form the cell's symmetry survives in. Each residue breaks σ ; their union does not. A statement about the pair may therefore be σ -covariant even though no statement about either residue alone can be.

6.3 The edge trichotomy

Definition 6.5 (Induced and boundary edges). [A] $E_{\text{int}}(W) = \{e \in E(X) : e \subseteq W\}$ and $\partial W = \{e \in E(X) : |e \cap W| = 1\}$.

Proposition 6.6 (Counts). [A] $|E_{\text{int}}(W)| = 3$, $|\partial W| = 4$, and $|E(X \setminus W)| = 14$, so that $3 + 4 + 14 = 21 = |E(X)|$.

Proof. Exhaustive over the twenty-one edges; V17f. $\square$

Theorem 6.7 (Each induced edge has its own fate). [D] *Under the atom map of Section 3, the three edges of $E_{\text{int}}(W)$ are pairwise distinct in fate:*

$C10b$ – $C11$ retained, $C4b$ – $C10b$ consumed by the sulfur insertion,

and every edge of ∂W is severed. The retained edge is the C_{β} – C_{γ} bond of Met; the severed induced edge is the one cut the two residues share.

Proof. The fate of each edge is read from the atom map and the cut lists; V17f. That the induced fates are three and distinct is then immediate from Proposition 6.6. $\square$

Corollary 6.8 (Six skeletal bonds, all accounted for). [D] *The cell destroys six edges of X as carbon–carbon bonds, namely the four of ∂W together with $C4b$ – $C5$ and $C4b$ – $C10b$. Transporting by σ the five severances the corpus records for the second sulfur residue, gives exactly these six. No edge destroyed here is absent from the corpus's own rows, and none of its rows is unused.*

Proof. σ -transport of the published row, compared against the cell's edge set; V17b, V17c. $\square$

Scholium 6.9. An earlier form of this corollary asserted that one of the six, the central edge, was absent from the published rows, being recorded there as a decoration rather than as a cut; and a further proposition followed, amending the corpus's completeness check to cover edges induced on a retained set. Both were wrong. The corpus severs the central edge in the second residue's own row, and the

verification block supporting the claim compared the cell against a list entered by hand from which that row's fifth entry had been dropped.

The manuscript records this rather than absorbing it, and records also what it is an instance of. The corpus warns that a check may agree with a claim because it is testing the wrong object; this is that failure, committed a third time in the same programme and caught only by re-reading the published table. Appendix D carries the entry and Appendix B now marks which verification blocks compute and which merely tabulate, that being the distinction under which the error was invisible.

which both residues carry the thioether is excluded, the two retained sets not being disjoint.

Proof. Exhaustive over the three pairings; V16a. $\square$

Scholium 6.14. Proposition 6.13 states the cost of confining this section to the skeleton. The alternative pairing severs fewer edges and leaves the unit in one piece, so on the bookkeeping of this section it is the cheaper outcome. What distinguishes the two is not the strip but what can bridge it, and that is Section 6.

6.4 Where the asymmetry sits

Theorem 6.10 (The asymmetry is carried by one orbit). **[D]** σ acts on $E_{\text{int}}(W) \cup \partial W$ with four orbits:

$\{C4a-C4b, C10a-C10b\}$, $\{C5-C6, C11-C12\}$, $\{C4b-C10b\}$, $\{C4b-C5, C10b-C11\}$.

On the first two both members are severed; the third is a fixed point and is consumed; on the fourth the two members differ, one severed and one retained. Exactly one orbit has members of differing fate.

Proof. The orbit decomposition is a finite check, and the fates are those of Theorem 6.7; V17f. $\square$

Scholium 6.11. Theorem 6.10 is the sharpest statement this section makes. The cell is centrosymmetric and its outcome is not, and one might expect the discrepancy to be diffuse. It is not: on seven edges the fate map is σ -equivariant, and it fails on one orbit of two. The question of what selects $C4b-C5$ for severance rather than $C10b-C11$ is therefore the whole of the cell's symmetry breaking at the level of the skeleton, and it is posed here and answered in Section 6.

Proposition 6.12 (The remnant). **[A]** $X \setminus W$ has two connected components, of seven vertices each, and σ exchanges them. One carries ring A together with C12, the other ring D together with C6; each retains the ether oxygen of its tether.

Proof. Connected components after deletion of W ; V17g. $\square$

Proposition 6.13 (A second pairing is not excluded here). **[A]** Let $W' = \{C5, C11\}$ be the strip of the pairing in which both residues terminate in a thiol. Then $E_{\text{int}}(W') = \emptyset$, $|\partial W'| = 4$, and $X \setminus W'$ is connected on sixteen vertices. No statement of this section excludes W' , and the pairing in

7 Balance

Section 4 counted bonds. This section counts electrons. The purpose is to determine what the cell must draw from the medium beyond the two heteroatom species, and the result is that under one hypothesis it draws nothing — at a price, stated in Corollary 7.11.

7.1 Non-implications

Proposition 7.1 (Non-implications of this section). [A] *None of the following is asserted below.*

- (i) *That the balance is a mechanism. It is global: it shows the carbon frame can supply the electrons the sulfur sink demands, and says nothing about how those electrons reach the sulfur–sulfur bond from two benzylic carbons at opposite ends of the skeleton. A reader will supply the stronger reading and it is not available.*
- (ii) *That a balance establishes feasibility. Theorem 7.9 shows the transformation is not excluded on electron-counting grounds. It says nothing about any barrier.*
- (iii) *That the oxidation index is a physical charge. It is the standard formal bookkeeping device of Definition 7.2 and is used for its additivity alone.*
- (iv) *That the sources of Hypothesis 7.5 are established. They are named premises and each is entered in the falsification register.*
- (v) *That $v(k)$ is unaffected by the pyramidalisation of Section 9. The move dearomatises a ring and changes the oxidation level of ring carbons; whether Corollary 7.10 survives its admission is Target 11.7 and is not settled here.*
- (vi) *That the asymmetry of Corollary 7.11 is the same asymmetry as that of Theorem 6.10. Whether the two are one choice or two is Open problem 7.13.*

7.2 The index

Definition 7.2 (Oxidation index). [A] For an atom a in a structural formula let

$$\omega(a) = \sum_{b \sim a, \chi(b) > \chi(a)} m(a, b) - \sum_{b \sim a, \chi(b) < \chi(a)} m(a, b),$$

where $m(a, b)$ is the bond order and χ the electronegativity, bonds between atoms of one element contributing nothing. For a set S of atoms write $\omega(S) = \sum_{a \in S} \omega(a)$.

Remark 7.3. [A] ω is additive over atoms and local to bonds, so for a transformation T carrying a molecular graph G to G' the quantity $\Delta_\omega(T) = \omega(G') - \omega(G)$ depends only on the atoms whose incidences change. All sums below are taken over that set.

Definition 7.4 (External demand). [D] The *external demand* of the cell is $v = \Delta_\omega^C + \Delta_\omega^S + \Delta_\omega^N$, the three summands

being taken over the carbon, sulfur and nitrogen atoms respectively. The cell is *redox-self-sufficient* when $v = 0$.

7.3 Sources

Definition 7.5 (Sources). [D] The cell draws sulfur as a disulfide, in which each sulfur has $\omega = -1$, and nitrogen as ammonia, in which $\omega = -3$. Both carboxyl oxygens are carrier-internal: one is the phosphate oxygen at C_β and one the 2'-oxygen of the adenosine ribose, to which C' is esterified.

Proposition 7.6 (Carbon closure). [A] *The cell holds twenty-two carbons: eighteen of the skeleton and four of the two tether glycol units. The products hold twenty-two: three in Cys, five in Met, and fourteen in the remnant of Proposition 6.12.*

Proof. V16f. □

Proposition 7.7 (Nitrogen is neutral and sulfur is a sink). [D] *Under Definition 7.5, $\Delta_\omega^N = 0$, the nitrogen passing from ammonia to an amine without change of index; and $\Delta_\omega^S = -2$, each of the two sulfurs passing from -1 in the disulfide to -2 in a thiol and in a thioether respectively.*

Proof. V16i, V17h. □

7.4 The remnant parameter, and uniqueness

The two remnant components of Proposition 6.12 each terminate at a benzylic carbon, C12 and C6 respectively, carrying the ether oxygen of its tether. Each may terminate at the alcohol level or at the aldehyde level, and these differ in index by two.

Definition 7.8 (Remnant parameter). [D] Let $k \in \{0, 1, 2\}$ be the number of remnant components terminating at the aldehyde level.

Theorem 7.9 (The external demand is affine in k). [D] *Under Definition 7.5 and the atom map of Section 3,*

$$\Delta_\omega^C(k) = 2k, \quad \text{hence} \quad v(k) = 2k - 2.$$

In particular $v(0) = -2$, $v(1) = 0$ and $v(2) = +2$.

Proof. The index change is computed atom by atom over the twelve carbons whose incidences change, with the two remnant termini supplied by k ; V17h. The stated values follow with Proposition 7.7. □

Corollary 7.10 (Self-sufficiency is attained at exactly one value). [D] $v(k) = 0$ if and only if $k = 1$.

Corollary 7.11 (The remnants cannot be equivalent). [D] *If the cell is redox-self-sufficient then its two remnant components, which are exchanged by σ as graphs, differ in oxidation state: one terminates as an aldehyde and one as an alcohol.*

Scholium 7.12. Corollary 7.11 is the section's substantive consequence and is a prediction rather than an observation. The two components are interchangeable by every structural criterion available to Section 4, and the electron count nonetheless forbids their being interchangeable in fact. A cell that produced two equivalent remnants would be balanced only by drawing two electrons from the medium, and the claim that sulfur is the single species the carrier cannot supply would fail with it.

Open problem 7.13 (Are the two asymmetries one?). [D] The cell breaks σ at the edge orbit of Theorem 6.10 and again at the remnant parameter of Corollary 7.11. Determine whether the second is a consequence of the first — the severed member of the orbit lying on the component that is oxidised further — or whether the two are independent choices. Nothing below Section 6 decides this.

7.5 Falsification register for these sections

statement	what would refute it
Proposition 6.6, Theorem 6.10, Proposition 6.12	a recomputation disagreeing with V17f, V17g
Theorem 6.7	an atom map assigning two induced edges the same fate
Corollary 6.8	a seventh skeletal bond destroyed, or a sixth accounted for as an insertion
Theorem 7.9	an index computation giving Δ_{ω}^C not affine in k , or not $2k$
Corollary 7.11	a self-sufficient cell exhibiting two remnants of equal oxidation state
Definition 7.5	a sulfur source other than a disulfide, or a carrier-external carboxyl oxygen

8 The bridge, and what it excludes

Section 5 left two pairings admissible on the skeleton, and observed that the one this paper does not adopt is the cheaper of the two by every measure available there. Section 6 described

the fracture and Section 7 the electron balance, and neither distinguishes them. This section supplies the distinction. It is the paper's principal result and it is obtained without any appeal to energy.

The argument has three steps. A bridge between two sulfur sites closes a ring whose size is determined by a graph distance; the admissible sizes do not by themselves exclude the competing pairing; and the geometry of an inversion does. The third step is exact.

8.1 Non-implications

Proposition 8.1 (Non-implications of this section). [A] *None of the following is asserted below.*

- That a pairing formed by two independent deliveries is excluded. Theorem 8.13 excludes a bridge, and the exclusion has force only under Hypothesis 8.19. The hypothesis, and not the theorem, carries the selection.*
- That migration is excluded. Theorem 8.13 concerns the sites a pairing retains; that a sulfur does not reach them from elsewhere is Hypothesis 8.20 and is assumed, not shown.*
- That the adopted pairing is favourable. Nothing below compares energies, and no barrier is estimated; the scope of Section 2 forbids it. What is established is that one pairing admits the bridge and the others do not.*
- That the bridged species is observed. It is an intermediate required by the construction and is not claimed to have been isolated.*
- That ring size decides the question. Proposition 8.7 is stated precisely so that its insufficiency can be recorded at Scholium 8.10.*
- That the idealised geometry of Lemma 8.11 is a computation of structure. It is a rigid planar model with fixed bond lengths, and the bound of Theorem 8.13 is stated so as to survive any relaxation that preserves the inversion.*

8.2 Sites and valence

Definition 8.2 (Sulfur site). [D] A *sulfur site* of a pairing is a vertex of X at which one of the two sulfur atoms is first attached. The sites of Cys + Met are {C5, C10b} and those of Cys + Cys are {C5, C11}.

Lemma 8.3 (Valence at a fusion vertex). [A] *The six vertices of degree three in X are the chord endpoints $C4a, C4b, C6a, C10a, C10b, C12a$. A degree-three vertex carries no hydrogen and admits an exocyclic substituent only after one of its three edges is removed. The vertices $C5$ and $C11$ have degree two and admit a substituent without removal.*

Proof. The degree sequence of X ; V1 of the corpus, recomputed at V16a. $\square$

Corollary 8.4 (The cut that frees the site is not a new move). [D] *The site $C10b$ is freed by removal of $C10a - C10b$, which is one of the four cuts the corpus already records for Met. The pairing Cys + Met therefore requires no edge removal beyond those its residues require in any case.*

Scholium 8.5. Corollary 8.4 is stated because the competing pairing needs no such removal at all, both of its sites having degree two. On the ledger of moves the adopted pairing is again the more expensive, and the section does not conceal this: what it establishes is an exclusion of the alternative, not an economy of the adopted.

8.3 The bridge and its ring

Definition 8.6 (Disulfide bridge). [D] Let u, v be sulfur sites and let X' be the skeleton after the removals of Corollary 8.4. A *disulfide bridge* on $\{u, v\}$ is the configuration in which one sulfur is bonded to u , the other to v , and the two to each other.

Proposition 8.7 (Ring size from graph distance). [A] *A disulfide bridge on $\{u, v\}$ closes a cycle whose length is*

$$|\text{ring}| = d_{X'}(u, v) + 3,$$

the cycle consisting of a shortest $u-v$ path together with the two sulfurs. In the present cell

$d(C5, C4b) = 1, \quad d(C5, C10b) = 2, \quad d(C5, C11) = 3,$
giving rings of four, five and six members respectively.

Proof. The cycle is the path together with $u-S$, $S-S$ and $S-v$, so its length exceeds the path length by three. The three distances are shortest paths in X' ; V16n. $\square$

Remark 8.8 (The three sizes, chemically). [C] A saturated four-membered CCSS ring is not a motif of the literature. The five-membered ring is the 1,2-dithiolane, of which lipoic acid is the familiar instance. The six-membered ring is the 1,2-dithiane, which is likewise a known motif [FPS⁺22].

Corollary 8.9 (The bridge to $C4b$ is excluded). [D] *Of the two sites available to Met, only $C10b$ admits a bridge, the bridge to $C4b$ closing a four-membered ring.*

Scholium 8.10. Proposition 8.7 does not decide the section's question, and it is important that this be said where the proposition is stated rather than at the end. Both the five-ring of the adopted pairing and the six-ring of the competing one are known motifs, so ring size excludes the bridge to $C4b$ and nothing else. An argument resting here would be an argument from the absence of a precedent, which is not an argument. What excludes the competing pairing is Theorem 8.13, and it excludes it for a reason that has nothing to do with how many atoms are in the ring.

8.4 The exclusion

Write z for the centre of the inversion σ , which is the midpoint of the edge $C4b-C10b$, and for a vertex v write $n(v)$ for the unit vector along the exocyclic direction at v , that is the direction opposite to the mean of the directions to the neighbours of v in X' .

Lemma 8.11 (The exocyclic direction points away from the centre). [D] *In the rigid planar model of the skeleton, $n(v) \cdot (v - z) > 0$ for $v \in \{C5, C11\}$, with $\|v - z\| = 1.85 \text{ \AA}$ and $n(v) \cdot (v - z) = +1.40$.*

Proof. V16o. The sign is a consequence of z lying inside the ring system and v on its periphery, and is therefore stable under any deformation keeping the skeleton convex at v . $\square$

Lemma 8.12 (Sulfurs at σ -related sites are antipodal). [D] *Let v be a site and σv its image, and let the sulfur attached at each lie along the exocyclic direction at bond length ℓ . Since σ is the point inversion $x \mapsto 2z - x$, one has $n(\sigma v) = -n(v)$ and hence*

$$S(\sigma v) = 2z - S(v), \quad \text{so} \quad \|S(v) - S(\sigma v)\| = 2\|S(v) - z\|.$$

Proof. Immediate from $\sigma(x) = 2z - x$ applied to v and to the substituent direction. $\square$

Theorem 8.13 (No bridge closes between σ -related sites).

[D] Let $\{v, \sigma v\}$ be a σ -orbit pair of sites. Then

$$\|S(v) - S(\sigma v)\|^2 = 4 \left(\|v - z\|^2 + 2\ell n(v) \cdot (v - z) + \ell^2 \right) > 4 \|v - z\|^2,$$

so that $\|S(v) - S(\sigma v)\| > 2\|v - z\|$. A bridge therefore requires $\|v - z\| < 1.02 \text{ \AA}$, half the sulfur–sulfur bond length. No peripheral vertex of a fused four-ring aromatic satisfies this; in the rigid model $\|v - z\| = 1.85 \text{ \AA}$, giving a separation above $3.70 \text{ \AA}$. No disulfide bridge closes on such a pair. In the present cell $\{C5, C11\}$ is such a pair and $\{C5, C10b\}$ is not.

Proof. Expand $\|S(v) - z\|^2$ with $S(v) = v + \ell n(v)$ and apply Lemma 8.12; the cross term is positive by Lemma 8.11, so the inequality is strict and the bound does not depend on ℓ . The numerical values and the verification that $\sigma(C5) = C11$ while $\sigma(C5) \neq C10b$ are at V16m, V16o. $\square$

Scholium 8.14. The inequality is strict independently of the sulfur–carbon bond length, and the condition it imposes, $\|v - z\| < 1.02 \text{ \AA}$, is not a quantity the model supplies: it is two thirds of one carbon–carbon bond, and no vertex on the periphery of a fused four-ring system lies that close to its centre. The exclusion is therefore not a numerical accident of the model, and the figure $3.70 \text{ \AA}$ is an illustration rather than the ground. Its content is that a substituent on a peripheral vertex points away from the inversion centre, and an inversion sends that direction to its negative: two such substituents recede from one another at exactly twice the rate at which either departs from the centre. Any deformation preserving the inversion and the convexity at v preserves the conclusion. This is why the exclusion survives the absence of a relaxed geometry, and why the section can reach a result under the scope of Section 2.

Corollary 8.15 (Exactly one pairing admits a bridge). [D] Of the three pairings of Section 5, Met + Met is excluded by overlap of the retained sets, Cys + Cys by Theorem 8.13, and Cys + Met admits a bridge, at $\{C5, C10b\}$ and there only. The mixed pairing is the unique pairing whose sulfur sites are not σ -related.

Proof. Exhaustive over the three pairings; V16a, V16m, Corollary 8.9. $\square$

8.5 The delivery

Proposition 8.16 (The bridge requires pyramidalisation).

[D] At C5 and C10b the carbon is trigonal and its exocyclic direction is fixed by the ring, admitting no rotation. Sulfurs placed along those fixed directions stand $4.78 \text{ \AA}$ apart, against $2.05 \text{ \AA}$ for the bond that must join them. The five-membered ring therefore cannot close while both carbons remain trigonal: at least one must pyramidalise, and ring C is dearomatised in the closing.

Proof. The exocyclic directions and the separation; V16k. $\square$

Scholium 8.17. The analogy with the 1,2-dithiolane of lipoic acid carries the ring size and not the geometry. There the ring carbons are tetrahedral and their carbon–sulfur bonds rotate toward one another; here they are aromatic and do not, and the shortfall of $2.73 \text{ \AA}$ is not a rotational artefact. What the analogy establishes is that the product ring is a known one, not that it is reachable from the resting cell. Two consequences are carried forward. Section 9 admits pyramidalisation as a move and places it in the precedence relation, so the ledger rises. And Remark 8.18 states what the distortion does to Theorem 8.13, whose hypothesis concerns a conformation in which the inversion is realised.

Remark 8.18 (The distortion preserves the exclusion). [D]

Theorem 8.13 is stated of a conformation realising the inversion, and Proposition 8.16 shows the bridge closes on a distorted one. For the competing pairing the two sites are exchanged by σ , so any distortion that pyramidalises one and not the other destroys the pairing’s own symmetry without bringing the sites together, and any distortion that pyramidalises both symmetrically preserves the inversion and leaves the theorem in force. The exclusion therefore survives, but by this argument and not by the theorem alone, and the argument is stated here rather than assumed.

What is *not* established is that no asymmetric distortion brings the two σ -related sites within bonding distance. The bound of Theorem 8.13 holds only where the inversion holds, and a sufficiently large asymmetric distortion is outside it. Bounding that distortion requires a relaxed geometry and is Target 11.6.

Hypothesis 8.19 (Disulfide delivery). [D] The cell receives its sulfur as a disulfide, in a single event, and the two sulfurs of that disulfide become the two sulfurs of the pair.

Hypothesis 8.20 (No migration). [D] A sulfur does not move from the vertex or edge at which it is first attached to another. The site at which the bridge closes is the site the structure retains.

Scholium 8.21. Hypothesis 8.20 is stated because Theorem 8.13 excludes a bridge *between the sites a pairing retains*, and nothing in the geometry forbids a disulfide from closing at some other pair of vertices and a sulfur moving afterwards. Were migration available, the competing pairing would not be excluded and the selection of this section would fail. The hypothesis is not an incidental stipulation about a reagent: with Hypothesis 8.19 it is one of the two premises on which the paper's principal result stands, and Section 11 states both as targets.

Proposition 8.22 (The demand is met exactly). [D] *The cell demands two sulfur atoms, one terminal at C5 and one internal between C4b and C10b. A disulfide supplies two. Under Hypothesis 8.19 one delivery event therefore serves both structures, with no atom left over and none required from a second event.*

Proof. V16h. □

Scholium 8.23 (What has replaced what). The corpus states, as a hypothesis about the medium, that one delivery serving two structures is preferred to two deliveries that must coincide, and declines to establish it. Hypothesis 8.19 is not that statement. It is a claim about the species delivered, from which the service of two structures by one event follows by Proposition 8.22 rather than being assumed; and the preference for one pairing over another, which the corpus obtained from the medium, is obtained here from the symmetry of the carrier. Whether the medium in fact supplies sulfur in this form is not settled by this paper, and the falsification register records it.

Remark 8.24 (Where the weight now rests). [A] By Proposition 8.1(i), the exclusion of Theorem 8.13 bears on the competing pairing only if the two sulfurs arrive bonded to one another. The selection therefore rests on two premises and not on the carrier alone: Hypothesis 8.19, that the sulfurs arrive bonded, and Hypothesis 8.20, that neither afterwards moves. Together they are the successor to the corpus's hypothesis about the medium. Neither is established here.

Open problem 8.25 (Two sites, one choice). [D] The bridge is available at {C5, C10b} and equally, by σ , at {C11, C4b}. Which is realised is the choice recorded at the edge orbit of Section 6 and, on the reading offered there, the same choice that fixes the remnant parameter of Section 7. Determine whether the bridge site fixes both.

8.6 Falsification register for this section

statement	what would refute it
Lemma 8.3, Proposition 8.7	a recomputation disagreeing with V16a, V16n
Theorem 8.13	a disulfide bridge closing between two sites exchanged by an inversion, in any system
Corollary 8.15	a fourth pairing, or a second bridge site for the mixed pairing
Hypothesis 8.19	a sulfur source that is not a disulfide, or delivery of the two sulfurs in separate events
Proposition 8.22	a cell demanding other than two sulfur atoms

9 The staged transformation

Section 8 established which pairing the cell can bridge. This section states the transformation that carries the bridged cell to the two residues, as a sequence of stages, and determines how much of the sequence is forced.

The result is that three stages are totally ordered by valence and existence alone, and that the fourth is ordered against them only in part. A second result is obtained in passing and is the more useful: the choice made at the bridge is the choice that resolves the edge orbit of Section 6, so the two are not independent, and half of the open problem left there is closed.

9.1 Non-implications

Proposition 9.1 (Non-implications of this section). [A] *None of the following is asserted below.*

- (i) *That the order of the stages is a chronology of anything beyond one reaction. It is a precedence relation among events within a single cell, established by valence and by what must exist before what. It bears on no assignment, no code and no priority of one mapping over another, and the refusal of the corpus on that point stands unweakened.*
- (ii) *That the stages are elementary steps. Each may comprise several, and Open problem 9.14 records that whether stage III is concerted is not settled here.*

- (iii) That the precedence relation is complete. Proposition 9.6 states what is not ordered, and nothing below supplies an order for it.
- (iv) That the loss of two aromatic rings is accounted anywhere. The balance of Section 7 counts electrons; nothing counts aromaticity, which is the dominant energetic term of the transformation and which the scope of Remark 2.5 excludes from computation. It is named here and nowhere quantified.
- (v) That the ledger of Table 2 is minimal. It is the smallest set of moves the present construction requires, and the count rises by one against the corpus; Scholium 9.15 says where.

9.2 The stages

Definition 9.2 (The stages). [D] Under the atom map and Hypothesis 8.19, the transformation of the cell comprises the following.

	event
0	the resting cell; no exogenous atom present
I	removal of C10a–C10b, freeing a valence at C10b
II'	pyramidalisation at C5 and C10b, dearomatising ring C; required by Proposition 8.16 before the ring can close
II	delivery of the disulfide and closure of the bridge at {C5, C10b}
III	reduction of S–S; the second sulfur displaces C4b–C10b to give the thioether, the first is protonated to the thiol
IV	amination at each C _α ; the transannular bonds C6 _α –C5 and C12 _α –C11; esterification of each C' to its ribose 2'-oxygen; the four boundary cuts and C4b–C5, releasing the residues

Proposition 9.3 (Distribution of the destroyed edges). [D] Of the six edges of X destroyed by the cell, one falls at stage I, one at stage III, and four at stage IV. The edge destroyed at stage III is the σ -fixed edge, and it is not severed but consumed by the insertion.

Proof. Assignment of each edge to its stage; V17j, with the edge list of V17c. $\square$

9.3 What is forced

Theorem 9.4 (The first three stages are totally ordered). [D] Stage I precedes stage II', which precedes stage II; stage II precedes stage III, and stage III precedes the cut C4b–C5 of stage IV. The grounds are respectively:

- (a) C10b has degree three in X and by Lemma 4.3 carries no exocyclic substituent until one of its edges is removed, and stage II' lies between stage I and stage II, the ring being unable to close on trigonal carbons (Proposition 8.16);
- (b) a bond cannot be reduced before it exists;
- (c) while S–S is intact the two structures are joined through it, so severing C4b–C5 first would release one molecule and not two.

Proof. Each clause is a finite statement about valence or about the existence of a bond; V17i. $\square$

Scholium 9.5. Clause (c) is the one worth reading. The shared cut of Section 6 is the cut that separates the two residues, and the bridge is what holds them together until it is resolved. The order of the transformation is therefore not imposed: the bridge that Section 8 requires for selection is the same object that fixes when the pair may come apart.

Proposition 9.6 (What is not ordered). [D] The amination at C6_α and C12_α is ordered against no stage. Its site is on the tether, at distance from every sulfur site and from every edge destroyed at stages I to III, and no valence argument constrains it.

Proof. V17i. The tether carbons are not vertices of X; V16g. $\square$

Lemma 9.7 (The transannular bond is constrained, the amination is not). [D] C5 has degree two in X and carries one hydrogen. Attachment of the sulfur consumes that hydrogen; the transannular bond C6_α–C5 therefore requires a further valence and cannot form while both ring bonds at C5 are intact. It follows the removal of C5–C6. The same statement at C11 requires no sulfur, that vertex carrying none.

Scholium 9.8. Lemma 9.7 is why stage IV is stated as a stage rather than as a set of free events. Part of it is constrained and part is not, and the constraint is local to C5. A reader wishing to place the amination early may do so; a reader

placing the transannular bond early may not.

for it, or record that none is available. Nothing in this paper's scope permits estimating what it costs.

9.4 Where the symmetry breaks

Theorem 9.9 (The bridge site resolves the edge orbit). [D] *The bridge of stage II may close at {C5, C10b} or, by σ , at {C11, C4b}. The first fixes the terminal site at C5, hence the retained sets $R_{\text{Cys}} = \{\text{C5}\}$ and $R_{\text{Met}} = \{\text{C11, C10b, C4b}\}$, hence the severance of C4b–C5 and the retention of C10b–C11 at stage IV; the second gives the σ -image throughout. The choice of bridge site therefore determines the resolution of the orbit {C4b–C5, C10b–C11}, which by Section 6 is the whole of the cell's skeletal symmetry breaking.*

Proof. The retained sets follow from the site by the atom map; the fates of the two edges of the orbit follow from the retained sets by Section 6; V17i, V17j, and V17f. $\square$

Corollary 9.10 (The break is made early and realised late). [D] *The cell ceases to be σ -symmetric at stage II, and the edge orbit in which that asymmetry is visible on the skeleton is not resolved until stage IV.*

Scholium 9.11. Corollary 9.10 answers a question Section 6 could pose and not settle. There the asymmetry was located on a single orbit and its origin left open; here it is identified with the site at which the disulfide binds. What remains open is narrower and is stated below: whether the same choice also fixes the remnant parameter of Section 7. Nothing in the present section decides that, the two remnant components being distinguished by no event of Definition 9.2.

Open problem 9.12 (Does the bridge site fix the remnant parameter?). [D] Section 7 shows that redox self-sufficiency forces exactly one remnant component to the aldehyde level. Theorem 9.9 identifies the choice that breaks the symmetry on the skeleton. Determine whether the two are the same choice — that is, whether the component bearing the severed member of the orbit is the one oxidised further — or whether the cell makes two independent choices.

Open problem 9.13 (The aryl–aryl insertion). [D] At stage III the second sulfur displaces C4b–C10b, which is the central bond of a fused aromatic system. Insertion of a heteroatom into an aryl–aryl bond is not a routine operation, and this step, rather than any other, is where the chemical plausibility of the account is decided. Exhibit a precedent

Open problem 9.14 (Concertedness). [D] Stage III comprises a reduction, a displacement and a protonation. Whether these are concerted is not determined by any argument of this paper and is outside the scope declared in Section 2.

9.5 The ledger

Scholium 9.15 (Where the count rises). The corpus admits ten moves and records that the count once fell. Against that ledger this paper consolidates and adds. The sulfur chemistry is one row and not two: the disulfide delivers both atoms, and the difference between a thiol and a thioether is the site rather than the move, which is the same consolidation the corpus made at its decarboxylative scission. The transannular attack is stated σ -covariantly and so covers both residues in one row where a naive statement would need two.

The count nonetheless rises by two. The α -nitrogen has no row in the corpus, whose nitrogen row is gated by a defective register and therefore cannot be the universal one: every residue carries an α -amino group and the structure carrying no side-chain nitrogen carries an α -amino group too. The corpus row is accordingly rescoped to side-chain nitrogen and a new row is admitted, forced by that observation and scoped without exception. The addition is recorded here rather than absorbed.

The second addition is pyramidalisation, admitted at stage II'. It is forced by a single case — the bridge cannot close on trigonal carbons — and scoped to the two bridge sites. It was not in the first form of this account, which took the 1,2-dithiolane analogy to carry the geometry as well as the ring size; Appendix D records the correction. Its cost is stated plainly: the move dearomatises a ring, which is the largest energetic term in the transformation, and the scope of Remark 2.5 forbids estimating it.

move	stage	scope
removal of a framework edge	I, IV	every edge destroyed as a carbon–carbon bond
pyramidalisation of a ring carbon, dearomatising its ring	II'	the two bridge sites; forced by Proposition 8.16
delivery of sulfur as a disulfide, bridging two sites, each sulfur terminating as thiol or as thioether by its site	II, III	the pair of this paper; the only move requiring a source outside the carrier and the nitrogen row below
transannular attack forming the bond to the terminal vertex, stated σ -covariantly	IV	both residues
cleavage of the arm at its ether bond	IV	both residues
delivery of α -nitrogen at the tether C_α	IV	every residue, without exception
delivery of side-chain nitrogen, gated by a defective register	—	the nitrogen-bearing side chains; rescoped from the corpus
esterification of C' to the ribose $2'$ -oxygen	IV	both residues

Table 2: Moves admitted by the cell, with the stage at which each is forced and its scope.

9.6 Falsification register for this section

statement	what would refute it
Proposition 9.3	a recomputation disagreeing with V17j
Theorem 9.4	a route reaching the bridged cell without prior removal at C10 <i>b</i> , or releasing two residues with S–S intact
Proposition 9.6	a valence or geometric constraint placing the amination relative to stages I–III
the aryl–aryl insertion at stage III	a demonstration that a heteroatom cannot be inserted into the central bond of a fused arene under any conditions available to the medium
Theorem 9.9	a bridge site leaving the orbit {C4 <i>b</i> –C5, C10 <i>b</i> –C11} unresolved
Table 2	a residue formed by a move not listed, or a listed move unforced by the stage against it

10 The product contact

The two residues leave the cell carrying sulfurs that were, one stage earlier, bonded to one another. This section states what becomes of that proximity, and states equally plainly what cannot be settled here.

The section’s position in the paper is itself a claim. An earlier form of this account placed a sulfur–hydrogen–sulfur contact at the head of the argument and asked it to select the pairing. It cannot: such a contact is worth a kilocalorie or two, and a selection resting on it would rest on a quantity this paper has no means to compute. Section 8 selects the pairing by an exclusion that is exact, and the contact appears here, downstream, as something the transformation produces rather than something

it requires.

10.1 Non-implications

Proposition 10.1 (Non-implications of this section). [A] *None of the following is asserted below.*

- (i) *That the contact selects the pairing. It is a consequence of Section 9 and enters no argument of Section 8. Nothing in the paper would change if the contact did not form.*
- (ii) *That the contact is established. Proposition 10.4 places the two sulfurs at a separation compatible with one; the angular condition is not met in the model available and is stated as open at Open problem 10.8.*
- (iii) *That the contact has been quantified. No interaction energy is computed or cited as a computation; the reference figures of Remark 10.3 are imported.*
- (iv) *That the two residues remain associated. Proposition 10.10 states what holds them, and the duration of that holding is not in view.*
- (v) *That the rigid planar model determines the product geometry. It determines the skeleton, and Lemma 10.7 states exactly where it ceases to determine anything.*

10.2 What the cleavage leaves

Definition 10.2 (The contact). [E] The *contact* is the sulfur–hydrogen–sulfur interaction in which the thiol of Cys is donor and the thioether sulfur of Met acceptor. It is a molecular reading and enters no proof.

Remark 10.3 (Reference figures). [C] A sulfur–sulfur bond is about 2.05 Å [AKW⁺87]. A sulfur–hydrogen–sulfur hydrogen bond is characterised by a donor–acceptor separation of some 3.6 to 4.2 Å, with the donor hydrogen approximately on the donor–acceptor line, so that the carbon–sulfur–sulfur angle at the donor lies near the carbon–sulfur–hydrogen angle of a thiol, about 96°. Such interactions are weak by comparison with their oxygen and nitrogen analogues [GRFC91].

Proposition 10.4 (Separation after stage III). [D] *In the rigid planar model, immediately after stage III and before any bond at C5 is severed, the thiol sulfur and the thioether sulfur stand at 3.80 Å. The two sulfurs, bonded at 2.05 Å in the bridge, therefore separate by 1.75 Å and no more.*

Proof. The thioether sulfur is displaced from the plane by the geometry of its two carbon–sulfur bonds across the former σ -fixed edge; the thiol sulfur lies along the exocyclic direction at C5; V16t, V16u. $\square$

Corollary 10.5 (The separation is in range). [D] *The separation of Proposition 10.4 lies within the interval of Remark 10.3. The distance condition for the contact is met by the geometry the transformation produces, with no further approach required.*

Scholium 10.6 (Why the distance is not a coincidence). Corollary 10.5 is less remarkable than it looks and should be read as such. The two sulfurs are where they are because they arrived bonded: the bridge sets their separation at 2.05 Å and the cleavage of Section 9 permits them to recede only as far as the new bonds require, which is 1.75 Å further. A contact at the resulting distance is what a disulfide cleaved in place must leave. The observation is worth stating because it is the mechanism, and not the contact, that does the work: had the two sulfurs been delivered independently, nothing would place them at this separation.

10.3 The angle is not determined here

Lemma 10.7 (The model constrains the skeleton, not the substituent). [D] *In the rigid planar model the carbon–sulfur–sulfur angle at the donor is 33°, which is some 63° from the value of Remark 10.3. The model holds C5 within the ring by both of its ring bonds. After C4b–C5 and C5–C6 are severed at stage IV, the exocyclic direction at C5 is no longer fixed by the ring, and the angle is not determined by any statement of this paper.*

Proof. V16t. $\square$

Open problem 10.8 (The angular condition). [D] Determine, on a relaxed geometry of the released pair, whether the carbon–sulfur–sulfur angle at the donor is compatible with the contact. The scope declared in Section 2 places this outside the present paper, and the figure of Lemma 10.7 is not evidence either way: it is the angle of a conformation that stage IV destroys.

Scholium 10.9. The angle is the section's weak joint and is named as such. It would have been possible to report the separation, which is favourable, and to omit the angle, which is not determined; the separation alone would then have read as a result. The two conditions of Remark 10.3 are of equal standing, one is met in the model and the other is not addressed by it, and a reader is entitled to both statements in the same place.

10.4 What holds the pair

Proposition 10.10 (Anchoring). [D] *At the close of stage IV each residue remains bound, through the ester at its C', to the 2'-oxygen of its own adenosine, and the two adenosines are carried on arms leaving the skeleton toward opposite faces. Neither residue is free in the medium at the moment of release.*

Proof. The esterification is an event of stage IV; the opposite faces are Corollary 4.16. $\square$

Scholium 10.11 (Three things that bear on the contact, of differing standing). Three circumstances are commonly adduced for a contact of this kind, and they are not of equal weight here.

The separation is a consequence of the mechanism and is established, in the model, at Proposition 10.4. The anchoring is established at Proposition 10.10 and bears on whether the two residues remain within reach of one another, although nothing here says for how long. The relief of ring strain at the destruction of ring *B* and ring *C* is a reading only: it is plausible that it leaves the two sulfurs on a short carbon path, and no statement of this paper establishes it. The first two are cited below; the third is recorded here and nowhere else.

Open problem 10.12 (Whether the contact has a function). [E] The contact, if it forms, joins the two residues at the moment both are released and both are still anchored.

Whether it bears on anything — the fate of the pair, the geometry at which the pair is presented, or nothing at all — is not addressed by this paper, which establishes only that the transformation leaves the two sulfurs in proximity.

10.5 Falsification register for this section

statement	what would refute it
Proposition 10.4, Lemma 10.7	a recomputation disagreeing with V16t, V16u
Corollary 10.5	a relaxed geometry placing the two sulfurs outside the interval of Remark 10.3
Proposition 10.10	a release in which the ester to the ribose 2'-oxygen is not formed, or is cleaved at stage IV

11 Non-implications restated; targets; conclusion

11.1 The refusals, restated

Section 3 placed ten refusals before the constructions they guard, and each section added its own. Three are restated here because they are the three a reader of the foregoing is most likely to have set aside.

Proposition 11.1 (The three most at risk). [A] *None of the following is asserted anywhere in this paper.*

- (i) *That the pairing is selected by an argument of the carrier alone. Theorem 8.13 excludes a bridge between σ -related sites and is exact; but it bears on the competing pairing only if the two sulfurs arrive bonded to one another, which is Hypothesis 8.19. The selection rests on that hypothesis and on nothing else, and the hypothesis is not established here.*
- (ii) *That any stage is favourable. The paper establishes what is excluded and what is forced given its premises. It computes no energy and estimates no barrier, the scope of Section 2 forbidding both, and the word favoured occurs in no numbered statement.*
- (iii) *That the order of Section 9 is a chronology of anything beyond one reaction. It is a precedence among events within a single cell, established by valence and by what must exist before what. No assignment, no code and no priority of one mapping over another follows from it, and the refusal of the corpus on that point stands unweakened by anything in this paper.*

Scholium 11.2. Clause ((i)) is the one to read twice. The corpus carries a headline result on a hypothesis about the medium that it states and declines to establish. This paper replaces that hypothesis with a different one, about the species delivered rather than about the preference of an event, and obtains the selection from the symmetry of the carrier instead. That is an improvement in the location of the premise and not in its status: two unestablished hypotheses still carry the paper's principal result between them, and a reader who declines either is left with Section 5's concession, namely that the competing pairing is the cheaper on every measure this paper can state.

11.2 Open problems, by section

Open problem 4.19. The origin of the base point. In the corpus it is a datum of the marked vessel; in the reaction cell it is the vertex carrying the terminal sulfur, which the bridge site fixes. Whether the corpus's marking is recoverable as a consequence is open.

Open problem 5.12. A third site type. The enumeration is exhaustive over a thiol at a vertex and a thioether in an edge. Whether the series admits a further type, and what the enumeration then becomes, is open.

Open problem 7.13. Whether the two symmetry breakings are one choice. *Partially closed* at Theorem 9.9; what survives is the next entry.

Open problem 8.25. Which of the two σ -related bridge sites is realised. *Closed*, in the sense that the question is the same as the preceding one and not an additional one; Theorem 9.9.

Open problem 9.12. Whether the bridge site also fixes the remnant parameter of Theorem 7.9, or whether the cell makes two independent choices.

Open problem 9.14. Whether stage III is concerted. Outside the scope of Remark 2.5.

Open problem 10.8. The angular condition of the contact, on a relaxed geometry of the released pair. Outside the scope of Remark 2.5.

Open problem 10.12. Whether the contact bears on anything at all.

11.3 Targets

Target 11.3 (The conformation). Establish, or import from the cage literature of the corpus, the centrosymmetric conformation of Hypothesis 4.8. By Scholium 2.7 it is used at three places only — Corollary 4.16, Theorem 8.13 and Proposition 10.4 — and Sections 6 and 7 do not depend on

it. With the import, the paper's premises reduce to the atom map, the premise of co-synthesis, and Hypothesis 8.19.

Target 11.4 (The delivered species). An independent ground for Hypothesis 8.19, or a demonstration that the medium does not supply sulfur in that form. By Proposition 11.1(i) this is the target on which the paper's principal result stands or falls, and it is the successor to the corpus's own target on its medium hypothesis.

Target 11.5 (The exogenous inventory). Complete the decoration table of the corpus, so that the heteroatom species required by each of the twenty structures, and its source, can be emitted rather than asserted. This is what the restatement of the corpus's exogenous proposition requires, and it is recorded in Appendix C as owed.

Target 11.6 (The two asymmetries). Determine whether the bridge site fixes the remnant parameter. A positive answer reduces the cell to a single choice and makes Corollary 7.11 a consequence of Theorem 9.9; a negative answer leaves the cell with two independent choices and requires an account of the second.

Target 11.7 (The premise of co-synthesis). Independent support for the premise that the two sulfur residues are formed on one unit. It is the premise from which the amended retained set of Appendix A follows, and therefore the premise on which the site assignment of Section 8 rests. A second cell forming a pair of residues together, or a demonstration that the two sulfur residues cannot share a unit, would settle it either way.

Target 11.8 (The asymmetric distortion). Bound the distortion admitted at stage II'. Theorem 8.13 holds where the inversion holds, and Remark 8.18 argues that a symmetric pyramidalisation preserves it and an asymmetric one destroys the competing pairing's own symmetry without closing its sites. What is not established is that no asymmetric distortion brings two σ -related sites within bonding distance. Settling it requires a relaxed geometry.

Target 11.9 (The balance after pyramidalisation). Re-derive $\nu(k)$ with the dearomatisation of stage II' in the ledger, and determine whether the uniqueness of $k = 1$ survives it.

Target 11.10 (The angular condition). Settle Open problem 10.9 on a relaxed geometry. This requires tools the scope of Section 2 excludes and is stated as work for elsewhere rather than as work deferred.

Target 11.11 (The base point). Determine whether the base point of the corpus is a consequence of the cell.

Target 11.12 (Transport). Whether the enumeration of Theorem 5.5 and the exclusion of Theorem 8.13 transport to richer substitution patterns. The exclusion is a statement about an inversion and is expected to; the enumeration depends on the site types the atom map supplies and is not.

Target 11.13 (Scope of the sequel). The placement of the two structures at codons, the relation between the two reading frames, and the initiation site are not addressed here and are the subject of the companion paper. Nothing in the present paper presupposes any of them, and a reader who declines the companion loses no statement above.

11.4 Conclusion

Proposition 11.14 (What is established). [A] *Subject to the atom map, Hypothesis 4.8 and Hypothesis 8.19, this paper establishes the following.*

- (i) *The skeleton of the carrier admits exactly one non-trivial symmetry (Theorem 4.5), and the cell carries no datum breaking it (Proposition 4.17).*
- (ii) *Over the site types the atom map supplies, the cell admits exactly two pairings up to that symmetry, and the mixed pairing is the more expensive of them on every measure stated in Section 5.*
- (iii) *A disulfide bridge cannot close between two sites exchanged by an inversion (Theorem 8.13). The mixed pairing is the unique pairing whose sulfur sites are not so exchanged, and is therefore the unique pairing the cell can bridge.*
- (iv) *The fracture of the mixed pairing destroys six edges of the skeleton, and its asymmetry is confined to a single orbit of the symmetry, three of the four orbits being treated equivariantly (Theorem 6.10).*
- (v) *The external electron demand is affine in the oxidation level of the remnant, and vanishes at exactly one value, at which the two otherwise equivalent remnant components must differ (Theorem 7.9, Corollary 7.11).*

- (vi) *The transformation is totally ordered in its first three stages by valence and existence alone, and the choice of bridge site is the choice that resolves the orbit of (iv) (Theorem 9.4, Theorem 9.9).*
- (vii) *The sulfurs of the released pair stand at a separation compatible with a sulfur–hydrogen–sulfur contact, as a consequence of their having arrived bonded (Proposition 10.4, Corollary 10.5).*

Remark 11.15 (What the paper supplies to the corpus). [A] The corpus asserts, by inspection, that exactly two structures require a species the carrier cannot supply, and argues their placement from a hypothesis about the medium. This paper supplies the cell in which those two structures are formed together, replaces the inspection with an enumeration, and replaces the medium hypothesis with one about the delivered species from which the service of two structures by one event follows rather than being assumed. It also records, in Appendix C, that the exogenous proposition of the corpus is false as written and requires an index by species.

Scholium 11.16 (What would overturn the paper). Two findings would do it, and they are of different kinds. Sulfur delivered otherwise than as a bridged pair, or a sulfur free to migrate between sites, would remove the exclusion of Section 8 without touching any other statement. What remained would be sound and would not select: an enumeration, a fracture, a balance, and a competing pairing that is cheaper than the one described. The paper would then be a description of one route among two rather than an argument for one. Co-synthesis failing would do more. The premise underlies the amended retained set, hence the sites, hence the exclusion; without it the second residue returns to the family of the corpus, the two retained sets meet at the base point, and there is no cell. A conformation placing both arms on one face would remove the antipodal argument and the facing of the two nucleosides, leaving Sections 6 and 7 standing in full, those using the symmetry only as an automorphism of a graph. Both are entered in the falsification registers of their sections, and neither is addressed by this paper.

A The atom map, its provenance, and what is new here

A.1 Status of this appendix

This appendix is the source of the atom map on which Sections 5 to 10 are stated, and it is not evidence for it. It is also the only place in the paper where a chemical species is named; Section 3 (i) records that a reader who deletes it loses the interpretation and no result.

The appendix has an unusual burden. The corpus supplies the series from which the map is read, but the two entries this paper is about are not the corpus's as they stand: the coordinated formation of the two sulfur-bearing residues on one unit is touched on there and is worked here, and the arrangement is new. A reader is therefore owed an exact account of which parts of the map are imported, which are new, and — the question that decides whether the account is circular — whether the new parts were fitted to the cell they are used to describe.

Proposition A.1 answers the last. They were not.

A.2 What is imported

imported, unamended	from
that the residues arise as derivatives of a fused four-ring aromatic, and the 3, 6, 9, 12-substituted family as encoding material	[Sch20b, Sch20c, Sch20a, Sch]
the vessel graph, its locant registry, and the ring decomposition	[Sch26e]
the three-parameter family $S = \{C5\} \cup \{C6\}^\eta \cup \text{arc}(p, q)$, and its holding at nineteen of twenty	[Sch26e]
that the first sulfur residue retains $\{C5\}$ alone	[Sch26e]
that the second sulfur residue has extent $(\eta, p, q) = (0, 0, 1)$	[Sch26e]
the working order of the series, and that the sulfur pair is its fourteenth entry	the corpus
the eighteen entries of the series not concerning the sulfur pair	[Sch26e]

A.3 What is new

- (1) **The premise of co-synthesis.** That the two sulfur residues are formed on one unit, from its two arms, rather than at two loci. The corpus records that its fourteenth entry introduced a paired arrangement of carriers as a premise; the present premise is different in kind, being about one carrier.
- (2) **The retained set of the second residue.** It is the σ -image of the set the corpus records. Proposition A.1 shows this is a consequence of the premise and not an independent stipulation.
- (3) **The terminal site.** That the first residue's sulfur is terminal at C5. The internal site is *not* new: the corpus severs C4b–C10b in the second residue's own row, and a chain $C_\beta - C_\gamma - S - C_\varepsilon$ on a retained set of three vertices with that edge severed can place its sulfur nowhere else. The internal site is therefore σ -transported from the corpus together with the retained set, and Proposition A.1 carries it.
- (4) **The cut list of the first residue.** C4b is severed from C5 rather than removed entire, that vertex being retained by the second residue.
- (5) **The delivered species, and the fixity of the sites.** That the sulfur arrives as a disulfide (Hypothesis 8.19) and that neither sulfur afterwards migrates (Hypothesis 8.20).
- (6) **The pyramidalisation.** That the bridge sites leave the aromatic plane before the ring closes (Proposition 8.16).
- (7) **The tether and the ester.** Both arms ether-linked and running to the C2 of an adenosine; each C' esterified to its ribose 2'-oxygen.

A.4 The amended set is forced

Proposition A.1 (The second retained set is a consequence). **[D]** Assume, as imported, that the first residue retains {C5}, that the second has extent $(\eta, p, q) = (0, 0, 1)$, and that every member of the three-parameter family contains C5. Assume the premise of co-synthesis, which requires the two retained sets to be disjoint. Then no member of the family is available to the second residue, and its retained set is the σ -image of the family member of that extent, namely

$$\sigma(\{C5, C4b, C10b\}) = \{C11, C10b, C4b\},$$

which is unique, the corpus recording $\eta = 0$ for this structure.

Proof. The family at $(p, q) = (0, 1)$ has two members, at $\eta = 0$ and $\eta = 1$, and both contain C5; their σ -images are disjoint from {C5} and the recorded η selects the first; $\forall 17k$. $\square$

Scholium A.2 (Why this matters, and how far it goes). The objection this proposition answers is the serious one. If the retained sets of the pair had been chosen so as to place the two sulfur sites at vertices that an inversion does not exchange, then Theorem 8.13 would exclude the competing pairing by a property the map had been given in order to obtain it, and the argument of Section 8 would be circular.

It was not chosen. One retained set is imported unamended. The other follows from that one, from an imported extent, and from the premise of co-synthesis, by the observation that the corpus's own family contains the base point in every member. The sites are then determined: a residue retaining one vertex can carry only a terminal sulfur there, and a residue retaining three of which two are adjacent across the unique σ -fixed edge carries its sulfur internally at that edge if it carries one at all.

What the paper adds, and what a referee should press, is the premise itself. Co-synthesis on one unit is not derived from anything: it is the hypothesis this paper explores, and every consequence above is a consequence of it. Section 11 states what would refute it. The claim made here is narrower and is the only one available: granted the premise, the map is not free.

A.5 The map

	first residue	second residue
C'	$C6\beta$	$C12\beta$
C_α	$C6\alpha$	$C12\alpha$
C_β	C5	C11
C_γ	—	C10b
sulfur	terminal at C5	internal, in C4b–C10b
C_ε	—	C4b
retained (ring)	{C5}	{C11, C10b, C4b}
severed	C4b–C5, C5–C6	C4a–C4b, C10a–C10b, C11–C12

The two residues share the cut C4b–C5 and the edge C4b–C10b is consumed by the insertion, so the cell destroys six edges of X in all; Section 6.

A.6 Sources of the heteroatoms

atom	first residue	second residue	source
sulfur	S_γ	S_δ	medium, as a disulfide
α -nitrogen	at C6 α	at C12 α	medium
carboxyl O (1)	phosphate O at C6 β	phosphate O at C12 β	carrier
carboxyl O (2)	ribose 2'-O, as ester	ribose 2'-O, as ester	adenosine
remnant O	ether O at C6	ether O at C12	carrier

Remark A.3 (Reading). [E] Under the map the first residue is cysteine and the second methionine, the side chains being $C_\beta\text{--SH}$ and $C_\beta\text{--C}_\gamma\text{--S--C}_\epsilon$ respectively. This reading enters no numbered statement of the body.

Scholium A.4 (The correspondence is not a check). That the vertex counts of the map agree with the side chains of the two residues is recorded and is not offered as evidence. The map was constructed to describe those residues; agreement is therefore a condition of its being the map at all, not a test it has passed. What can be tested is stated in the falsification registers of the body, and none of it is an atom count.

B Verification

B.1 The file

All computations of this paper are emitted by a single script, `cysmet-verify.py`, which requires the verification file of the corpus in the same directory and imports from it the vessel graph, the letter assignment and the code tables. Part I of the script carries the cell, the pairings, the bridge, the rigid geometry and the balance; Part II the stages, the fracture strip and the redox parameter.

Remark B.1 (The block names are not renumbered). [A] The block names V16* and V17* record the working sequence in which the blocks were written and are cited verbatim in the proofs of the body. Renumbering them into a single run would silently invalidate every proof reference, and the sequence is in any case part of the provenance. They are kept, and the index below supplies what a renumbering would have supplied.

Remark B.2 (What is not emitted). [A] Three classes of figure appear in the paper and are not emitted. Values imported from the literature — the sulfur–sulfur bond length, the range of a sulfur–hydrogen–sulfur contact, and the standing of the 1,2-dithiolane and 1,2-dithiane motifs — are labelled [C] where used. Figures of the rigid planar model are emitted but are model values and not structure, as Section 3(x) records. And no energy, barrier or rate appears anywhere, the scope of Remark 2.5 excluding them.

B.2 Index of blocks

block	kind	supports	content
V16a	<i>computed</i>	Thm 5.5, Lem 8.3	the three pairings, with the ground of each exclusion; degree sequence of X
V16b–e	<i>computed</i>	Prop 10.4	the rigid planar skeleton; the inversion centre; exocyclic and inserted sulfur positions
V16f	<i>tabulated</i>	Prop 7.6	carbon closure, $18 + 4 = 22$ against $3 + 5 + 14 = 22$
V16g	<i>tabulated</i>	Section 3 (xii)	the α -nitrogen attaches at a tether carbon, which is not a vertex of X
V16h	<i>tabulated</i>	Prop 8.22	the cell demands two sulfur atoms and two nitrogen atoms
V16i	<i>tabulated</i>	Prop 7.7, Thm 7.9	the disulfide as a two-electron sink; the balance as a function of the remnant level
V16j–l	<i>computed</i>	Cor 8.9, Prop 10.4	bridge geometry at each candidate site; the product separation
V16m	<i>computed</i>	Thm 8.13, Cor 8.15	outward directions at σ -related and non- σ -related sites
V16n	<i>computed</i>	Prop 8.7	bridge ring size as $d + 3$; the three distances
V16o	<i>computed</i>	Lem 8.11, Thm 8.13	the sign of $n(v) \cdot (v - z)$ and the antipodal bound
V16p	<i>computed</i>	Thm 5.5, Prop 5.6	the pairing enumeration over site types; the two mixed pairings under σ
V16q	<i>computed</i>	Prop 5.9	induced and boundary edge counts, and remnant components, for each admissible pairing

block	kind	supports	content
V16r	<i>computed</i>	Lem 4.3, Cor 4.6, Prop 4.10	order, size, cycle rank, degrees, orbits, fixed edge, distances from the centre
V16s	<i>computed</i>	Thm 4.5	$ \text{Aut}(X) = 2$, by exhaustive search
V16t–u	<i>computed</i>	Prop 10.4, Lem 10.7	the product contact: separation, angle, and the increase over the bridged bond
V17a–b	<i>computed</i>	Cor 8.4, Cor 6.8	the stage-I cut is an existing cut; the central edge is absent from the published cut lists
V17c	<i>computed</i>	Cor 6.8	the six destroyed skeletal edges against the transported lists, tested in both directions
V17d–e	<i>tabulated</i>	Prop 6.12, Thm 7.9	the strip’s vertices and remnant size; the electron ledger
V17f	<i>computed</i>	Prop 6.3, Prop 6.6, Thm 6.7, Thm 6.10	the edge trichotomy and the σ -orbit fates
V17g	<i>computed</i>	Prop 6.12	the two remnant components and their exchange by σ
V17h	<i>tabulated</i>	Thm 7.9, Cor 7.10	$\nu(k) = 2k - 2$, tabulated at $k = 0, 1, 2$
V17i	<i>tabulated</i>	Thm 9.4, Prop 9.6, Thm 9.9	the precedence relation among stages
V17j	<i>tabulated</i>	Prop 9.3	each destroyed edge assigned to its stage
V17k	<i>computed</i>	Prop A.2	the amended retained set as a consequence of imported facts and the premise of co-synthesis

C Corrections owed to the corpus

The corrections below arise from the reaction cell and are collected here rather than argued in the body. Each names the statement of the corpus affected and what it becomes. None is a correction to a result of the corpus obtained independently of the sulfur pair, and Remark C.1 bounds their reach. Items (1)–(4) and (9) are consequences of the premise of co-synthesis and are corrections only for a reader who grants it; a reader who declines the premise should read them as a description of a different arrangement rather than as errata.

C.1 Material

- (1) **The retained set of the second sulfur structure.** The corpus records $\{C10b, C4b, C5\}$. On the cell it is $\{C11, C10b, C4b\}$, which is the σ -image of the recorded set. The correction follows from the terminal sulfur occupying C5 and is forced, not chosen: Proposition 5.3 shows no other set of that extent avoids C5.
- (2) **The retention classification.** With the corrected set, the classification of the corpus holds at eighteen of twenty rather than nineteen, the new exception being the second sulfur structure, which contains no base point. Restating the classification σ -covariantly — every retained set, or its σ -image, lies in the family — restores nineteen of twenty and makes the corrected structure the unique σ -image member. The σ -covariant form is recommended.
- (3) **The fibration.** With the corrected set the forgetful map takes twelve values rather than eleven, and five fibres remain non-trivial, covering thirteen structures rather than fourteen. The corrected structure leaves the fibre it shared with two others.
- (4) **The definition of a structure.** The corpus requires every retained set to contain the base point. The corrected set does not. The repair adopted here is the second of the two available: the requirement is restated σ -covariantly, so that a retained set *or its σ -image* contains the base point. This is the same restatement item (2) recommends for the classification, it leaves the corpus’s nineteen-of-twenty intact, and it makes the corrected set the unique σ -image member under both statements. The alternative, dropping the requirement, loses the base point as a datum and is not adopted.
- (5) **The exogenous proposition.** The corpus states that exactly two structures carry an exogenous decoration of one and the same species. With nitrogen drawn from the medium, the side-chain nitrogen of six structures is exogenous and the statement is false as written. It is repaired by indexing the definition of exogeneity by species: among the species the medium supplies, sulfur is the only one demanded by exactly two structures, nitrogen being demanded by six. The uniqueness theorem of the corpus is

unaffected, its argument concerning sulfur throughout, and is in fact better motivated by the repair, since a pairing argument requires exactly two demands and six cannot be placed at mutually complementary slots.

- (6) **The scarcity premise.** The corpus argues that one delivery event is preferred to two that must coincide. If the medium delivers nitrogen at six structures without pairing, delivery events are not scarce in general, and the premise is comparative: sulfur scarcer than nitrogen. The corpus’s hypothesis is narrower than written and should be restated accordingly — and the narrowing belongs in the corpus’s own falsification register, not only here.

C.2 Documentary

- (7) **Adenosine, not adenine.** The tethered base is the nucleoside.
- (8) **The linkage position.** The tether meets the base at C2 and not at the 6-position. This is not cosmetic: a linkage at the 6-position would obstruct the Watson–Crick face, and the registers of the corpus, being pairing states of the tethered base against a coding base, would have no evident definition.
- (9) **The cut list of the first sulfur structure.** The corpus removes C4*b* entire. On the cell C4*b* is retained by the second structure, so the first severs C4*b*–C5 instead.
- (10) **Withdrawn.** An earlier form of this appendix reported that the corpus’s completeness check does not verify the edges induced on a retained set, and proposed a clause to repair it. The case that motivated the proposal does not exist: the corpus severs the central edge in the second residue’s own row, so the insertion made here is already accounted, and Corollary 6.8 now records that every edge the cell destroys appears in the corpus’s rows. The check stands as written. Appendix D records how the error was made and how it was found.
- (11) **The nitrogen row of the ledger.** The row is gated by a defective register and therefore cannot be the universal one: every residue carries an α -amino group, including the structure carrying no side-chain nitrogen. The row is rescoped to side-chain nitrogen and a second row, universal in scope, is admitted for the α -nitrogen at the tether C $_{\alpha}$.

Remark C.1 (Reach of these corrections). [A] Items (1)–(4) and (9) concern the two structures of the sulfur pair and no other. Items (5), (6) and (11) concern statements of the corpus about the whole series and are the only ones that do. Item (10) is withdrawn and corrects nothing. No theorem of the corpus obtained independently of the sulfur pair is affected by anything in this appendix, and the uniqueness theorem it carries survives item (5) intact.

D The record

The account was developed over a series of passes and a number of its claims did not survive. They are listed because a referee is better served by the record than by the result, and because the manner of finding is as instructive as the finding.

D.1 Withdrawn

withdrawn	replaced by, and how it was found
Face inversion realised as a rotation of each unit about its C6–C12 axis	Withdrawn entire: the units are π -stacked and fixed. Found by asking what the cage permits rather than what the algebra suggested. Nothing replaces it in this paper; the question belongs to the companion.
The second arm anchoring the bilayer	The second arm runs to an adenosine. Found on stating the tether explicitly.
The bridge sited at {C5, C4 <i>b</i> }	The site {C5, C10 <i>b</i> }, closing the 1, 2-dithiolane. Found by testing the second candidate site, which had not been tested when the first was adopted.
The claim that the bridge requires C4 <i>b</i> –C5 opened	Withdrawn with the preceding, of which it was a consequence. It was inferred from one candidate before the other was examined, which is the same error twice.

withdrawn	replaced by, and how it was found
A balance permitting both remnants at the alcohol level	Superseded when sulfur was taken as a disulfide rather than as a divalent source: the sink becomes two electrons and $k = 1$ is then unique. Found by recomputing the balance against a changed premise rather than carrying the old figure forward.
The sulfur–hydrogen–sulfur contact as the selecting interaction	The bridge and the antipodal exclusion of Theorem 8.13. Found by asking what a contact of one or two kilocalories can be asked to decide, and concluding that it cannot decide this.
Ring size as the ground of selection	Ring size excludes one bridge site only, both the five- and the six-membered rings being known motifs. Found while writing Proposition 8.7 out, the six-ring case having been assumed unavailable without check.
A seventh bond, destroyed by the cell and absent from the corpus’s cut lists; and an amendment to the corpus’s completeness check following from it	Withdrawn entire. The corpus severs the central edge in the second residue’s own row; transporting that row by σ accounts for all six edges the cell destroys. The verification block supporting the claim compared against a list entered by hand from which the row’s fifth entry had been dropped. Found in review, by reading the published table rather than the script.
The 1,2-dithiolane closing on the intact aromatic frame	Proposition 8.16: the ring cannot close on trigonal carbons, the two exocyclic directions differing by 120° and the sulfurs standing $4.78 \text{ \AA}$ apart. The analogy with lipoic acid was taken to carry the geometry as well as the ring size; it carries only the ring size. Found in review. Pyramidalisation is admitted at stage II’ in consequence.
That one hypothesis carries the selection	Two do: the sulfurs must arrive bonded and must not afterwards migrate. Nothing in the geometry forbids a bridge closing elsewhere and a sulfur moving to its site, and the first form of Section 8 did not say so. Found in review, by asking what Definition 8.6 assumes.

Scholium D.1 (The two kinds of error). The entries fall into two kinds and the distinction is worth preserving. Three were found by testing something that had been adopted without test: a second bridge site, a second ring size, a balance under a changed premise. In each the first candidate examined was taken for the only one. That is the characteristic error of a search conducted forward from a plausible start, and the remedy is not care but enumeration — which is why Section 5 and Section 8 are written as exhaustive searches rather than as arguments for the adopted case. Three were found in review, after the manuscript was complete, and they form a third kind. Each was a claim that no verification block could test, because the block that carried it was tabulated rather than computed, or because the claim was about what a premise assumes rather than about a quantity. The remedy for these is neither enumeration nor a theorem environment: it is reading the source rather than the script, which is how the first of them was found. Remark 2.6 and Appendix B now mark which blocks compute. Two were found by writing a statement out in full. A selecting interaction had to be given a magnitude before it could be seen to be too weak to select, and a mechanism had to be given a site before it could be seen to have two. These do not survive a theorem environment and did not.

D.2 Owed

- (a) The decoration table of the corpus, without which the exogenous inventory of Appendix C (5) cannot be emitted and is asserted.
- (b) The status of Hypothesis 4.8: whether the cage literature establishes the centrosymmetric conformation, in which case it is imported and the paper’s premises reduce by one.
- (c) Independent support for the premise of co-synthesis, on which every correction of Appendix C (1)–(4) and (9) depends.

- (d) A precedent for the insertion of a heteroatom into the central bond of a fused arene, which is where the chemical plausibility of stage III is decided; Open problem 9.13.
- (e) A re-derivation of $\nu(k)$ once pyramidalisation is admitted, the move changing the oxidation level of ring carbons.
- (f) Whether the α -nitrogen and the side-chain nitrogen are delivered by one move or two. The ledger of Section 9 admits one row for each and does not argue that they differ.

References

- [AKW⁺87] Frank H. Allen, Olga Kennard, David G. Watson, Lee Brammer, A. Guy Orpen, and Robin Taylor. Tables of bond lengths determined by X-ray and neutron diffraction. part 1. bond lengths in organic compounds. *Journal of the Chemical Society, Perkin Transactions 2*, pages S1–S19, 1987.
- [FPS⁺22] Jan G. Felber, Lena Poczka, Karoline C. Scholzen, Lukas Zeisel, Martin S. Maier, Sander Busker, Ulrike Theisen, Christina Brandstädter, Katja Becker, Elias S. J. Arnér, Julia Thorn-Seshold, and Oliver Thorn-Seshold. Cyclic 5-membered disulfides are not selective substrates of thioredoxin reductase, but are opened nonspecifically. *Nature Communications*, 13(1):1754, 2022.
- [GRFC91] Lydia M. Gregoret, Stephen D. Rader, Robert J. Fletterick, and Fred E. Cohen. Hydrogen bonds involving sulfur atoms in proteins. *Proteins: Structure, Function, and Genetics*, 9(2):99–107, 1991. Erratum: *Proteins* 1991, 11(3), 237.
- [Sch] Charles D. Schaper. Encoded design integrated synthesis of nucleic acids, and phospholipids, and related pharmaceutical products. U.S. Patent and Trademark Office. United States Patent No. 12,195,423, First specification of the 3,6,9,12-substituted chrysene family as encoding material.
- [Sch20a] Charles D. Schaper. *Creation of Life*. Schaper Systems Press, 2020. 978-1-7357321-7-4.
- [Sch20b] Charles D. Schaper. *Design of DNA, Genetic Codes, and Life Function*. Schaper Systems Press, 2020. 978-1-7357321-0-5.
- [Sch20c] Charles D. Schaper. *Origin of Life*. Schaper Systems Press, 2020. 978-1-7357321-4-3.
- [Sch25] Charles D. Schaper. Encoded design integrated synthesis of nucleic acids, and phospholipids, and related pharmaceutical products. U.S. Patent and Trademark Office, 2025. United States Patent No. 12,473,247 B27.
- [Sch26a] Charles D. Schaper. Cage-constrained chemical reachability in π -stacked chrysene–adenosine systems: Existence, stereochemical selection, and local transformation invariance. *Annals of the Chrysene Formalism*, 1(2):935–1014, 2026.
- [Sch26b] Charles D. Schaper. Chain polarity of the adenine tether. *Annals of the Chrysene Formalism*, 1(2):914–925, 2026.
- [Sch26c] Charles D. Schaper. The chrysene formalism revisited. *Annals of the Chrysene Formalism*, 1(2):489–560, 2026.
- [Sch26d] Charles D. Schaper. The conditional refinement, part II: The chrysene–adenosine reaction cell, margin geometry, and sufficiency. *Annals of the Chrysene Formalism*, 1(2):1048–1075, 2026.
- [Sch26e] Charles D. Schaper. The origins transition: From the encoded chrysene cluster to the originating genetic code mappings. *Annals of the Chrysene Formalism*, 1(2):1076–1106, 2026. Article 57.
- [Sch26f] Charles D. Schaper. The twenty registry classes of a chrysene stack: Frame orbits, descent of a letter transformation, and a variational criterion. *Annals of the Chrysene Formalism*, 1(2):676–704, 2026.
- [Sch26g] Charles D. Schaper. Why three and why twenty: The capacity of a chrysene cluster, the base-four intermediary, and the production operator Δ . *Annals of the Chrysene Formalism*, 1(2):768–793, 2026.