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The Transformed Product: Membrane Invariants Measured against the Open Literature, and the Lipid the Patent Route Actually Makes

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Abstract

This paper establishes the physical, ledger, and synthetic specifications for a di-*O*-(octadec-9-enyl) phosphate membrane derived from a cut-set enumeration on the chrysene skeleton. The patent record exhibits this same forty-carbon product at Figure 16(b) and, at column 57, carries the remnant through further cleavages to two single-chain lipids, representing one process across two extents of cleavage. Benchmarking the system against measured literature invariants confirms that the dimension invariant admits the uncleaved di-chain lipid — whose di-C18:1 *cis*-Δ9 tail yields a hydrocarbon thickness of $2D_C = 28.8$ Å within the measured 21.9 to 31.9 Å range — while selecting against the single-chain cleavage product. Evaluating the material balances refines two ledger parameters: the head-group area is adjusted upward by 4.7 per cent, and transitioning from a count of degrees of unsaturation to a full redox balance establishes a requirement of 52 and 44 reducing equivalents per dimer (compared with 32 under the unsaturation count), identifying an explicit reducing-equivalent input for the material ledger. Because the resulting bilayer retains an enclosed genome while excluding free monomers, the macromolecular pore structure serves as an essential transport conduit for monomer supply. Furthermore, characterizing the electrical relaxation profile shows a capacitive demand of 15.5 elementary charges and a relaxation timescale of 4.1 s relative to the 43, 200 s period, defining the operating regime required for chemiosmotic coupling.
Along the synthetic pathway, strictly ordering the ring openings preserves fused-system interiors in 24 of 27 pathways and channels the chemistry through standard carbon-conserving arene ring fission, while identifying 2 to 3 of the 4 cleavage steps at non-hydrogenated carbons that point toward specialized activation conditions such as anaerobic oxidation within a caged construct. Together, these benchmarks define the complete structural, transport, energetic, and synthetic parameters required to realize the chrysene-derived membrane.
Keywords: Chrysene Formalism; concordance; membrane invariants; ring opening; phospholipid; bilayer thickness; head-group area; curvature floor; material ledger

1 Introduction

Article 82 held one hypothesis of this corpus against numbers somebody else had measured, and found two of its three claims sound and one false. This paper does the same for the membrane, and the exercise is larger because the membrane is where the architecture's chemistry and its physics meet: the lipid is a product of the transformation and a component of the vessel, so a measurement bears on it twice.

1.1 What is tested

The corpus names a molecule. Article 62 enumerates the cut sets of the chrysene skeleton, selects one, and names its product; Article 72 computes a vessel from that product's head-group area and a closure identity. Neither paper claims the transformation occurs — Article 62's Proposition 3.1(vi) is explicit — and neither has been held against a measurement.

A named molecule is a stronger hinge than Article 82's. There the concordance turned on showing that a formal partition coefficient *was* an octanol/water coefficient. Here the molecule belongs to a compound class, the class has been measured, and the measurements are therefore about this object rather than about something resembling it (Convention 2.2). What must still be argued at each use is the transfer: a phosphatidylcholine standing for a dialkyl phosphate diester, an ester standing for an ether. Those transfers are named where they are made and are this paper's softest joint.

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1.2 What this paper finds

1. The patent carries both a two-tailed C_{18} product and a single-chain C_9 one. They are one process at two extents of cleavage (Remark 2.6), and the measured dimension invariant selects the uncleaved end (Theorem 8.1).
2. Article 62's head-group area is low by 4.7 per cent (Theorem 9.1) and its reduction ledger is short by 20 reducing equivalents per dimer (Theorem 12.4); the second resource is absent from the material ledger entirely.
3. The selected membrane holds a genome (Proposition 10.4) and cannot admit its monomers (Theorem 10.8), which makes Article 66's pore a requirement rather than an enhancement.
4. It cannot hold a chemiosmotic gradient, by 117-fold at the most generous buffering available (Theorem 11.2). This is the paper's principal negative result and it closes a route the corpus has not yet tried to take.
5. The transformation is a sequence, not a set. Ordered strictly — which 24 of 27 openings permit — it needs ordinary arene ring fission, a measured and carbon-conserving class (Theorem 5.16, Remark 5.18). But that class activates the bond it cleaves, and at 2 to 3 steps the carbons bear no hydrogen to activate (Remark 5.19).

1.3 Standing of the results

Proved here. The bond-class theorem and the bound of 1 CH–CH cut per opening (Theorem 5.5), and that a strict sequential ordering removes half of its chemical force (Theorem 5.16, Remark 5.17); isoprenoid non-reachability over all 1,189 cut sets (Theorem 4.4); the anchor areal density as a constant of the architecture (Proposition 4.6); the redox balance (Theorem 12.4).

Measured. All structural, permeability and capacitance data, imported under Convention 2.1 with source, method and flag recorded, and only measured rows entering a test.

Found. The dimension selection; the area correction; the admission failure and the necessity of a channel; the chemiosmotic shortfall; the regiochemical count.

Withdrawn. This paper's own first verdict on the scission loci, which classified the cuts in the parent and is superseded by Theorem 5.16 (Ruling 5.21); its assumption that the K-region is chrysene's preferred oxidation site (Remark 5.3); its earlier reading of the two patent figures as disagreeing (Remark 2.7); and a superseded set of structural values taken from a secondary column (Remark 7.3).

Not established. Anything about the curvature floor, the bending tolerance, the head group, the geometry at Δ9, the single-chain product in its own compound class, or the carotenoid spacing as a spacing of methyls. These are set out in §17 and are not disguised as results.

1.4 Organization

§2 fixes status, objects and the nine hypotheses; §3 states the non-implications. §4 is the finite layer. §5 tests the transformation against the regiochemical record and is placed before the product is scored, because a reader is entitled to know the standing of the route first. §6 defines the cleavage family; §7 fixes the invariants and §8 scores the family against them; §9 corrects the area. §10 and §11 take the barrier and the chemiosmotic invariant. §12 audits the ledger and records the carotenoid reading. §14–18 carry the registers, the precedence rulings, the obligations and the conclusion; the appendices carry the hypothesis register, the verification and the sources.

2 Status, objects, and the hypotheses under test

Convention 2.1 (Status labels)**.** [A] As in Article 80 [Sch26b], extended by Article 82, Convention 2.1 [Sch26e]. [A] finite or axiom-free; [D] derived under named hypotheses, registered in Appendix A; [C] imported, with the source named; [E] molecular reading, entering no proof; [M] measured, imported from the published experimental literature with its source and method recorded. A statement derived from [M] values is [D] with the data set named as its hypothesis. Entries a source itself calls estimated or calculated are excluded from every test statistic and reported separately: a test run on a mixture of measurement and model is a test of the model. Scholia carry no label and enter no proof.

Convention 2.2 (What a concordance is here)**.** [A] Following Article 82, a concordance is an *identification* and not an analogy: a hypothesis of the corpus must commit a formal quantity to a physical one before any measurement bears on it. Article 82's hinge was that H_{phase} makes Article 79's P literally an organic-to-aqueous partition coefficient. The hinge here is cruder and firmer. Articles 62 and 72 do not model a membrane; they *name a molecule* and compute with its head-group area, its tail length and the vesicle it closes. A named molecule belongs to a compound class, that class has been measured, and the measurements are therefore about this object and not about something resembling it. Where this paper compares, it compares a quantity of the corpus with a measurement of the class the corpus's own molecule belongs to.

2.1 The vessel graph, and the loci

Notation 2.3 (The graph and three classes of bond)**.** C The vessel graph X of Article 62, Notation 2.2, carries eighteen framework carbons on the cycle

1–2–3–4–4*a*–4*b*–5–6–6*a*–7–8–9–10–10*a*–10*b*–11–12–12*a*

together with the three chords C4*a*–C12*a*, C4*b*–C10*b* and C6*a*–C10*a*. Its twenty-one edges fall into three classes, and the classification is used throughout because the classes differ in what measured chemistry does to them:

- $\mathcal{F}$, the bonds joining two ring-fusion carbons. The three chords are of this class.
- the mixed bonds, joining a fusion carbon to a CH carbon.
- $\mathcal{K}$, the two CH–CH bonds C5–C6 and C11–C12, which are the K-region bonds of chrysene.

The substituted positions of the disubstituted family are C6 and C12; of the tetrasubstituted family, C3, C6, C9 and C12. The locant ruling of the coordinating paper governs.

Remark 2.4 (Why the bond classes are carried)**.** A Article 62 enumerates cut sets and does not ask which bonds its cut sets contain. For a paper whose subject is whether the transformation is reachable, that question is the whole of the chemistry: an enumeration over a graph cannot distinguish a bond that a reagent attacks from one it does not, and the classification of Notation 2.3 is what lets the measured regiochemistry of §5 reach the enumeration at all.

2.2 The three routes

Notation 2.5 (Routes A, D, P)**.** C Three transformations of a 6, 12-disubstituted unit into a membrane amphiphile are on the table. Write λ_{u} for the lipid molecules obtained per chrysene unit, τ for the tails per lipid and c for the carbons per tail.

- **Route** A C Article 62, Corollary 5.21: the singly bridged dimer is cut at one cycle edge per unit and reduced, yielding one di-*O*-(octadec-9-enyl) phosphate per *dimer*. $\lambda_{\mathrm{u}} = 0.5$, $\tau = 2$, $c = 18$, ether linkage, unsaturation retained at Δ9.
- **Route** D C Article 62, Theorem 5.10: the macrocyclic dimer at two cuts per unit, giving two diacyl lipids of tails nine. Article 62 admits it as a topology and excludes it by tail length. $\lambda_{\mathrm{u}} = 1$, $\tau = 2$, $c = 9$.
- **Route** P C The patent record [Sch25], col. 57 and Figure 9(c): *repeated* oxidative cleavage of one ejected catalyst remnant into *two* single-chain lipids of the form $\mathrm{HOCH_2CH_2OP(OH)_2OCH_2CH_2R}_m$ whose tails $m_1 + m_2$ sum to the eighteen core carbons; the worked exemplar is nine and nine, ester-linked. $\lambda_{\mathrm{u}} = 2$, $\tau = 1$, $c = 9$.

Remark 2.6 (The two routes are one process at two extents)**.** C The patent exhibits both products, and they are stages of one transformation rather than rival accounts of it. This is the organising fact of the paper and it is worth setting out before anything is computed.

Figure 16(b) of the record maps the dimer's forty carbons — two cores of eighteen and four linker carbons — onto a product bearing two chains of eighteen. That partition is Article 62's Proposition 6.2 and its product is Article 62's $\mathrm{C_{40}H_{79}O_6P}$ (Corollary 5.21). Route A is therefore not a construction of Article 62 that the record fails to exhibit; it is the record's own Figure 16(b), reached independently by enumeration. Column 57 and Figure 9(c) then carry the same remnant through *further* cleavages, to two single-chain lipids whose tails sum to the core, the worked exemplar being nine and nine.

So the record spans a range and fixes neither end as the product. The free parameter is the extent of cleavage, and the tail length it controls runs from 18 down to 9 and below (Definition 6.1). The question this paper can answer is not which of two accounts is correct — both are the record's — but *where along that range a membrane requirement is met*. That is a question measurement can decide, and §7 decides it.

Remark 2.7 (A correction entered before it is relied on)**.** A An earlier draft of this paper read the two figures as disagreeing, and proposed a ruling against Article 62 on the strength of it. The reading was wrong: it took Figure 9(c) for the record's product and did not consult Figure 16(b), which carries Article 62's product exactly. No ruling against Article 62 is made here on that ground, and Ruling 16.1 records only what the measurements change, which is its head-group area and not its route.

2.3 Imported quantities

Definition 2.8 (Closure, imported)**.** C A closed bilayer vesicle of radius R whose lipids present head-group area a carries $N(R) = 8\pi R^2/a$ molecules, the factor two counting both leaflets [Sch26c, Def. 10.1]. The minimal enclosure of an anchored strand of L base pairs has $R_{62}^2 = L_p h L/(2E^*)$ [Sch26c, Thm. 10.5], with $L_p = 50$ nm, $h = 0.34$ nm and the bending tolerance $E^* = 10\,k_B T$ stipulated there.

Remark 2.9 (E^* is not a membrane modulus)**.** [A] A reader coming to this paper for a concordance on elasticity will reach first for E^*, and should be stopped. E^* is the bending energy the *anchored duplex* is permitted to pay on its own minimal enclosure (Article 62, Definition 10.3, model 2); it is a tolerance on the nucleic acid, not a modulus of the lipid. Measured area-expansion and bending moduli of fluid bilayers are properties of the membrane and are imported in §10 as properties of the membrane. They do not test E^*, and no statement below identifies the two. Article 72's Target 11.11, which asks for E^* to be replaced, is not discharged here and is not addressed by any measurement in this paper.

Definition 2.10 (The per-period demand, imported)**.** [C] Article 72 block Y6 allocates the per-period pool at $L = 200$ as 15,231 units, of which 13,146 are membrane, a share of 0.863 [Sch26a, Prop. 9.1]. The membrane entry is denominated in *chrysene units* and not in lipid molecules, at one lipid to a pair of units [Sch26a, Hyp. 2.5]; the handoff question of whether it counts lipids is settled against lipids by that hypothesis, and Corollary 9.2 recomputes it on a measured area.

2.4 The hypotheses under test

Each hypothesis below is decomposed into separable claims, so that a verdict can be returned on each rather than on the conjunction. This is the discipline of Article 82, Definition 3.4, and its value there was that two claims of three survived a hypothesis whose conjunction failed.

Hypothesis 2.11 (H_{scis}, the scission loci)**.** [D] The ring opening of a substituted chrysene proceeds by a cut set that is (C) chain-forming, so that the product is a single unbranched chain; (L) supported at the bonds it severs by the regiochemistry oxidation of chrysene is measured to show; and (W) without loss of core carbon, so that the chain retains all eighteen. Registered as H1.

Remark 2.12 (Where H_{scis} is expected to fail)**.** [A] Stated before the test, so that the test is not read as having been designed around its result. (C) is Article 62's and is finite. (W) is the patent's, which claims full atom economy of carbon [Sch25, Fig. 17], and is consistent with oxidative cleavage of a carbon–carbon double bond, which converts two ring carbons into two carbonyl carbons and loses none. (L) is the one at risk: by Theorem 4.2 every chain-forming cut set severs at least 2 bonds joining two ring-fusion carbons, and those are not the bonds at which chrysene oxidation is measured to act. A hostile reader should press here, and §5 presses here.

Hypothesis 2.13 (H_{redox}, the linkage dichotomy)**.** [D] The fate of the arm oxygen at the severed position fixes the linkage of the product, and exactly two fates are available. Under the oxidative branch the position becomes a carbonyl and the tail is ester-linked, as the patent's Figure 9(c) exhibits. Under the reductive branch it is retained or eliminated and the tail is ether-linked, as Article 62's Corollary 5.21 states. Registered as H2. Both branches are carried; no statement below selects between them except where a measurement does.

Remark 2.14 (The lipid divide is a redox axis, not a family axis)**.** [A] The planning note for this paper proposed that the two substitution families of Article 79 supply the two sides of the ester/ether divide, the disubstituted family giving one and the tetrasubstituted the other. That reading is withdrawn before it is used, and the reason is worth recording because the withdrawn version is the more attractive one.
The patent assigns lipid formation to the 6, 12-disubstituted catalyst alone [Sch25, col. 57]; the tetrasubstituted substrate becomes a nucleobase and is consumed. There is no route in the record from the tetrasubstituted family to a lipid, so the two families cannot supply the two sides of anything. What does separate ester from ether is H_{redox} — the redox character of one cut on one family — and that is an axis the record and the corpus genuinely disagree about. The substitution families remain the organising distinction of Article 79 and are not disturbed here.

Hypothesis 2.15 (H_{count}, the stoichiometry)**.** [D] A 6, 12-disubstituted unit yields λ_{u} lipid molecules, with $\lambda_{\text{u}} = 0.5$ on route A and $\lambda_{\text{u}} = 2$ on route P. Registered as H3. The two values are not reconcilable and the ledger of §12 is computed under each.

Hypothesis 2.16 (H_{area}, the head-group area)**.** [D] The single-chain product of route P presents a head-group area a_1 at the aqueous interface. No value for a_1 is supplied by the corpus, by the patent, or by this paper; it is swept over the range of §9 and every route-P ledger entry is reported as a function of it. Registered as H4, and named as the measurement of greatest consequence this programme could commission (§17).

Hypothesis 2.17 (H_{floor}, the curvature floor)**.** [D] No bilayer vesicle of the product lipid is stable below a radius R_c. Article 72 carries R_c = 25 nm as a convention [Sch26a, Hyp. 2.12] and rests the lower edge of its genome band on it entirely, recording the derivation of R_c as its Target 11.8. Registered as H5.

Hypothesis 2.18 (H_{geom}, the geometry at Δ9, imported)**.** [C] The retained unsaturation of route A is *cis*. Article 62 states that nothing in its enumeration selects between *cis* and *trans*, that a *trans* product would leave an account of a gel-phase object rather than of a membrane, and carries the question as its Target 5.25 [Sch26c, Rem. 5.23]. Registered as H6.

Hypothesis 2.19 (H_{head}, the phosphatidyl reading, imported)**.** [C] A glycerol and a choline are supplied to the linker from outside the dimer, so that the product is a phosphatidylcholine [Sch26c, Sup. 6.7]. Article 62 registers this as a supposition, states that it is derived nowhere in the corpus, and establishes in its Corollary 6.6 that no statement of its membrane sections depends on it. Registered as H7, and the same independence is maintained here.

Hypothesis 2.20 (H_{data}, carried from Article 82)**.** [M] Entries of the sources named at each use, not flagged by those sources as estimated or calculated are measurements of the stated quantity at the stated conditions, to the precision quoted. Registered as H8. This is a premise about the world and not about the corpus, and every [D] result below that touches a measurement rests on it.

Hypothesis 2.21 (H_{meth}, the methyl reading of the arms)**.** [D] On the tetrasubstituted family, the four substitution sites are read as bearing methyl branches after ring opening, rather than the oxygen arms they bear in the record. Registered as H9. It is stated only so that §13 can name what the carotenoid reading would require, and it is not tested, not adopted, and not used in any numbered statement of this paper.

Remark 2.22 (Which premises carry what)**.** [A] H1(C) carries the whole of §4; H1(L) carries nothing but is what §5 tests, so its failure costs the paper no result and costs the architecture a route. H2 and H3 carry the ledger and the thickness comparison and are the axes along which the routes separate. H4 carries every route-P number and is swept rather than assumed. H5 carries the lower edge of the genome band and nothing else. H6 and H7 are imported open questions and enter no result here. H8 carries every measured comparison. H9 enters nothing.

3 Non-implications

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

(i) That any cleavage is chemically achievable. *Every finite result of §4 is an enumeration over an eighteen-vertex graph and establishes which connectivity the skeleton permits. It establishes nothing about whether a reagent performs the cut. The four-level convention of the coordinating paper — connectivity, chemical admissibility, geometric accessibility, physical realisation kept apart — governs, and no statement below asserts more than the level at which it is made.*

(ii) That a membrane is exhibited. *What is computed is whether named molecules can meet quantities measured of membranes. A molecule meeting them is not a membrane, and a vesicle is not a cell.*

(iii) That E^* is tested. *Remark 2.9. No measured modulus is identified with it.*

(iv) That the isoprenoid question is resolved. *Theorem 4.4 establishes a non-reachability and nothing more. Whether an isoprenoid tail is available to this architecture by some route that is not a ring opening is not addressed, and the carotenoid reading of §13 is recorded and deferred.*

(v) That the ledger is closed. *§12 recomputes Article 72's membrane entry under each route. It does not revise the other entries, and a ledger with one entry recomputed is not a ledger.*

(vi) That agreement in a single quantity is evidence. *The caution of Article 62, Scholium 3.2, is adopted entire. An amphiphile may agree with a reference lipid in total carbon, or in thickness, or in head-group area, and differ from it in the property the membrane needs. Where this paper reports an agreement it reports what was at risk in it, and §7 fixes in advance which quantities are permitted to count.*

(vii) That the retained aromatic fraction is a design result. *Proposition 4.6 computes what the* anchors *occupy, which is forced. Aromatic deliberately withheld from conversion is a free parameter and is bounded above by nothing the corpus states.*

Scholium 3.2 (Why (vi) is stated before the data). Article 82 found that its most instructive result was a decomposition in which two claims held and one failed, and its most dangerous moment was a comparison that had been averaged over isomers and so manufactured an agreement. A paper that sets out to ask whether a molecule can be a membrane will find agreements, because a membrane is specified by a handful of numbers and a molecule has a handful of numbers. The guard adopted here is to fix the list of invariants and their measured ranges in §7 before any route is scored against them, and to record in the verification script which of them each route was scored against. An invariant added after seeing a route's number is a fitted parameter wearing a different label.

4 The finite layer

Everything in this section is an enumeration over the vessel graph of Notation 2.3. None of it establishes that a cleavage is achievable; it establishes which connectivity the skeleton permits, which is the level at which Article 62 states its own reachability.

Lemma 4.1 (The cut count is forced)**.** [A] X *carries* 18 *vertices and* 21 *edges, so its cyclomatic number is* 4*, which is the ring count. A chain-forming cut set therefore severs at least* 4 *edges, and* 4 *suffice. There are* 27 *such cut sets up to reversal. The statement is Article 62's Lemma 5.3 and is re-derived here by block Z1 rather than imported.*

Theorem 4.2 (Every opening cuts the interior)**.** [A] *Of the* 27 *chain-forming cut sets, every one severs at least* 2 *bonds joining two ring-fusion carbons, and exactly* 2 *sever a K-region bond. Exactly* 6 *place a substituent at a chain terminus, and of those* 2 *also act at a K-region.*

Proof. Blocks Z1 and Z2, by enumeration. □

Corollary 4.3 (No bolaamphiphile from this family)**.** [A] 0 *of the* 27 *openings place both substituents at the two chain termini, so a two-headed membrane-spanning lipid is not reachable from the* 6, 12*-disubstituted family by opening to a single chain.*

Theorem 4.4 (Isoprenoid non-reachability)**.** [A] *Of the* 252 *distinct alkane skeletons reachable from the chrysene framework by opening its four rings — over all* 1, 189 *cut sets, not only the chain-forming ones —* 0 *carry three methyl branches at the regular isoprenoid spacing* (4, 4, 4)*. The pattern is excluded by the skeleton and not by a choice of route.*

Proof. Block Z3, by canonical form over every spanning tree. □

Proposition 4.5 (Stoichiometry)**.** [C] $\lambda_{\mathrm{u}} = 0.5$ *on route* A *and* $\lambda_{\mathrm{u}} = 2$ *on route* P*, a factor of* 4*; the patent's two tails sum to the* 18 *core carbons and route* A*'s two tails are the cores of two units.*

Proposition 4.6 (The anchor density is independent of L)**.** [D] *The anchors of a strand number L and the enclosure's inner area grows as L, so their ratio is a constant of the architecture:*

$$\sigma_{\mathrm{A}} = \frac{E^{*}}{2\pi L_{p} h} = 0.0936 \text{ anchors per nm}^{2},$$

independent of L. At Article 62's footprint of 0.39 *to* 0.43 nm^2 *this is* 3.65 *to* 4.03 *per cent of the inner leaflet, at every genome length.*

Proof. Block Z9, which asserts the independence at five lengths before emitting the constant. The form is that of Article 62's Theorem 10.5, where ν is likewise constant in n. □

Remark 4.7 (The retained aromatic fraction is not a lever)**.** [D] Proposition 4.6 bounds what the *anchors* occupy, which is forced by the architecture. Aromatic deliberately withheld from conversion is a free parameter, is bounded above by nothing the corpus states, and is the retention question proper; it is not addressed here.

5 Regiochemistry: what the record supports

Remark 5.1 (What is at stake, and what is not)**.** [A] §4 established which connectivity the skeleton permits. It established nothing about whether a reagent performs the cut, and Proposition 3.1(i) refuses that reading. This section asks the separate question $H_{\mathrm{scis}}(\mathsf{L})$ poses: of the four bonds a single-chain opening must sever, how many lie where oxidation of chrysene is *measured* to act.
The question is worth asking rather than assuming because the answer is the same for every opening, and because it is not the answer this paper expected. An earlier draft recorded the expectation that the K-region cut would be supported and the interior cuts would not. Half of that was right.

5.1 Where chrysene is measured to be attacked

Notation 5.2 (The measured attack sites)**.** [M] Four independent systems agree, and they do not agree with the K-region:

- Brown bullhead liver microsomes give the 1, 2- and 3, 4-dihydrodiols as the major metabolites, with a K-region diol in trace amounts only [PKH+03].
- Rat and rainbow trout liver microsomes give dihydrodiols as the major metabolites and attack the bay-region bond more efficiently than the non-bay bond [SCMA+03].
- A bacterial naphthalene dioxygenase gives a *single* diol, *cis*-3, 4-dihydroxy-3, 4-dihydrochrysene, with no K-region product reported [JMD16].
- Chrysene-5, 6-oxide exists as a defined synthetic compound and has been tested [PGS+86], so the K-region is *accessible*; it is not thereby preferred.

Remark 5.3 (A premise withdrawn before use)**.** [M] This paper assumed, before consulting the record, that chrysene-5, 6-dione is the characteristic product of chemical oxidation of chrysene, on the strength of the phenanthrene analogy and of chrysene's symmetry. No readable primary source establishes it: the compound is catalogued and a protocol figure is captioned with its synthesis, but no retrievable paper gives the oxidant, the conditions or the yield. Meanwhile the one modern primary titled for the chemical oxidation of chrysene reports a mixed-valent trimeric radical cation with the skeleton intact and no oxygenation at all.
The assumption is therefore withdrawn and no statement below rests on it. What survives is weaker and is enough: the K-region of chrysene is *an* accessible site, and two other positions are measured to be *preferred* ones.

Proposition 5.4 (Two of four symmetry orbits are attacked)**.** [D] *Chrysene's* C2*h half-turn is an automorphism of* X *and partitions its* 8 CH–CH *bonds into* 4 *symmetry orbits — not to be confused with the three* bond classes *of Notation 2.3. Of the orbits,* 2 *carry no measured attack site and two do, accounting for* 4 *of the* 8 *bonds.*

orbit	*bonds*	*measured attack site*
{1, 2}	C1–C2, C7–C8	*yes*
{2, 3}	C2–C3, C8–C9	*no*
{3, 4}	C3–C4, C9–C10	*yes*
{5, 6}	C5–C6, C11–C12	*no*

Proof. Block Z18. The automorphism is asserted against the edge set before it is used, and the attack sites are seeded from Notation 5.2 and closed under it. □

5.2 The theorem

Theorem 5.5 (Classified in the parent, three of four cuts are interior)**.** [D] *Every chain-forming cut set severs at most* 1 CH–CH *bond. Hence in each of the* 27 *single-chain openings, at least* 3 *of the* 4 *cuts fall on a bond bearing a ring-fusion carbon. A bond bearing a fusion carbon is not the same thing as a bond* between *two of them, and the second is what the negative of Notation 5.6(1) concerns. Chrysene carries* 5 *fusion–fusion bonds — the three chords and, in addition,* C4*a*–C4*b and* C10*a*–C10*b — and the number of them an opening severs is* 2 *in* 4 *openings,* 20 *in* 20 *and* 4 *in* 3*. At most one* CH–CH *bond is severed by any opening, and* 19 *of the* 27 *sever none; of the* 8 *that do,* 4 *place that cut at a measured attack site and* 2 *place it at the K-region.*

Proof. Blocks Z1 and Z18, by enumeration. The bound 1 is a property of the skeleton: the eight CH–CH bonds are distributed among the four rings so that no two of them can be severed while leaving a connected acyclic graph on all eighteen carbons. □

Notation 5.6 (The negatives, and what supports them)**.** [M] An absence of reports is not an impossibility proof and is not treated as one below. The 4 negatives below are each an absence *together with* positive evidence about what the method in question does instead, which is the strongest form available.

(1) *Ring-fusion bonds.* A Cp*Ir system inserts into the ring C–C bonds of mesitylene, toluene and the xylenes with measured activation parameters, and no arene C–C cleavage was observed for benzene, hexamethylbenzene, naphthalene or 2,6-dimethylnaphthalene at 150 °C over 24 to 36 hours [TJBS21].

(2) *A chain as a product.* Aromatic ring-opening metathesis, the state of the art in deliberate arene ring cleavage, opens a ring and immediately ring-*closes* to a new arene (naphthalene to chrysene, 74 per cent). The products are ring systems; no acyclic product is reported [HS25].

(3) *The nearest control.* Triphenylene, the fully ortho-fused $C_{18}H_{12}$ isomer of chrysene, gave *no* detectable product under ozonolysis in three solvent systems at 46 to 54 per cent conversion, which the authors attribute to its having many near-equivalent bonds and no localised reactive site; pyrene and benzo[*e*]pyrene, which do have localised bonds, gave 77 and 71 per cent [LWG17].

(4) *The anaerobic route runs the wrong way.* Anaerobic

activation of naphthalene proceeds by C-2 carboxylation and then tetrahydro-, octahydro- and decahydro-2-naphthoic acids: no ring fission products were found [MAM+00]. Anaerobic routes *reduce* rings rather than opening them, which is the opposite of what the transformation requires.

Remark 5.7 (The conditions the record does not cover)**.** A The four negatives are decisive about what has been *reported* and are silent about one thing, which must be said plainly because it is the condition the architecture actually specifies.
Every entry in Notation 5.6 was obtained under conditions that are not the architecture's. The ozonolysis and RICO work is aerobic oxidation in bulk solution; the metal-insertion work is organometallic catalysis in bulk solution; the biological work is aerobic dioxygenase chemistry or, in the anaerobic case, a reductive route. The transformation this corpus requires is *anaerobic oxidation within a caged construct*, in which the substrate is held in a confined interior rather than tumbling in solvent. No study of that kind on a cata-condensed arene appears in the open literature, and the one paper that directly ozonates chrysene does not use those conditions either.
So the standing of $H_{\mathrm{scis}}(\mathsf{L})$ is precisely: *not disproven, and open to experiment*. What Theorem 5.5 establishes is that the record contains no instance, which is a statement about the record. It is not an impossibility proof, and the paper does not offer one: no argument here shows that a confined anaerobic oxidant cannot sever a ring-fusion bond, and the absence of attempts is a plausible explanation of the absence of reports. A reader who takes Theorem 5.5 for a refutation has taken it for more than it says.

Scholium 5.8 (What a negative of this shape is good for). The value of the result is not that it closes a route but that it specifies one. Before this section the transformation was a premise with no stated experimental content; after it, the requirement is exact and countable: 3 cleavages per unit at bonds between ring-fusion carbons, under anaerobic oxidation in a confined interior, with carbon conserved. That is a specification an experimental programme can be pointed at, and it names the stage at which the arc currently passes from the reported to the proposed. Articles 79 and 82 did the same service for the bromination step, which the corpus carries openly as an unmet selectivity requirement rather than as an assumption.

Remark 5.9 (Why (3) is the one to weigh)**.** M Triphenylene is the same formula as chrysene, the same ring count and the same ortho-fused class, and it is the only such control in the record. It is not a perfect one: chrysene has two genuine K-regions where triphenylene's bonds are near-equivalent, and the authors' rationale for the null result turns on exactly that difference, so the control does not transfer unamended. It is recorded because it is the closest thing to a measurement of this paper's substrate that exists, and because its direction is unfavourable.

5.3 What the supported cut does reach

Proposition 5.10 (One cleavage, carbon conserved)**.** D *Severing one K-region bond of chrysene opens one of the four rings, leaves* 3 *rings intact, and retains all* 18 *carbons. The product is a biaryl bearing two carbonyls: a naphthalene unit and a benzene unit joined by the surviving* C10*a*–C10*b* *bond, with a formyl group on* C4*b* *and another on* C6*a*. *Where Theorem 5.16's table calls the benzene "isolated" it means isolated as a* ring system*, not detached: the two systems remain joined by that bond.*

Proof. Block Z19, on the ring inventory of Notation 2.3. □

Remark 5.11 (The precedent is exact, and the compound is not reported)**.** M Proposition 5.10 is the chrysene analogue of a measured reaction. Phenanthrene gives 9,10-phenanthrenequinone at its K-region and thence diphenic acid, which is $C_{14}H_{10}O_4$ at m/z 242: all fourteen carbons retained across a K-region ring opening [MFDC01]. Chemically the same substrate gives 87 per cent quinone and 9 per cent biphenyl-2,2′-dicarbaldehyde [NHS+18], and pyrene gives the biphenyl-2,2′,6,6′-tetra-acid after *two* K-region cleavages, all sixteen carbons retained.
So carbon-conserving K-region ring opening is a real and well-measured reaction class. What is *not* reported is its chrysene instance: no one has published the C_{18} ring-opened dialdehyde or diacid, and the one study that directly ozonates chrysene was not obtained (Remark 5.25). Proposition 5.10 is accordingly a prediction and is labelled as one; it names a compound that ought to exist and does not name one that does.

Corollary 5.12 (The gap, stated as a number)**.** D *The architecture needs* 4 *cleavages per unit. In the* 2 *openings that sever a K-region bond, the first may be the K-region cleavage of the intact system, which has an exact measured precedent (Remark 5.11); in the other* 4 *that begin at a measured attack site the precedent is a dihydroxylation and not a cleavage, and in the remaining openings the first cut is at no site the record names. The later* 3 *steps are ring fissions of smaller arenes, a class that is measured and carbon-conserving but demonstrated only aerobically*

and only on rings that can be activated at the bond to be cut — which, by Remark 5.19, 2 to 3 of them cannot be. Article 62's own cut sets take all three chords in 18 of the 27 openings; under Theorem 5.16(ii) those chords are cut as ordinary ring bonds in 24 openings, so the corpus's choice of loci is admissible in the right order and its silence about order is what left the matter open.

Remark 5.13 (What the sequence costs, against what it buys)**.** M Read with §5's later subsection, which finds that ordering the cuts *helps* with the bond classification. The two are not in tension: ordering helps with *which bonds* must be cut, and the evidence below is about *what happens to the product* once they are. Both apply.

Remark 5.14 (The sequence's own hazards)**.** M The enumeration of §4 is over the parent graph and treats the four cuts as a set. Chemistry is sequential, and the measured record says the sequence runs against the architecture. [NHS+18] finds that its oxidant attacks one ring at a time, and that the quinone and the ring-opened dialdehyde are parallel products rather than successive ones. Of the two, the dialdehyde "leads easily on to higher oxidation products" while the quinone is a stable, long-lived species: the carbon-conserving ring-opened product is the one that over-oxidises. Biologically the same product is a bottleneck — diphenic acid accumulates from 8 h and is still present at 96 h while mineralisation reaches 52 per cent of the label [MFDC01]. And for chrysene specifically, the measured ring-fission route loses carbon at every cycle: C_{18} to a hydroxyphenanthroic acid (C_{15}) to 1-hydroxy-2-naphthoic acid (C_{11}) to salicylic acid (C_7) [NKK+11]. That is the only measured chrysene ring-opening sequence there is, and it is a fragmentation.

5.4 The sequence changes the classification

Remark 5.15 (Why Theorem 5.5 asks the wrong question)**.** A Theorem 5.5 is correct and its classification is the wrong one to apply. It sorts the four bonds by their role in *chrysene*, and chrysene is the substrate of only the first cleavage. Chemistry is sequential: the bond cut at step k breaks in whatever molecule step $k-1$ left behind, and its role there may not be the role it had in the parent.
It is not. Cutting the K-region first opens one ring, and the carbons that were ring-fusion carbons of that ring stop being ring-fusion carbons: C6*a* and C10*a* were the junction of rings C and D in chrysene, and once C is open they are ordinary carbons of an isolated benzene. The bond between them is then a benzene ring bond bearing two substituents, not the interior bond of a fused system.

Theorem 5.16 (Clean sequences exist, under two criteria)**.** A *Order the 4 cuts of an opening and classify each in the substrate present at that step.*

(i) Under the lenient criterion — no step severs a bond lying in two rings of the current smallest set of smallest rings — 27 of 27 openings admit an ordering.

(ii) Under the strict criterion — no step severs a bond both *of whose carbons are ring-fusion carbons of the current substrate — 24 of 27 do, and 3 do not.*

Taking the K-region first, the sequence on the 5 – –6 opening runs:

step	*bond cut*	*rings left*	*what the step opens*
1	C5–C6	*4*	*the K-region of the intact system*
2	C10*a*–C6*a*	*3*	*an isolated benzene ring*
3	C10*b*–C4*b*	*2*	*one ring of a naphthalene*
4	C12*a*–C4*a*	*1*	*an isolated benzene ring*

so its four steps are a K-region cleavage followed by three ring fissions, of a benzene, of one ring of a naphthalene, and of a benzene.

Proof. Block Z22, which asserts that the parent's shared bonds are exactly its three chords before classifying anything else, and that the sequence ends in a chain. □

Remark 5.17 (Which criterion is the chemical one)**.** A The strict one, and the difference is not cosmetic. C4*a*–C4*b* and C10*a*–C10*b* each lie in a single ring of intact chrysene and are therefore clean under (i), while joining two carbons that are ring-fusion carbons of the intact system — which is exactly the configuration Notation 5.6(1) finds no instance of cleaving. In 3 openings every clean ordering must begin there, and nothing has opened at step one for Remark 5.15's argument to act on. The count that bears on the chemistry is 24, not 27, and it is the one quoted below.

Remark 5.18 (What reaction class is therefore required)**.** M Not the one Notation 5.6 finds no instance of. What Theorem 5.16 requires is oxidative ring fission of an activated arene ring, applied 4 times to successively smaller substrates. That class is measured, and it conserves carbon:

- Catechol to *cis,cis*-muconic acid, EC 1.13.11.1: $C_6H_6O_2 \rightarrow C_6H_6O_4$, all six carbons retained [HH50, HKR57].
- Biphenyl-2,3-diol to 2-hydroxy-6-oxo-6-phenylhexa-2,4-dienoate, EC 1.13.11.39: $C_{12}H_{10}O_2 \rightarrow C_{12}H_9O_4^-$, all

twelve carbons retained *and the partner ring untouched* [RHE].

The second is the close structural analogue of this paper's stage-two substrate: one ring of a biaryl opened while the other survives, with no carbon lost. 2 entries, both measured.

Remark 5.19 (And what the class still does not supply)**.** [M] Three things, and the second is an obstruction rather than a gap.

Both entries are *aerobic* dioxygenases and consume O_2 directly. The architecture specifies anaerobic oxidation, so the class transfers as a class and not as a protocol, and Remark 5.7 stands unchanged.

Both cleave the bond *between the two carbons that carry the activating diol*: catechol 1,2-dioxygenase cuts between the two hydroxylated carbons, and the biaryl dioxygenase cuts C1–C2 where C2 bears the hydroxyl. A carbon that already bears a carbon substituent and no hydrogen cannot take that hydroxyl without a prior cleavage. Counting, over the clean orderings, the steps whose bond has no hydrogen on either carbon: the minimum is 2, reached by 15 openings, and 12 openings need 3; the displayed sequence needs 3. So at 2 to 3 of the 4 steps the activation the cited class requires cannot be installed where the class requires it. This is positional and is not repaired by enumerating regiochemistry. Two formyl groups appear on the substrate after step one, and they deactivate a ring toward dioxygenation, which runs the same way.

And carbon conservation belongs to the fission step alone. Where a measured pathway loses carbon — the chrysene route of [NKK+11], C_{18} to C_{15} to C_{11} to C_7 — the loss is at the downstream hydrolase that releases pyruvate, not at the fission. An architecture that stops at fission keeps its carbon, and one that does not, does not.

Scholium 5.20 (The barrier argument, and how much of it is answered). A reader may object that severing a bond between two ring-fusion carbons of a fused aromatic carries a high thermodynamic and kinetic barrier: such a carbon bears no hydrogen, carries three ring bonds, and cleaving one of them separates nothing, since both carbons remain held in a second ring. The objection is sound and is the likeliest reason the record of Notation 5.6 is empty.

The objection has two parts and Theorem 5.16 answers one of them. Under a sequential reading, in 24 of 27 openings no step severs a bond whose carbons are both still held in a second ring, so the *separation* half of the objection lapses. The *hydrogen* half does not: by Remark 5.19 at 2 to 3 steps neither carbon bears a hydrogen, which is what forecloses the activation. The sequential reading therefore buys the easier half of the objection and leaves the harder half standing, and a reader should not take it for more.

5.5 Disposition

Ruling 5.21 (On H_{scis})**.** [D] The hypothesis as registered at Hypothesis 2.11 asks of (L) whether the cuts are supported by the regiochemistry *oxidation of chrysene* is measured to show. The sequential argument changes the substrate after step one, so it answers a different question; both are returned here, and Remark 5.22 amends the hypothesis for the corpus.

(C) holds, finitely. The cut sets exist and are enumerated (§4).

(L) as registered: supported at the first cut only, and in a minority of 4 of 27 openings place their one CH–CH cut at a position chrysene is measured to be attacked at, and 2 at a K-region. Nothing in the record speaks to steps two through four, whose substrate is not chrysene.

(L) on the sequential reading: the class is right and the activation is Ordered strictly, 24 of 27 openings never cut a bond whose carbons are both fusion carbons of the current substrate (Theorem 5.16(ii)), so the class required is ordinary arene ring fission, which is measured and carbon-conserving (Remark 5.18). But at 2 to 3 of the 4 steps neither carbon of the bond bears a hydrogen, and the cited class installs its activating diol on exactly those carbons (Remark 5.19). The class therefore transfers for the first cleavage and for at most one later step, not for all 4.

(W) holds at the fission step and is not yet shown for the sequence. Carbon is conserved across a K-region ring opening and across both ring-fission entries. The hypothesis as registered asks for conservation across the whole transformation, and the architecture does not stop at one fission: it needs 3 more, and in the one measured chrysene sequence the step between two fissions is the hydrolase that loses the carbon (Remark 5.13).

Remark 5.22 (The hypothesis, amended for the corpus)**.** [A] H_{scis}(L) was written against chrysene because the first draft read the transformation as a cut set rather than a sequence. It should read: *supported, at each step, by the regiochemistry the substrate present at that step is measured to show*. Under the amended form the verdict is the third item above. The amendment is recorded rather than applied silently, because a hypothesis rewritten after seeing its test is a fitted parameter unless the rewriting is declared.

Remark 5.23 (Step three is outside both entries)**.** [M] A further limit on Remark 5.18. Its two entries are a monocyclic catechol and a biaryl, and the biaryl's partner ring is joined by a single bond. Step three of Theorem 5.16's sequence opens one ring of a *naphthalene*, whose partner ring is *fused*. That is a different reaction, the measured chemistry for it was not obtained, and the paper does not claim the class covers it.

Remark 5.24 (What this does and does not do to the corpus)**.** [A] It changes no result of this paper and no result of Article 62, and the reason is worth stating precisely rather than leaving as a relief.

Article 62 declares at its Proposition 3.1(vi) that it does not assert the transformation occurs, and fixes reachability at the level of connectivity. Theorem 8.1 and §10 are conditional in the same way: they establish what the route-A product *would* do in a membrane, given that it exists. That conditional is the whole of what they claim and it survives intact.

What this section does is price the condition. The arc from bulk chrysene to a dividing protocell is complete as connectivity and, at this step, incompletely supported as chemistry — and the corpus has 12,530 units per period to cleave at $L = 200$. This is the largest single gap in the arc, it is larger than the bromination regioselectivity that Article 79 [Sch26f] already carries openly, and it should be carried at least as openly.

Remark 5.25 (Two things not obtained)**.** [A] Named rather than worked around.

(1) A primary source for chrysene to chrysene-5, 6-dione. The paper therefore does not assert that the K-region dione is the characteristic chemical oxidation product (Remark 5.3).

(2) The chrysene 5, 6-ring-opened C_{18} dialdehyde or diacid. The one study that directly ozonates chrysene, at *Environ. Sci. Technol.* **36**(5), 869 (2002), was not obtained, and it is the single most valuable acquisition outstanding against this section.

Target 5.26 (The three cleavages)**.** Attempt the sequence of Theorem 5.16 under anaerobic oxidation in a confined interior: a K-region cleavage, then three ring fissions of successively smaller arenes, each requiring its own activation. The regiochemistry of those 3 activations is not enumerated here and is the first thing to settle. Independently, establish whether the architecture can reach a lamellar amphiphile from a *partially* opened chrysene — the biaryl dialdehyde of Proposition 5.10 is itself amphiphilic once its arms are phosphorylated, and the question of what membrane *it* forms has not been asked.

Scholium 5.27 (The shape of the result). A concordance can fail in two ways: the formal object can disagree with a measurement, or it can turn out to have no route to existence. The first three sections of this paper tested the product and found it good, within the range the record spans. This section tested the route. A first pass put three of its four steps outside the reported record; a second, following the mechanism rather than the graph, put all four inside a measured reaction class and left the conditions outside it. Both are concordance results and the second is the more consequential, because a membrane that cannot be made has no properties worth measuring.

The honest summary is therefore narrower than the one the earlier sections invite. What is established is that *if* the route-A lipid is made, it is a membrane of the right dimension that holds a genome and cannot feed it; and that the making is a sequence of 4 ring fissions of a measured and carbon-conserving class, none of which has been attempted anaerobically, in a cage, or with the activation each later stage needs.

6 The cleavage family

Definition 6.1 (The cleavage family)**.** [C] Let a 6, 12-disubstituted remnant be opened to a single chain of 18 carbons (§4), and let it then be cleaved further at interior positions. One further cleavage at position m leaves tails of m and $18 - m$. Write $\mathcal{F}$ for the family of products so reached, parameterised by the extent of cleavage. Its two named members are the record's own, and the family runs down to a tail of 1:

A : no further cleavage, tails 18; P : one further cleavage, $m = 9$.

Remark 6.2 (What the family does to the question)**.** [A] Article 62 selected within its enumeration by asserting that tails of nine fall in the micelle-forming range and tails of eighteen in the lamellar one (its Corollary 5.16 and Remark 5.17). The assertion is correct in direction and is nowhere measured in that paper. Under Definition 6.1 it becomes a quantitative question with a measured answer, and §7 supplies it. The corpus's selection is thereby either confirmed on evidence it did not have, or overturned; it is not left as an assertion either way.

7 The invariants, fixed before the routes are scored

Convention 7.1 (How an invariant is admitted)**.** [A] An invariant is a quantity that any membrane must present, stated with a measured range, *and the range is fixed from the measured record before any product of $\mathcal{F}$ is placed against it*. The guard matters: a membrane is specified by a handful of numbers and a molecule has a handful of numbers, so a range chosen after seeing a candidate's value is a fitted parameter wearing a different label (Proposition 3.1(vi)). Each invariant below therefore names its comparand class, its source, and its range, and the scoring follows in §8.

7.1 I1. The dimension of the bilayer

Notation 7.2 (The dimension series)**.** [M] Hydrophobic thickness d_{hc} and area per lipid a for fluid-phase diacyl phosphatidylcholines, measured by joint small-angle X-ray and neutron scattering on unilamellar vesicles and fitted with the scattering-density-profile model [KNK11]. One laboratory, one method, the whole series, so a difference taken inside the table cancels method bias. Each lipid is quoted at the lowest temperature at which that source reports it fluid.

lipid	chain	T (°C)	$2D_C$ (Å)	A (Å^2)
DLPC	C12	20	21.9	59.6
DMPC	C14	30	25.7	59.9
DPPC	C16	50	28.5	63.1
DSPC	C18	60	31.9	63.8
DOPC (di-C18:1)	C18:1	30	28.8	67.4

The di-C18:1 row is from the same laboratory and the same method [KNS+08], whose DPPC entry reproduces the series to the last digit. Area is a fit to measured scattering through the Gibbs dividing surface and so is one inferential step from the data; the source says so and this paper repeats it wherever the area is used.

Remark 7.3 (A superseded set, and why it is named)**.** [M] An earlier draft of this paper carried DLPC 63.2/20.9, DMPC 60.6/25.4, DOPC 72.4/26.8 and POPC 68.3/27.1 as measured structure. They are not measurements but the literature column of a water-permeability paper [MTNNZ08], quoted there from standalone-X-ray analyses which [KNK11] states overestimated lipid area by about ten per cent. The error is recorded rather than silently corrected because the superseded area would have changed the test of §9 by more than that test's own effect, and because the discipline of Article 82's Convention 2.1 is that a provenance failure is itself a finding.

Proposition 7.4 (Thickness against tail length)**.** [D] *Over the saturated series of Notation 7.2, least squares gives*

$$d_{\mathrm{hc}} \;=\; 1.64\,n_c \;+\; 2.40\,\text{Å}, \qquad R^2 = 0.9969,$$

on H_{data}. The measured thicknesses span 21.9 *to* 31.9 *Å.*

Proof. Block Z11, computed over the four saturated rows. □

Remark 7.5 (The fit's slope is a lower bound)**.** [A] Each lipid enters at the lowest temperature at which its source reports it fluid, so temperature rises along the series; a bilayer thins as it warms, and the slope at fixed temperature is therefore steeper than 1.64. This runs against the conclusion drawn below — a steeper slope puts the short-tail member further from the measured range, not nearer — and is stated here rather than left for a reader to find.

7.2 I2. The chemiosmotic invariant

Notation 7.6 (Specific capacitance)**.** [M] The measured specific capacitance is $0.7771 \pm 0.0048\ \mu\mathrm{F\,cm^{-2}}$ for films made without retained alkane, by AC bridge against a photographically measured area [Whi78]. The film is *GMO/squalene* — a *monoacylglycerol*, neutral, and neither a phosphatidylcholine nor a dialkyl phosphate — so this is a third compound-class transfer, and an unflagged one in the first draft; it is registered at Remark 7.10 and carried wherever the capacitance is used. It is *not* the $1\ \mu\mathrm{F\,cm^{-2}}$ of a biological membrane, and on the same lipid films retaining *n*-decane measure 0.40 to 0.43 [Whi73]. The spread is set by residual solvent rather than by lipid chemistry, so the quantity is invariant only once the phase is named, and the solvent-free value is the one a protocell argument needs.

Remark 7.7 (A thickness read off a capacitance is not imported)**.** [A] The sources convert capacitance to a thickness through an assumed dielectric coefficient. That is a model output and is excluded by Convention 2.1; only the capacitance itself is imported.

7.3 I3. The permeability barrier

Notation 7.8 (Water permeability)**.** [M] Osmotic water permeability of unilamellar vesicles by stopped flow at 30 °C, one laboratory and one method [MTNNZ08]:

lipid	P_f (10^{-3} cm/s)	T (°C)
DMPC	8.3 ± 0.76	30
DLPC	10.4 ± 0.50	30
POPC	13.0 ± 0.44	30
DOPC	15.8 ± 0.58	30
DOPC + 40% cholesterol	6.8 ± 0.57	30

Only P_f is imported from that source; its structural columns are literature and are superseded (Remark 7.3).

Remark 7.9 (What a permeability comparison can resolve)**.** M On DOPC alone, four laboratories report P_f between 0.0067 and 0.0158 cm s^{-1}, a factor of 2.4 [MTNNZ08]. Any cross-source permeability comparison is therefore blind below that factor, which is larger than several effects a reader might expect this paper to resolve. In particular the ether-against-ester water permeability of the matched pair [GGP+09] is measured at mismatched temperatures, 48 against 50 °C, and the authors' temperature-corrected ratio is 1.1 with a stated uncertainty of at least 0.2. That does not resolve a difference, and no statement of this paper asserts one.

7.4 The transfers, registered

Remark 7.10 (Three transfers, ranked by what measures the target)**.** A Every measured comparison in this paper reaches the route-A product through a compound class that is not its own, and the transfers differ in strength. Ranked:

(1) *Tail to tail.* Route A's tails are di-C18:1 *cis*-Δ9 and so are DOPC's. Nothing is transferred across chain length, unsaturation or position — but the *molecules* still differ, and Remark 7.11 says how.

(2) *Ester to ether*, bounded by a matched pair at one laboratory [GGP+09], and bounded at less than the effects reported here.

(3) *Phosphatidylcholine, and monoacylglycerol, to dialkyl phosphate diester.* Unbounded: nothing measures the target class. This carries the head-group area, the proton permeability and the capacitance.

Transfer (3) is this paper's softest joint and the one Target 17.2 and Target 17.4 ask to close.

Remark 7.11 (What "the same tail" does not mean)**.** A The tails are identical; the molecules are not, and the quantities compared are sensitive to the difference. Against DOPC the route-A product has no glycerol backbone, no choline, and — the difference nowhere stated in the first draft — a different *charge*: a dialkyl phosphate diester is anionic where a phosphatidylcholine is zwitterionic. Head-group area, proton permeability and specific capacitance are all head-group and charge sensitive. So Theorem 9.1's direction is known for a di-C18:1 phosphatidylcholine ether, and for an anionic head group the electrostatic contribution runs the other way from the steric one. Theorem 9.1 and Ruling 16.1 should be read as holding *if transfer (3) holds*, which is what Target 17.2 exists to settle.

Hypothesis 7.12 (H_{pos}, the position of the retained unsaturation)**.** C Of the nine aromatic double bonds of the skeleton, the one retained sits at the chain centre, giving Δ9 [Sch26c, Thm. 5.20]. Registered as H10. It is what makes DOPC and the $d = 27$ row of Notation 10.1 the same tail as the product; if the retained unsaturation sits elsewhere, transfer (1) of Remark 7.10 fails and both comparands change. Article 62 derives the position from its cut set and this paper does not re-derive it.

7.5 What is not obtained

Remark 7.13 (Six quantities the paper does not have)**.** A Named so that no statement rests on a number that was never read at source, and so that the obligations travel with the numbers rather than being discovered by a reader. The paper's scope is cut to match.

(1) Proton permeability of a *dialkyl phosphate* bilayer. The phosphatidylcholine series was obtained after this list was first written and carries §10 and §11; what is still missing is the target class, under transfer (3).

(2) A nucleotide permeability *coefficient* for a two-tailed phospholipid membrane. The fatty-acid measurements were obtained and are used, by refusal rather than transfer (Theorem 10.8); the phospholipid case is reported qualitatively by that source and not as a number.

(3) The shortest single chain that forms a bilayer, C8 against C10. A secondary review relays C8 and is not cited.

(4) Dialkyl phosphate vesicles: transition temperature, thickness, area per molecule. The route-A product is a dialkyl phosphate diester and this is its own compound class; the paper reaches it only through phosphatidylcholines, which is a transfer and is marked as one wherever it is made.

(5) Proton permeability of fatty-acid vesicles.

(6) Permeability asymmetry between the two leaflets. No measured value was found; the related measured contrast is in flip-flop kinetics, which is a different quantity

and is not substituted for it.

2 of these were obtained after the list was first drafted and are used in §10 and §11; what remains open in both cases is the compound class and not the quantity. Item (6) is untouched, so the asymmetry invariant is carried as a target and not scored.

8 Scoring the family

Theorem 8.1 (The dimension invariant selects the uncleaved end)**.** [D] *On H_{data} and Proposition 7.4:*

*(i) The route-*A *product carries di-C18:1 tails unsaturated at* Δ9*. Its measured comparand, differing only in linkage and backbone, is DOPC at $d_{\text{hc}} = 28.8$ Å, which lies inside the measured range* $[21.9, 31.9]$.

*(ii) The route-*P *product carries a tail of* 9*. Proposition 7.4 puts it at* 17.2 Å*, below every fluid bilayer in the measured record, the thinnest of which is* 21.9 Å.

Hence of the two members of $\mathcal{F}$ the record names, the dimension invariant admits A*. It does not admit* P*: that verdict rests on the extrapolation, which is weak for the reason given in the proof, and the paper claims no more for it than that nothing measured supports a fluid bilayer that thin.*

Proof. Block Z11. The comparison in (i) is direct and requires no fit: DOPC's tails are the route-A tails. The comparison in (ii) is an extrapolation of Proposition 7.4 below the range of its own data, and it is weaker still than that: the fit is over *diacyl* lipids, whose two tethered chains pack against one another, and the route-P product is single-chained, where packing is governed by headgroup repulsion and the critical packing parameter rather than by chain–chain contact. A diacyl scaling has no standing as a predictor for that class. The extrapolated figure is therefore reported as an indication and not as the ground of the exclusion; the ground is Remark 8.2, which argues in the right comparand class. □

Remark 8.2 (Route P fails twice, and the second failure is the firmer)**.** [M] The route-P product is *single-chained*, so the diacyl series is not its comparand class at all and Theorem 8.1(ii) understates the case. Its class is the single-chain amphiphiles, where the measured record is that decanoic acid, one carbon longer, requires 39 mM and a transition window about 0.2 pH units wide near pH 7.2 to form vesicles at all [JRZ+19]. Whether a C9 single chain forms a bilayer under any conditions is item (3) of Remark 7.13 and was not obtained. So the verdict on P is: not admitted. An extrapolation runs against it and its own comparand class was not measured. Neither is a measurement of P, and the paper does not claim one.

Scholium 8.3 (What the corpus gains, and it is not a vindication). Article 62 chose route A over route D by asserting that tails of nine are micelle-forming. Theorem 8.1 reaches the same selection from measurements that article did not have, which is worth having; but the two are not the same statement. Article 62's assertion was about an aggregate's phase, and what is measured here is a thickness. A tail length can be lamellar and still give a bilayer too thin to be a membrane, and the measurement speaks to the second. The selection is confirmed; the reasoning is replaced.

Theorem 8.4 (The chemiosmotic demand is not binding)**.** [D] *On H_{data} and the measured capacitance of Notation 7.6, a closure vesicle at $L = 200$ must separate* 15.5 *elementary charges to hold* 150 *mV across its membrane. Article 72 carries $N_\lambda = 558.6$ osmolyte particles for that vessel, so the charge demand is* 2.78 *per cent of the osmolyte the vessel already holds.*

Proof. Block Z13, from $Q = C \cdot A \cdot V$ at the closure radius. □

Remark 8.5 (A check on the corpus, found in passing)**.** [D] Article 72's osmolyte count has no stated concentration behind it. At the closure vesicle's volume, $N_\lambda = 558.6$ corresponds to 100 mM, which is exact to the precision carried. The corpus's osmolyte bookkeeping is therefore at a physiologically ordinary concentration, and was not set to be.

Remark 8.6 (What Theorem 8.4 does not establish)**.** [A] That a potential can be *held* is not that it can be *maintained*. The charge is a capacitive demand and says nothing about the leak, which is the proton permeability of Remark 7.13(1). A membrane can be easy to charge and unable to stay charged, and this paper computes only the first. The invariant is discharged in its capacitive half and open in its kinetic half.

9 The area, and what it does to the ledger

Theorem 9.1 (Article 62's head-group area is low)**.** [D] *Article 62 stipulates $a_2 = 0.65$ nm² and records its sign as unknown (its Remark 10.7). The sign is now known. The measured di-C18:1 ester area is* 67.4 Å² *[KNS+08], and the measured ether-minus-ester shift at matched chain length and one laboratory is* +0.8 Å² *[GGP+09], giving* 68.2 Å² *for a di-C18:1 ether. The stipulated value is low by* 4.7 *per*

cent.

Proof. Block Z12. □

Corollary 9.2 (The membrane entry falls)**.** [D] *At $L = 200$, closure at 68.2 Å^2 needs 6,265 lipids and 12,530 units, against the 6,573 lipids and 13,146 units the stipulated area gives, a fall of 4.7 per cent. Since the membrane is 0.863 of the per-period pool, the whole pool falls by very nearly as much.*

Remark 9.3 (The route-P ledger, for completeness)**.** [D] Route P is excluded on dimension (Theorem 8.1), so its ledger is recorded and not used. Its head-group area is not supplied by anything (H_{area}), so the entry is a sweep rather than a number: over the range swept it needs between 6,104 and 8,545 units against route A's 13,146.

a_1 (nm^2)	lipids	units	vs. route A
0.25	17,090	8,545	0.65×
0.28	15,259	7,630	0.58×
0.30	14,242	7,121	0.54×
0.32	13,352	6,676	0.51×
0.35	12,207	6,104	0.46×

Remark 9.4 (Why this is a small number and still worth stating)**.** [A] A five per cent revision to one ledger entry changes no conclusion of Articles 72 or 80, and none is claimed. It is stated because it is the first entry in the material ledger to rest on a measurement rather than on a stipulation, and because it runs in the direction that relieves the architecture: fewer units are required, not more.

10 The barrier, measured against thickness

Notation 10.1 (The permeation series)**.** [M] Permeability coefficients for protons, potassium ions, water, urea and glycerol across six phosphatidylcholines with monounsaturated chains of fourteen to twenty-four carbons, the double bond at the chain centre, extruded to unilamellar vesicles and all liquid-crystalline at 30 °C [PVVH+96]. One laboratory, one series, one temperature. Protons by pyranine fluorescence after a half-unit pH jump, with valinomycin present to dissipate any diffusion potential.

d (Å)	log $P_{\mathrm{H^+}}$	log $P_{\mathrm{K^+}}$	log P_{water}	log P_{urea}	log P_{gly}
20.0	-1.89	-9.82	-1.61	-5.47	-5.21
23.5	-2.74	-11.03	-1.71	-5.61	-5.43
27.0	-3.29	-11.46	-1.82	-5.85	-5.56
30.5	-3.80	-11.62	-1.95	-5.97	-5.67
34.0	-4.10	-11.66	-2.15	-6.11	-5.88
37.5	-4.31	-11.77	-2.30	-6.22	-5.97

d is the hydrophobic thickness the source assigns from [LE83]; it is an assigned structural value and not one that paper measured.

Remark 10.2 (Why this series and this row)**.** [M] The row at $d = 27$ Å is di-C18:1 with the double bond at the chain centre. That is the route-A tail exactly, under H_{geom} in its *cis* branch, so no transfer is made across chain length, across unsaturation or across position: the tail is the same tail. The *molecule* is not, and Remark 7.11 says what differs.
Two cautions travel with it. The thickness assigned here, 27 Å, differs by 6 per cent from the 28.8 Å measured for the same lipid by scattering (Notation 7.2); the two are different methods and are not merged in any column. And the lipid is an ester where route A under the reductive branch of H_{redox} is an ether; the matched pair of [GGP+09] bounds that difference in area and in water permeability, and bounds it at less than the effects reported below.

Proposition 10.3 (The barrier spans nearly ten decades)**.** [D] *At $d = 27$ Å, $\log P$ runs from -1.82 for water to -11.46 for potassium, a span of 9.6 decades, on H_{data}; the proton sits between them at -3.29. A membrane is the object that presents that span: it must pass water freely and hold ions.*

10.1 Retention

Proposition 10.4 (The genome is retained)**.** [D] *For a sphere of radius R losing a solute through a membrane of permeability P, the content relaxes with time constant $R/(3P)$. At the closure radius 13.04 nm and the potassium row of Notation 10.1, that is 35 hours, against a forcing period of 43,200 s. A nucleic-acid backbone carries one negative charge per residue and is larger than a potassium ion by orders of magnitude in both dimensions that restrict permeation, so the potassium row is a generous upper bound on its permeability and the retention is a fortiori.*

Remark 10.5 (The vessel's smallness works against it here)**.** [A] The relaxation time scales as R, so the closure vesicle

— the smallest object the corpus contemplates — holds its contents worse than a larger one, having more membrane per unit volume. The margin in Proposition 10.4 is nonetheless 35 hours against a twelve-hour period at the *worst* case the corpus carries, and the genome's own figure is far better.

10.2 Admission, and why the lipid cannot supply it

Notation 10.6 (Nucleotide permeation)**.** [M] Measured on fatty-acid vesicles at 23 °C [MSK+08]. Nucleoside phosphorimidazolides, which carry a single negative charge at pH 8.5, equilibrate across 100 nm vesicles with a half-time of about 12 hours. AMP, ADP and ATP, with two, three and four negative charges, show negligible leakage over 24 h without magnesium. The same source states that nucleotides cross a phospholipid (DMPC) membrane only through defects formed at the gel-to-liquid transition.

Proposition 10.7 (Admission would be fast enough, on that membrane)**.** [D] *Scaling the half-time of Notation 10.6 by R, a closure vesicle of radius* 13.04 *nm equilibrates an activated nucleotide with a half-time of* 3.1 *hours, which is* 3.8 *half-times within one forcing period. The retention figures of Proposition 10.4 are* $1/e$ *time constants* $\tau = R/3P$*; the corresponding half-time is* $\ln 2\,\tau$*, and the two are compared on that footing below rather than as if commensurable. Were the protocell membrane a fatty-acid membrane, admission would not be limiting.*

Theorem 10.8 (But the selected lipid does not admit nucleotides)**.** [D] *The membrane selected by Theorem 8.1 is a two-tailed dialkyl phosphate of the phospholipid class, not a single-chain fatty-acid membrane. Proposition 10.7 therefore does not transfer, and the measured record runs the other way:*

(i) [MSK+08] reports that nucleotides cross a phospholipid membrane only through transition defects, which a membrane held fluid throughout its cycle does not present.

(ii) Both sources agree that charge is the dominant restriction on permeation, and at $d = 27$ *Å the measured coefficient for a* monatomic *singly charged ion is already* -11.46*, giving* 35 *hours as a* $1/e$ *constant and about two thirds of that as a half-time (Proposition 10.4) — still twice the* 3.1 *hours of Proposition 10.7. A mononucleotide is larger and no less charged.*

*Hence the same property that retains the genome excludes its monomers. Passive admission across the route-*A *membrane is not available.*

Remark 10.9 (What this costs, and what already pays it)**.** [C] The architecture is not short of a component here; it is short of an argument it had not made. Article 66 [Sch26d] builds a selective trimeric pore, and Article 72 computes that one such pore over-supplies a closure vessel's nitrogen demand by a factor of 773,410, at a cost of nine units per strand per period [Sch26a, Prop. 9.3]. What Theorem 10.8 adds is that the pore is not an enhancement but a *requirement*: the corpus's own lipid cannot feed the vessel, and the corpus's own pore is what does. The two articles were written independently and the dependence between them was not stated.

Remark 10.10 (Does the pore fit the membrane it must sit in?)**.** [D] Remark 10.9 makes the pore necessary and says nothing about whether it fits. The question is a hydrophobic-mismatch question and the corpus supplies half of what it needs. Article 62 gives the π-stacking repeat of these units as 3.4 Å (its Proposition 7.3); the core selected in Theorem 8.1 is 28.8 Å and the head-to-head distance of the same comparand is 36.7 Å. A chrysene tower spanning the core therefore needs 8.5 stacked units, and one spanning head group to head group needs 10.8.
Whether Article 66's trimeric pore [Sch26d] is built of towers of that height is not something this paper can say: that article is not held against these numbers here, and a tower materially shorter or taller than 8.5 units would sit in a core it does not match, with the usual consequences — local thinning, tilt, or exclusion from the fluid phase. The requirement is stated so that the next article can check it, and Target 10.11 records it. A reader should not take Remark 10.9 as establishing that the architecture's pore and its membrane are mutually compatible; it establishes only that the architecture needs a pore.

Target 10.11 (The pore in this membrane)**.** Check Article 66's trimeric pore against a core of 28.8 Å: a spanning tower needs 8.5 π-stacked units at 3.4 Å. Hydrophobic mismatch is the standard failure mode for a rigid species in a fluid bilayer and the corpus has not tested for it.

Scholium 10.12 (A tension resolved in the architecture's favour). It is worth noticing what would have happened had the dimension invariant selected the other end of the cleavage family. A C9 single-chain product would have been in the compound class [MSK+08] measures, and admission would have come free — but it would have failed Theorem 8.1 and, by Proposition 10.4's converse, would have retained its genome correspondingly less

well. The architecture cannot have both from the lipid alone, and that is a general statement about membranes rather than a defect of this one: a barrier that admits monomers leaks polymers. Resolving it requires a selective channel, which is what cells have and what Article 66 supplies.

11 The chemiosmotic invariant is not met

Remark 11.1 (Where this section stands)**.** [A] This is the paper's principal negative result and it is stated before its derivation. Theorem 8.4 established that the charge needed to hold a membrane potential is small. That was the capacitive half of the invariant. The kinetic half fails, and it fails by a margin no choice available to the architecture closes.

Theorem 11.2 (Neither the potential nor the gradient survives the period)**.** [D] *Two distinct quantities, relaxing differently, and both short.*

The potential. *At the measured capacitance of Notation 7.6 and the proton conductance implied by the* $d = 27$ *row, the RC time constant is* 4.1 *s against a forcing period of* 43,200 *s: short by* 10,530*. This is the quantity Theorem 8.4 charges* 15.5 *elementary charges to establish, and it is the stronger of the two results.*

The pH gradient. *Buffering the lumen lengthens its relaxation; carrying Article 72's entire osmolyte content as a perfect buffer at pH 7 — which is* 100 *mM not by assumption but because that is the concentration Article 72's own* $N_\lambda = 558.6$ *corresponds to at the closure volume (Remark 8.5), and which is generous twice over, since no osmolyte buffers perfectly and the corpus names none that buffers at all:*

β (mM/pH)	τ (s)	period/τ
0	0.000847	50,977,736
10	36.8	1,174
50	184	235
100	368	117

At 100 *mM the hold is* 368 *s, short by* 117.

Remark 11.3 (The unbuffered row is a formal limit)**.** [A] At the closure volume and pH 7 the lumen contains 5.6×10^{-4} free protons. The $\beta = 0$ row of the table is therefore a continuum statement about a species present in sub-unit number, and is printed as the limit of the sweep rather than as a physical relaxation; the 100 mM row is the one with a physical reading, and it is the one Theorem 11.2 quotes. That the buffered row's 558.6 titratable protons coincide with Article 72's own osmolyte count is the check of Remark 8.5.

Proof. Block Z16, from $\tau = R/(3P)$ and, for the buffered case, $\tau_\beta = \tau\,\beta/(\ln 10\,[\mathrm{H}^+])$; the electrical constant from $G = PF^2c/RT$ and $\tau_{RC} = C/G$. □

Corollary 11.4 (No thickness available to the architecture repairs it)**.** [D] *The proton permeability of Notation 10.1 falls with thickness, and at the thickest membrane in that record the unbuffered relaxation is* 0.0089 *s — an order of magnitude better and still far short. Since Theorem 8.1 already caps the architecture's tail at C18, no member of the cleavage family reaches even that thickness.*

Remark 11.5 (What is and is not refuted)**.** [A] Three things, because this result is the one most likely to be over-read.

It does not refute any published statement of the corpus. No article of this programme claims a proton gradient, a chemiosmotic coupling or a membrane potential, and none of their results depends on one. The vessel of Articles 72 and 76 runs on a photochrome brake and an osmotic gain, both of which are indifferent to this.

It does not show that a potential cannot be *established*. Theorem 8.4 shows the charge is trivial to supply; what fails is retention, and retention is the half that matters for storing energy.

What it does close is a route. A chemiosmotic protocell of this architecture would require continuous pumping against a 4.1 s electrical relaxation, or against 368 s if only a pH gradient is wanted, in a cycle whose only energy input is a twelve-hour photochrome forcing. A pump of that duty is not among the components the corpus carries, and the material ledger has no entry for one. Any future development proposing to extract energy across this membrane — a rotor, an ATP analogue, an ion-motive step — inherits this as its first obstruction and should be read as owing a pump before it owes anything else.

Target 11.6 (The pump, or the period)**.** Either exhibit a proton pump of duty cycle shorter than 4.1 s within the material ledger, or establish that the architecture's energetics require no transmembrane gradient at all. The second is the cheaper claim and is, on the present reading, the one the corpus is already making without having said so.

Scholium 11.7 (Why a negative result here is worth its space). A concordance that returned only agreements would be evidence that its invariants were chosen to agree. This one returns a sharp

disagreement at the first invariant whose kinetics were tested, and the disagreement is of the kind that cannot be absorbed: it is four orders of magnitude on the potential at the architecture's own geometry, and it worsens as the vessel gets smaller, which is the direction Article 72 shows the population moving. The dimension invariant was met and the barrier invariant was met; this one is not, and reporting all three is what makes the first two worth anything.

12 The ledger of the transformed product

Remark 12.1 (What this section expands, and what it does not)**.** [A] Article 72 block Y6 allocates the per-period pool at $L = 200$ among the genome, the membrane, the residues and the catalyst, denominated throughout in chrysene units. This section revises two membrane entries and leaves the others alone. A ledger with two entries recomputed is not a ledger, and Proposition 3.1(v) says so; what is offered is an audit of the part this paper's measurements reach.

12.1 The area entry, on a measurement

The first revision is Theorem 9.1 and Corollary 9.2: the stipulated head-group area is low by 4.7 per cent, the closure membrane needs 12,530 units rather than 13,146, and the revision runs in the direction that relieves the architecture.

12.2 The reduction entry, audited

Remark 12.2 (Why this can be checked without a mechanism)**.** [A] Article 62, Proposition 5.19, charges "sixteen hydrogens per tail and thirty-two per dimer" for the reduction, counting eight reduced carbon–carbon double bonds. The charge can be checked without reference to any route, because the oxidation state of the carbon skeleton is fixed at both ends of the transformation by the two structures Article 62 itself names: the 6,12-disubstituted core at one end and the named product at the other. Oxidation state is a state function, so the difference is what the transformation must be supplied whatever path it takes — including a path nobody has yet run (§5).

Convention 12.3 (The bookkeeping)**.** [A] For each of the 18 skeleton carbons, the oxidation number is the number of bonds to oxygen less the number of bonds to hydrogen, counting bond order; carbon–carbon bonds contribute nothing. The reducing equivalents required are the fall in the sum over the skeleton.

Theorem 12.4 (The reduction ledger is short)**.** [D] *Under Convention 12.3, the* 6,12*-disubstituted core sums to* −8*. The ether product, octadec-9-en-1-yl, sums to* −34 *and the ester product, oleoyl, to* −30*. Hence the transformation requires* 26 *reducing equivalents per tail on the ether branch of* H_{redox} *and* 22 *on the ester branch, against the* 16 *Article 62 charges.*

branch	*per tail*	*per dimer*	*per period at* $L = 200$
ether (reductive)	*26*	*52*	*325,780*
ester (oxidative)	*22*	*44*	*275,660*
Article 62, Prop. 5.19	*16*	*32*	*200,480*

The charge is short by 20 *per dimer on the ether branch and* 12 *on the ester branch; the true demand is* 1.62 *times what is carried.*

Proof. Block Z20, which asserts the hydrogen counts of both named products before using them. □

Remark 12.5 (Where the shortfall comes from)**.** [A] Article 62 counts the eight reduced double bonds and stops, which is sixteen of the 26 hydrogens required. The balance closes as 16 + 8 + 2: eight more for the four cuts, two carbons capped each; and two at the arm position, one hydrogen gained and one carbon–oxygen bond lost. Two further demands are therefore not counted, and both are consequences of its own Lemma 5.3.

A ring opening is not free of hydrogen. Article 62 writes that "the four rings are discharged by the cut set", which is correct as bookkeeping on degrees of unsaturation and is not a chemical balance: severing a carbon–carbon bond leaves two carbons that must each be capped, and four cuts therefore carry eight hydrogens the ledger does not charge. And C6 bears the arm rather than a hydrogen in the parent, while the corresponding chain carbon bears one.

Neither omission is an error in Article 62's own terms, since its Proposition 5.19 is explicitly a count of degrees of unsaturation rather than a redox balance. What is an error is using that count as the architecture's reducing-equivalent demand, which is how it has been read downstream.

Corollary 12.6 (The per-period demand)**.** [D] *At the* corrected *membrane entry of Corollary 9.2,* 12,530 *units per period at* $L = 200$ *— not the* 13,146 *this section has just superseded — the reduction demands* 325,780 *reducing equivalents per period on the ether branch and* 275,660 *on the ester branch, against* 200,480 *on Article 62's charge: an understatement of* 125,300 *per period.*

Remark 12.7 (The resource has no entry at all)**.** [A] The sharper point is not the size of the correction but that the quantity it corrects is absent from the ledger. Article 72's block Y6 allocates *carbon*, in chrysene units, among four demands. Reducing equivalents are a distinct resource, they are consumed at 325, 780 per period on the dominant branch, and the material ledger has no column for them and names no source.

Article 62 states at its Convention 6.1 that hydrogen "is admitted elsewhere in the architecture . . . and available to be placed where a structure requires", and treats it as unconstrained for that reason. That is a reasonable convention for a composition ledger in carbon. It is not available to a ledger that means to close, because a reducing equivalent at this scale is a flux and not a placement: the vessel must obtain them at a rate, from an environment, against a twelve-hour period. Target 12.9 records the obligation.

Remark 12.8 (An argument for the oxidative branch)**.** [D] Theorem 12.4 supplies the first quantitative reason to prefer one branch of H_{redox} over the other, and it favours the ester. The oxidative branch retains an oxidised carbon as the ester carbonyl, so it arrives at a membrane-forming lipid having spent $20 - 12$ fewer reducing equivalents per dimer, which is 325, 780 against 275, 660 per period.

The argument is worth exactly what it is, and no more. It is an argument from a resource the corpus does not yet budget, about a branch the corpus does not yet decide, on a transformation nobody has yet performed (§5). It does not select the branch. What it does is attach a cost to the choice, where before there was none.

Target 12.9 (The reductant)**.** Name the source of reducing equivalents and add a column for them to the material ledger. The demand is 325, 780 per period at $L = 200$ on the ether branch; the environment must supply them at that rate, and no article of the corpus says what supplies them.

Scholium 12.10 (What an audit is for). This finding was not sought. It fell out of carrying both branches of H_{redox} through the ledger, which was done for a different reason — to price the linkage — and the branch comparison required a redox balance that Article 62 had not computed. That is the ordinary yield of an audit pointed inward, and it is the second time in this paper that carrying two readings instead of choosing one has returned something neither reading would have given alone.

13 The carotenoid reading, recorded

Remark 13.1 (Why this is a scholium and not a section)**.** [A] The tetrasubstituted family is not a lipid precursor in the record: the patent assigns lipid formation to the 6, 12-disubstituted catalyst and consumes the tetrasubstituted substrate as a nucleobase (Remark 2.14). What follows is therefore recorded for the corpus and is deferred, and no numbered result of this paper rests on it.

Proposition 13.2 (The spacing is invariant and is not isoprenoid)**.** [A] *Of the* 27 *single-chain openings,* 6 *sever the* C10*a*–C10*b bond. In every one of them the four substitution positions of the tetrasubstituted family stand at the same spacing,* $(4, 5, 4)$*. That spacing is a contiguous run of the carotenoid interior* $(4, 4, 5, 4, 4)$ *and is not the phytanyl spacing* $(4, 4, 4)$ *of an archaeal diether core.*

Proof. Block Z4, by enumeration; the invariance is over all 6 paths. □

Scholium 13.3 (What it would take to read this as a tail). Two things, and the first is not a matter of degree. The spacing is a spacing of *substitution sites*, which bear oxygen arms in the record; reading them as methyl branches is H_{meth}, which this paper registers and does not test. Until that premise is discharged the agreement is between a pattern of arms and a pattern of methyls, which is a resemblance and not an identification — the distinction Convention 2.2 exists to enforce.

The second is Theorem 4.4: no opening of the chrysene skeleton, under any of the 1, 189 cut sets, places three methyls at the regular isoprenoid spacing. So even granting H_{meth}, what is reachable is the carotenoid pattern and not the archaeal one, and the archaeal branch of the lipid divide would need a carbon source the architecture does not have. The corpus should claim the carotenoid class or neither.

14 Consolidated register

This section states in one place what the paper answers and on what. It adds nothing. Its purpose is that a reader who has followed the argument should be able to see which answers are finite, which rest on a measurement, and which are open.

14.1 What is answered, and on what

Does the record name one lipid or a range?

A range. Figure 16(b) of the patent carries the two-tailed C_{18} product that is Article 62's $C_{40}H_{79}O_6P$; column 57 and Figure 9(c) carry the same remnant through further cleavages to two single-chain lipids of 9. The free parameter is the extent of

cleavage.
Rests on: Notation 2.5; Definition 6.1. *Standing:* [C] imported from the record.

Which member of that range can be a membrane?
The uncleaved end. The route-A tail is di-C18:1 cis-Δ9, whose measured comparand sits at 28.8 Å inside the measured range [21.9, 31.9]; the route-P tail extrapolates to 17.2 Å, below every fluid bilayer measured.
Rests on: Theorem 8.1; block Z11. *Standing:* [D] on H_{data}.

Is Article 62's head-group area right?
No; it is low by 4.7 per cent. The membrane entry falls from 13, 146 to 12, 530 units per period.
Rests on: Theorem 9.1, Corollary 9.2; block Z12. *Standing:* [D] on H_{data}.

Does the membrane hold the genome?
Yes, with margin: 35 hours of relaxation for a monatomic singly charged ion against a 43, 200 s period, and a polyanionic backbone is slower a fortiori.
Rests on: Proposition 10.4. *Standing:* [D] on H_{data}.

Does it admit the monomers?
No. Passive admission across a phospholipid-class membrane is not available, and the corpus's own pore is therefore a requirement rather than an enhancement.
Rests on: Theorem 10.8; Remark 10.9. *Standing:* [D] on H_{data}.

Can it hold a chemiosmotic gradient?
No. Fully buffered at 100 mM the hold is 368 s against 43, 200 s, short by 117; the capacitive half is trivial at 15.5 elementary charges.
Rests on: Theorems 8.4 and 11.2, Corollary 11.4. *Standing:* [D] on H_{data}.

Is the transformation supported by the record?
Partly. Ordered strictly — which 24 of 27 openings permit — every cut is an ordinary arene ring fission, a measured and carbon-conserving class. But the class activates the bond it cleaves, and at 2 to 3 steps neither carbon bears a hydrogen; and every measured instance is aerobic.
Rests on: Theorems 5.5 and 5.16, Ruling 5.21, Remarks 5.18 and 5.19. *Standing:* [D] on H_{data}.

What does the supported cleavage reach?
A C_{18} biaryl dialdehyde, all 18 carbons retained, 3 rings still intact. The compound is predicted and is not reported.
Rests on: Proposition 5.10, Remark 5.11. *Standing:* [A] for the connectivity; [M] for the precedent; a prediction for the compound.

Is the reduction ledger right?
No. The demand is 52 reducing equivalents per dimer on the ether branch and 44 on the ester, against 32 charged. The resource has no column in the material ledger at all.
Rests on: Theorem 12.4, Corollary 12.6; block Z20. *Standing:* [D]; the bookkeeping is mechanism-independent.

Is an isoprenoid tail reachable?
No, under any of the 1, 189 cut sets. The carotenoid spacing (4, 5, 4) is reachable and is invariant, and reading it as methyls is H_{meth}, which is not tested.
Rests on: Theorem 4.4, Proposition 13.2. *Standing:* [A], finite.

14.2 How much is finite

Remark 14.1 (The four kinds, counted)**.** [A] Of the numbered results: the enumerations over X — its 18 vertices, 21 edges and 4 rings — are [A] and need no premise beyond the skeleton; the stoichiometry and the redox balance are [A] and [D] respectively on structures the record names; everything touching a measurement is [D] on H_{data} and on the compound-class transfer named where it is made; and the two premises of H_{redox} are carried throughout rather than chosen. Nothing in the paper is [E].

Remark 14.2 (Where the premises are concentrated)**.** [A] Two places. H_{area} carries every route-P number and is swept rather than assumed, so its failure changes a sweep and not a conclusion. H_{data} carries every measured comparison, and its real content is not that the measurements are correct but that the compound-class transfers are admissible: phosphatidylcholines standing for a dialkyl phosphate diester (§9), fatty-acid vesicles standing for nothing, since that transfer is the one the paper refuses (Theorem 10.8). The transfers are named at each use and are the paper's softest joint.

15 Falsification register

Theorem 8.1. A measured fluid bilayer of hydrophobic thickness below 21.9 Å; or a measured $2D_C$ for a di-C18:1 ether differing materially from its ester comparand.

Theorem 9.1. A measured head-group area for a dialkyl phosphate diester at or below 0.65 nm^2. This is the obligation of Remark 7.13(4) and would settle the entry directly rather than through a transfer.

Proposition 10.4. A measured nucleotide or oligonucleotide permeability across a two-tailed phospholipid membrane fast enough to lose a genome within a period.

Theorem 10.8. A measured admission of activated nucleotides across a fluid two-tailed phospholipid membrane without transition defects and without a channel.

Theorem 11.2. A measured proton permeability for a membrane of this class at least 117-fold below the series of Notation 10.1; or a lumen buffer capacity far above the osmolyte Article 72 carries; or a pump within the material ledger.

Theorem 5.5. A chain-forming cut set severing two CH–CH bonds.

Theorem 5.16. A chain-forming cut set admitting no clean ordering; or a demonstration that ring fission of an activated

arene cannot proceed anaerobically, which would move the obstruction from the conditions back to the chemistry.

Theorem 12.4. An error in the oxidation-state bookkeeping of Convention 12.3, or a product formula other than the two Article 62 names.

Theorem 4.4. A cut set of X, outside the 1, 189 enumerated, placing three methyls at the spacing $(4, 4, 4)$.

16 Precedence

Corrected statements supersede earlier ones where they speak to the same object; the earlier text is not altered.

Ruling 16.1 (Against Article 62)**.** D Five entries, of which two are corrections and three are confirmations.

62.1 D **The head-group area is superseded.** $a_2 = 0.65$ nm^2 (Corollary 10.6) is low by 4.7 per cent against 68.2 Å^2 derived from measurement (Theorem 9.1). Remark 10.7 records the sign of this omission as unknown; it is now known and runs toward relief.

62.2 D **The reduction ledger is superseded.** Proposition 5.19's "sixteen hydrogens per tail and thirty-two per dimer" is a count of degrees of unsaturation and is correct as such. It is not a redox balance and must not be read as the architecture's reducing-equivalent demand, which is 26 and 44 per dimer on the two branches of H_{redox} (Theorem 12.4).

62.3 D **Corollary 5.16 is confirmed and its reasoning replace** The selection of route A over route D holds, on a measured thickness rather than on an assertion about micelle-forming tail length. The two are different statements and the Scholium following Theorem 8.1 says so.

62.4 D **Remark 5.4 is vindicated, in the right order.** The three chords are where the corpus records scission. Classified in the parent they are ring-fusion bonds and the record holds no instance of cleaving one (Theorem 5.5); cut in the order of Theorem 5.16 they are ordinary ring bonds of smaller arenes and the class is measured. Article 62's choice of loci is therefore admissible and its silence about order is what left the matter open.

62.5 C **Targets 5.25 and Supposition 6.7 are not discharged.** The geometry at Δ9 and the phosphatidyl reading remain open. H_{geom} is carried in its *cis* branch wherever a comparand requires it, and Corollary 6.6's independence from the head group is maintained here.

Ruling 16.2 (Against Article 72)**.** D

72.1 D **The membrane entry of block Y6 is superseded.** 13, 146 units per period at $L = 200$ becomes 12, 530 (Corollary 9.2). The other three entries are untouched and the allocation is not recomputed.

72.2 D **Hypothesis 2.10 acquires a necessity.** The pore of Article 66 was carried as a supply line whose tether was a reading. Theorem 10.8 makes a selective channel *necessary* for admission, whatever its tether, because the lipid cannot admit the monomers. Proposition 9.3's over-supply figure is unaffected.

72.3 A **A check, not a correction.** $N_\lambda = 558.6$ at the closure volume corresponds to 100 mM, which Article 72 does not state (Remark 8.5).

72.4 C **Target 11.8 is NOT discharged.** The curvature floor R_c for this lipid is not derived here and no measured value was obtained. The band's lower edge continues to rest on the convention $R_c = 25$ nm, which gives $L_{\min} = 735$ and excludes the $L = 200$ the corpus computes at; a floor at the closure radius itself, 13.04 nm, would give $L_{\min} = 200$, but that identity is Article 72's own Remark 10.2 and is not an independent determination.

72.5 C **Target 11.11 is NOT addressed.** E^* is a tolerance on the anchored duplex and not a membrane modulus. No measured modulus is identified with it (Remark 2.9).

Remark 16.3 (What the corpus may now cite)**.** A Three entries. That the architecture's lipid cannot feed its own vessel, so Article 66's pore is load-bearing for supply and not only for nitrogen. That reducing equivalents are a resource of the same standing as carbon and are absent from the material ledger. And that the arc's chemistry passes from the reported to the proposed at one identified step, with the requirement stated as a count (§5).

17 Obligations

Remark 17.1 (What was not obtained)**.** A 6 quantities were named in Remark 7.13 and 2 in Remark 5.25. Two of the first set have since been obtained and are used in §10 and §11. The rest stand, and the paper's scope was cut to match rather than estimated across.

Target 17.2 (The head-group area of a dialkyl phosphate)**.** Measure a_1 and a_2 for a dialkyl phosphate diester. The route-A product is of that class and the paper reaches it only through phosphatidylcholines. This is the measurement of greatest consequence to the ledger.

Target 17.3 (The curvature floor)**.** Measure the smallest radius at which a bilayer of this lipid is stable. It is Article 72's Target 11.8, it is not discharged here, and the lower edge of the genome band rests on it entirely.

Target 17.4 (Proton permeability of the architecture's own lipid)**.** The series of Notation 10.1 is phosphatidylcholine. Measure it for an ether-linked dialkyl phosphate, which would convert Theorem 11.2 from a transfer into a direct result.

Target 17.5 (The single-cleavage amphiphile)**.** Determine what membrane the biaryl dialdehyde of Proposition 5.10 forms once its arms are phosphorylated. It is one *supported* cleavage from the substrate, where the route-A lipid is four, and nobody has asked.

18 Conclusion

Proposition 18.1 (What is established)**.** [D] *Subject to Appendix A. Item (vi) is* [A]*, finite over* X*; items (i)–(v) are* [D] *on* H_{data} *and on the compound-class transfers of Remark 7.10.*

(i) The patent's two lipid figures are one process at two extents of cleavage, and the measured dimension invariant selects the uncleaved end: route A *at* 28.8 *Å inside the measured range, route* P *at* 17.2 *Å below all of it (Theorem 8.1).*

(ii) That membrane retains a genome and cannot admit its monomers, so a selective channel is necessary and the corpus already has one (Proposition 10.4, Theorem 10.8).

(iii) It cannot hold a chemiosmotic gradient, by 117*-fold at the most generous buffering the corpus admits, and no thickness available to the architecture repairs it (Theorem 11.2, Corollary 11.4).*

(iv) Article 62's head-group area is low by 4.7 *per cent and its reduction ledger is short by* 20 *reducing equivalents per dimer; the second resource has no column at all (Theorems 9.1 and 12.4).*

(v) The transformation, ordered strictly, avoids cleaving fused-system interiors in 24 *of* 27 *openings and so requires only ordinary arene ring fission, a measured carbon-conserving class (Theorem 5.16, Remark 5.18). It is not thereby supported: at* 2 *to* 3 *of the* 4 *steps the bond to be cut bears no hydrogen on either carbon, so the activation that class uses is unavailable, and the conditions are anaerobic where every measured instance is aerobic (Remark 5.19).*

(vi) Finite, over X*: a regular isoprenoid tail is unreachable under all* 1,189 *cut sets (Theorem 4.4); a bolaamphiphile is unreachable from the* 6, 12 *family by single-chain opening,* 0 *of* 27*; and the anchor areal density* $\sigma_{\mathrm{A}} = E^{*}/(2\pi L_{p} h)$ *is independent of genome length (Proposition 4.6).*

Remark 18.2 (What is not established)**.** [A] That any cleavage is achievable; that a membrane is exhibited; that E^{*} or the curvature floor is determined; that the head group is a phosphatidyl; that the geometry at Δ9 is *cis*; that the single-chain product is excluded in its own compound class, which was not measured; and that the carotenoid spacing is a spacing of methyls. The paper is a set of conditional statements about a molecule the record names and nobody has made.

Scholium 18.3 (The shape of the account). The paper set out to ask whether the membrane requirements can be met from the chrysene source. The answer it returns is in three parts and only the first was expected.

The product is good: at the uncleaved end of the range the record spans, it is a membrane of the right dimension that holds what it must hold. The function is partial: it cannot feed itself, which the architecture already pays for, and it cannot store energy across its own period, which the architecture does not. And the route is unperformed and partly unexplained: an ordered sequence of 4 fissions, of a measured class that cannot activate 2 to 3 of its own steps, none attempted under the conditions the architecture names.

A reader wanting one sentence should take the third. The first two are conditional on it, and a membrane that cannot yet be made is a specification rather than a result — which is what §5 ends by saying it should be read as.

A Hypothesis register

The 9 premises of §2, what rests on each, and what survives its failure. Emitted by block Z21, so a premise cannot be registered in the prose without appearing here.

	premise	what rests on it	what survives its failure
H1 H_{scis}	the scission loci	§5 entire	the connectivity results; everything in §7 onward, which is conditional on the product existing
H2 H_{redox}	ester against ether	the linkage, the area shift, the redox balance	the dimension result, which is indifferent to linkage
H3 H_{count}	lipids per unit	the ledger entries	the invariants, which are per molecule
H4 H_{area}	the single-chain head-group area	every route-P ledger number	everything: route P is excluded on dimension, not on area
H5 H_{floor}	the curvature floor	the lower edge of the genome band	everything else
H6 H_{geom}	*cis* at $\Delta 9$	the choice of comparand in the dimension test	the test itself, at the resolution of the measured range
H7 H_{head}	the phosphatidyl reading	nothing in this paper	everything; the independence of Article 62 Cor. 6.6 is kept
H8 H_{data}	the measured entries	every D result touching a measurement	the finite layer and the redox balance
H9 H_{meth}	the methyl reading of the arms	nothing; it is registered and not tested	everything

B Verification

The body's numbers come from 22 computed blocks. Every one is emitted by `verify_a83.py` into `verification_values_a83.tex`; every data table is emitted as a complete tabular environment. Nothing is typed into the manuscript. The script is standard library only, asserts rather than prints its claims, and exits non-zero on failure. The measured record it imports is in `data_a83.py`, one row per entry, each carrying its source, method and a flag of MEASURED, LITERATURE or CALCULATED; only MEASURED rows enter a test statistic.

block	content
Z1	single-chain openings, classified by bond class
Z2	terminal attachment, and the K-region coincidence
Z3	isoprenoid non-reachability over every spanning tree
Z4	the carotenoid spacing, invariant
Z5	the three routes and their stoichiometry
Z6	closure per route; the route-P sweep
Z8	the curvature floor and the genome band
Z9	the anchor areal density, independent of L
Z10	the cleavage family
Z11	the dimension series and its fit
Z12	the head-group area, and the ledger entry
Z13	the chemiosmotic charge demand
Z14	what a permeability comparison can resolve
Z15	the permeability barrier against thickness
Z16	proton relaxation, with the buffering sweep
Z17	admission, scaled to the closure vessel
Z18	the regiochemical standing of each required cut
Z19	what one supported cleavage reaches
Z20	the reduction ledger, audited
Z21	this appendix
Z22	the sequential model, under two criteria
Z23	the pore against the membrane it sits in

C Sources, by use

C.1 The corpus

source	used at	what is taken
The Enclosure [Sch26c]	Notation 2.3, Notation 2.5, Definition 2.8, Ruling 16.1	The vessel graph and its chords (Not. 2.2); the cut-set enumeration and route A (Lem. 5.3, Thm. 5.10, Cor. 5.21); the carbon budget (Prop. 6.2); the reduction count (Prop. 5.19); the closure identity and head-group area (Def. 10.1, Thm. 10.5, Cor. 10.6); the anchor footprint (Cor. 7.7).
The Integrated Cycle [Sch26a]	Definition 2.10, Theorem 8.4, Ruling 16.2	The per-period ledger and membrane entry (Prop. 9.1, block Y6); the closure radius and osmolyte count (block Y1); the curvature floor as a convention (Hyp. 2.12, Target 11.8); the pore's over-supply (Prop. 9.3); the forcing period.
The Completeness Condition [Sch26b]	Convention 2.1	The status labels.
The Partition Concordance [Sch26e]	Convention 2.1, Convention 2.2	The measured label M and its discipline; the concordance method, in particular that a hypothesis must commit a formal quantity to a physical one before measurement bears on it.
US 12,195,423 [Sch25]	Notation 2.5, Remark 2.6	Figure 16(b), the forty-carbon atom map to a two-tailed C_{18} product; column 57 and Figure 9(c), the repeated oxidative cleavage to two single-chain lipids summing to the core; the assignment of lipid formation to the 6, 12 catalyst.

C.2 The measured literature

Rows marked by their sources as estimated or calculated are excluded from every test statistic (Convention 2.1).

source	quantity	standing here
Kučerka *et al.* 2011 [KNK11]	$2D_C$, A, D_B for the PC series	The dimension invariant. One laboratory, one method, the whole series. Area is a fit to measured scattering and is one inferential step from the data.
Kučerka *et al.* 2008 [KNS+08]	DOPC and DPPC	The di-C18:1 comparand, which is the route-A tail exactly. Its DPPC row reproduces the 2011 series, which is the check that the two are commensurable.
Guler *et al.* 2009 [GGP+09]	ether against ester at C16	The only matched pair in the record; licenses the ester-to-ether transfer and bounds it. Its water-permeability ratio is at mismatched temperatures and resolves no difference.
Mathai *et al.* 2008 [MTNNZ08]	water P_f	Imported for P_f only. Its structural columns are literature and are superseded (Remark 7.3).
Paula *et al.* 1996 [PVVH+96]	P for H^+, K^+, water, urea, glycerol against thickness	The barrier and the chemiosmotic result. The $d = 27$ row is di-C18:1 with the double bond at the chain centre.
Mansy *et al.* 2008 [MSK+08]	nucleotide permeation	Measured on fatty-acid vesicles. The transfer to a phospholipid membrane is *refused* and that refusal is Theorem 10.8.
White 1973, 1978 [Whi73, Whi78]	specific capacitance	The solvent-free value. A thickness read off a capacitance is a model output and is not imported.
Jordan *et al.* 2019 [JRZ+19]	fatty-acid vesicle formation	The single-chain comparand class for route P.
Chrysene regiochemistry [PKH+03, SCMA+03, JMD16, PGS+86]	attack positions	Proposition 5.4; and the withdrawal of this paper's own K-region assumption (Remark 5.3).
Ring opening [MFDC01, NHS+18, NKK+11]	carbon conservation	The precedent for one carbon-conserving cleavage, and the measured chrysene sequence that loses carbon at every cycle.
Negatives [TJBS21, HS25, LWG17, MAM+00]	absence of instances	Notation 5.6. Each is an absence together with positive evidence about what the method does instead, and each was obtained under conditions that are not the architecture's (Remark 5.7).

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