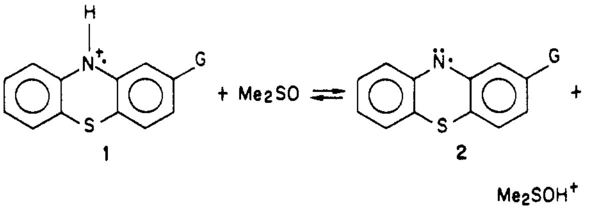
Table I. Equilibrium Acidities of Radical Cations Derived from Phenothiazine (Pz-H) and Fluorene (FlH$_2$), as Estimated from Acidity and Oxidation Potential Data (eq 1-4) in Me$_2$SO Solution at 25 °C.

HA	pK_{HA}	$E_{ox}(A^-)^e$	E_{ox}(HA)	p$K_{\cdot HA}{}^{+j}$
Pz-H	22.7[a]	-0.107	+0.985[f]	4.3[k]
2-MeO-Pz-H	22.5[b]	-0.119	+0.943[f]	4.6
2-Cl-Pz-H	20.8[a]	+0.038	+1.042[f]	3.9
2-F$_3$C-Pz-H	20.65[c]	+0.058	+1.084[f]	3.4
FlH$_2$	22.6[a]	-0.194	+2.1[g]	-16
2-MeO-FlH$_2$	22.75[d]	-0.189	+1.8[h]	-11
2,7-(MeO)$_2$FlH$_2$	22.95[d]	-0.195	+1.53[f,i]	-6

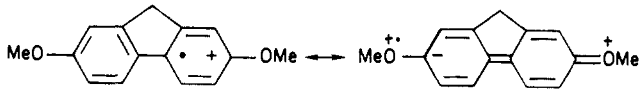
[a] Reference 8. [b] Measured by A. H. Clemens. [c] Present work. [d] Reference 9. [e] Irreversible oxidation potentials equal to the peak oxidation current measured by cyclic voltammetry using Pt and Ag/AgI working electrodes in Me$_2$SO solution with 0.1 M tetraethylammonium tetrafluoroborate electrolyte at a sweep rate of 100 mV/s (reproducible to <±10 mV); reversible ferrocene–ferrocinium redox couple at $E_{1/2}$ = 0.875 was used as a standard. [f] Reversible; the E_{ox} value is equal to one-half the sum of the voltages at peak oxidative and reductive currents. [g] Measured in CH$_3$CN; E_p for a shoulder preceding a wide irreversible wave with an E_p maximum at 2.4–2.5 V.[10] [h] Measured in CH$_3$CN; E_p for a narrow irreversible wave.[10] [i] Reversible in CH$_3$CN, but irreversible in Me$_2$SO.[10] [j] $pK_{\cdot HA}{}^+ = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)] \times 23/1.37$. These values are estimated to have an accuracy of ±2 pK units, based on the assumption that E_{ox} values are accurate to ±0.1 V. The value for fluorene itself is less certain. [k] Alkaitas[4] reports 4–5 in H$_2$O.

distributed between nitrogen and sulfur,[17] and the positive charge can be delocalized to the 2-substituent by resonance. The major effect of the 2-substituents on equilibrium 5 will be exerted on **1**, since remote substituent effects on radicals are small.[18] The decrease in acidity caused by the 2-MeO substituent and the increase caused by the 2-Cl and 2-CF$_3$ substituents is in line with their electron-donor and -acceptor effects, respectively. The p$K_{HA^{+\cdot}}$ for phenothiazine in Me$_2$SO is expected to be within one unit of that in water, as observed,[4] by analogy with the small difference in relative acidities of amine conjugate acids in these solvents.[19]



(5)

The high acidity found for the three fluorene radical cations in Table I is consistent with the high acidity reported for toluene[7] and for polymethylbenzene[20] radical cations. Also, the oxidation potential of 2,7-dimethoxyfluorene has been shown to be reversible when F$_3$CCO$_2$H is added to the CH$_2$Cl$_2$ solvent, suggesting that the irreversible behavior in its absence is associated with loss of a proton to the solvent.[21] The stronger acid-weakening effect of a methoxyl substituent on a radical cation C–H acid than on a radical cation N–H acid (Table I) is understandable since delocalization of the positive charge provides strong stabilization of the high-energy radical cation C–H acid formed by e_T^- from the π system (e.g., **3a**,**b**). Since the pK_{HA} and $E_{ox}(A^-)$ values for the three fluorenes differ but little (Table I), the acid-weakening MeO effects are caused almost entirely by differences in the E_{ox}(HA) values.[22] (The $\Delta pK_{HA^{+\cdot}}$ values calculated by method I of Nicholas and Arnold,[7] assuming a BDE value of 80 ± 5 kcal/mol for fluorene,[23,24] are −14, −9, and −5.) In contrast, the acid-weakening effect of the MeO substituent in 2-methoxy phenothiazine is relatively small because the radical cation N–H acid is formed by transfer of an electron from nitrogen (**1**). Note that the (reversible) E_{ox}(HA) for 2-methoxyphenothiazine is 0.59 eV more negative than the (reversible) E_{ox}(HA) of 2,7-dimethoxyfluorene (in CH$_3$CN).[10] In Me$_2$SO, the latter E_{ox}(HA) becomes irreversible, because the radical cation is deprotonated by the more basic solvent. Extension of this method to additional radical cation C–H and N–H acids, as well as to O–H and S–H acids, is in progress.



3a **3b**

Acknowledgment. This research was supported by the National Science Foundation. We are grateful to M. Chehel-Amiran and J.-P. Cheng for the measurements of the E_{ox}(HA) values of the fluorenes in acetonitrile. Discussions with D. R. Arnold during the development of this method were most helpful.

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New Isomeric Tetranuclear Cluster Anions $Mo_4Cl_{12}{}^{3-}$: Fragments of the $(Mo_6Cl_8)Cl_6{}^{2-}$ Octahedral Cluster Anion

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Received January 6, 1986

The paucity of known tetranuclear molybdenum clusters has prompted investigations which have begun to yield a rich and interesting chemistry. The first tetranuclear molybdenum clusters isolated were the ternary solid-state compounds $Mo_4S_4Br_4$[1] and MMo_4S_8[2] (M = Al, Ga), utilizing high-temperature preparations. Solid-state tetranuclear clusters were also found in the oxide compounds $M_xMo_8O_{16}$ (M = K, x = 2; M = Ba, x = 1.14).[3] Discrete molecular clusters are also exemplified by several recent discoveries. Thermal decomposition of $Mo(CO)_4I_3^-$ in chlorobenzene[4] and reaction between HI and $Mo_2(O_2CCH_3)_4$ in methanol[5] produced the butterfly cluster $Mo_4I_{11}{}^{2-}$. Rational synthetic pathways began to emerge with the addition of two quadruply bonded dimeric units to form $Mo_4X_8L_4$ compounds (X = Cl, Br, I; L = PR$_3$, RCN, MeOH, THF).[6] Similarly, the molecules $Mo_4(O\text{-}i\text{-}Pr)_8X_4$ (X = Cl, Br), formed by the coupling of two triply bonded dimeric molecules, were shown to adopt different geometric configurations depending on which halide was present.[7] More recently, the first discrete tetrahedral clusters, $Mo_4S_4(CN)_{12}{}^{8-}$[8,9] and $Mo_4S_4(S_2CNR_2)_6$,[10] have been isolated.

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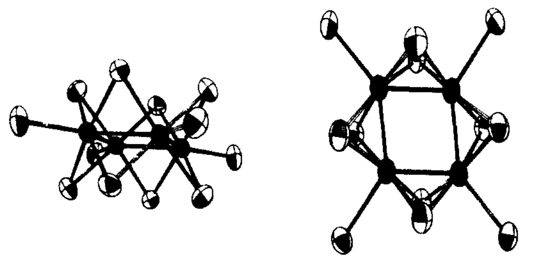

Figure 1. Two views of the planar cluster units found in $(Ph_4As)_2(Et_4N)Mo_4Cl_{12}\cdot 2CH_2Cl_2$ (V). Mo–Mo bond distances are 2.358 (2) and 2.653 (2) Å on the short and long edges of the rhombically distorted, rectangular cluster units. Average Mo–Cl distances are 2.434 (3) and 2.463 (3) Å for atoms bridging the long and short edges of the cluster, respectively, and 2.520 (3) Å for the terminal Cl atoms. The Mo–Mo–Mo bond angles are 99.06 (5)° and 80.94 (5)°. Mo atoms are represented by filled ellipsoids.

We report here the synthesis and characterization of novel tetranuclear chloromolybdate anions which are fragments of the larger hexanuclear anion, $(Mo_6Cl_8)Cl_6^{2-}$. These anions are also unusual because tetranuclear chloromolybdate anions have not previously been isolated although the remainder of the series of chloroanions, $MoCl_6^{3-}$,[9] $Mo_2Cl_8^{4-}$,[11] $Mo_2Cl_9^{3-}$,[12] $Mo_3Cl_{12}^{3-}$,[13] $Mo_5Cl_{13}^{2-}$,[14] and $Mo_6Cl_{14}^{2-}$,[15] have been previously reported. We have found that both $Mo_4Cl_{12}^{4-}$ and $Mo_4Cl_{12}^{3-}$ can be obtained, the latter in two different isomers.

The $Mo_4Cl_{12}^{4-}$ anion was first isolated from the reaction between $Mo_4Cl_8(MeOH)_4$[16] or $Mo_4Cl_8(NCEt)_4$ and $Et_4N^+Cl^-$ in refluxing dichloromethane (DCM), eq 1. The extremely air-sensitive,

$$Mo_4Cl_8(NCEt)_4 + 4Et_4N^+Cl^- \rightarrow \underset{\text{I}}{(Et_4N)_4Mo_4Cl_{12}} + 4EtCN \qquad (1)$$

insoluble purple product (I) precipitated in >95% yield. Reaction of I with methanol produced yellow $Mo_4Cl_8(OHMe)_4$, confirming retention of the tetranuclear cluster unit. However, in acetonitrile the cluster dissociates to produce the dimer $Mo_2Cl_4(NCMe)_4$.[17] Isolation of soluble salts $R_4Mo_4Cl_{12}$ with R = Ph_4P^+ (II), $(n\text{-}Bu)_4N^+$ (III), and $(n\text{-}Pr)_4N^+$ (IV) requires that the reactions between R^+Cl^- and $Mo_4Cl_8(NCEt)_4$ in dichloroethane be conducted at low temperature (>−10 °C) in order to prevent oxidation by the solvent.[18] Magnetic susceptibilities for I and II show that these compounds are diamagnetic over the range 8–300 K.[19]

One-electron oxidation of these compounds results in the formation of two isomers of $Mo_4Cl_{12}^{3-}$. The reaction between $Ph_4AsCl\cdot HCl$ and I in DCM, eq 2, provided black platelets of

$$(Et_4N)_4Mo_4Cl_{12} + 2Ph_4AsCl + HCl \rightarrow (Ph_4As)_2(Et_4N)Mo_4Cl_{12} + {}^1/_2H_2 + 3Et_4NCl \qquad (2)$$

$(Ph_4As)_2(Et_4N)Mo_4Cl_{12}\cdot 2CH_2Cl_2$ (V). An X-ray structure determination of V revealed the planar rhomboidal (distorted rectangular) cluster configuration shown in Figure 1.[20] Likewise, crystals of $(Pr_4N)_3Mo_4Cl_{12}\cdot 0.7C_2H_4Cl_2$ (VI) and $(Ph_4P)_3Mo_4Cl_{12}\cdot {}^1/_2Ph_4PI$ (VII), prepared by oxidation of IV and II with I_2 in DCE, were found to adopt structures having the $Mo_4Cl_{12}^{3-}$ anion with the same planar rhomboidal geometry.[21] On the other hand, oxidation of I with I_2, Cl_2, or $PhICl_2$ (1:0.5 mole ratio) in DCM resulted in an insoluble olive green powder, which after extended extraction with DCM provided a few crystals of $(Et_4N)_3Mo_4Cl_{12}$ (VIII). In VIII the $Mo_4Cl_{12}^{3-}$ cluster assumed the "butterfly" configuration shown in Figure 2.[22] Magnetic susceptibilities demonstrated the expected paramagnetism of VI and VIII, with moments of 1.72 and 1.63 μ_B, respectively.

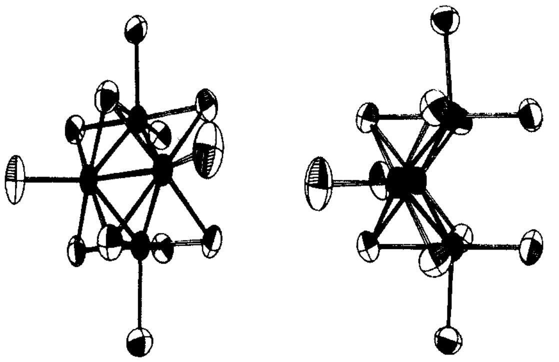

Figure 2. Two views of the butterfly cluster unit in $(Et_4N)_3Mo_4Cl_{12}$ (VIII). Some bond distances: Mo(basal)–Mo(basal) 2.598 (1); Mo(apical)–Mo(basal) 2.552 (1), 2.501 (1); Mo(apical)–Mo(apical) 3.392 (1); Mo–Cl(triply bridging) 2.501 (6), Mo–Cl(doubly bridging) 2.444 (6), Mo–Cl(terminal) 2.470 (6) Å. The dihedral angle between the two Mo_3 planes is 104°. Mo atoms are represented by filled ellipsoids.

Both isomers of $Mo_4Cl_{12}^{3-}$ can be viewed as fragments of the octahedral cluster anion $(Mo_6Cl_8)Cl_6^{2-}$. Removal of two trans Mo atoms along with their terminal Cl atoms from the latter would produce a planar cluster unit related to those observed here, while removal of two cis Mo atoms and their terminal Cl atoms would yield the butterfly cluster. The occurrence of both planar and butterfly isomers is reminiscent of the related structures found in $Mo_4(O\text{-}i\text{-}Pr)_8X_4$ compounds, where a square-planar cluster occurs for X = Cl and the butterfly cluster results when X = Br.[7] Factors favoring one configuration over the other are not known. In the alkoxide clusters the butterfly configuration appears to be favored in solution,[23] while in the $Mo_4Cl_{12}^{3-}$ case the planar unit is evidently the dominant solution species.

The planar isomer of $Mo_4Cl_{12}^{3-}$ apparently adopts the rhombically distorted rectangular geometry because of Jahn–Teller interactions. Extended Hückel[24] and Fenske–Hall calculations[23] show that the hypothetical square (D_{4h}) geometry for $Mo_4Cl_{12}^{3-}$ results in an ^2E_g ground state arising from a formally nonbonding HOMO with e_g^3 electron configuration. Rectangular distortion lowers the symmetry to D_{2h}, splits the orbital degeneracy to create additional bonding levels, and creates a $^2B_{3u}$ ground state. Further distortion driven by coupling of the ground state with a low-lying $^2B_{2u}$ excited state through a B_{1g} vibrationl mode produces the rhombic cluster unit. The actual bond distances and angles within these electronically pliant species also must be influenced somewhat by crystal packing forces.

Additionally, we note that the butterfly isomer of $Mo_4Cl_{12}^{3-}$ is closely related to the cluster $Mo_4I_{11}^{2-}$.[4] With X = Cl or I,

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(18) Satisfactory elemental analyses were obtained for I, II, and IV. The identity of III was determined by comparison of its visible and far-infrared spectra with I. All (I–IV) show identical bands at 347 (w), 300 (vs), and 279 (s) cm^{-1} in the far-infrared and at 563, 454, and 378 nm in the UV–visible spectra of Nujol mulls.

(19) Compounds I and II also failed to show any signal in the EPR spectra of the powdered materials.

(20) Structure was refined to $R = 0.055$, $R_w = 0.066$ in the monoclinic space group $P2_1/a$, $a = 17.018$ (3) Å, $b = 17.680$ (2) Å, $c = 13.072$ (3) Å, $\beta = 113.072$ (17)°.

(21) Relevant crystal data: VI, space group $P2_1/a$; $R = 0.062$; $a = 17.554$ (14) Å, $b = 15.854$ (7) Å, $c = 18.111$ (12) Å, $\beta = 102.92$ (5)°. VII, space group $P2_1/a$; $R = 0.091$; $a = 18.354$ (3) Å, $b = 31.571$ (4) Å, $c = 11.254$ (2) Å, $\beta = 105.27$ (1)°.

(22) Crystal data for VIII: space group $I4_1/acd$; $a = 24.181$ (7) Å, $c = 30.826$ (18) Å; 16 clusters/unit cell; $R = 0.054$, $R_w = 0.058$.

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$Mo_4X_{11}^{2-}$ can be obtained from $Mo_4X_{12}^{3-}$ by loss of X^- from an inner position of the cluster $(Mo_4X_8)X_4^{3-} \rightarrow (Mo_4X_7)X_4^{2-} + X^-$. Alleviation of steric congestion, caused by the large size of I atoms, presumably leads to loss of I^- and stabilization of $Mo_4I_{11}^{2-}$. Finally, the square-pyramidal cluster $Mo_5Cl_{13}^{2-}$ can be considered as a fragment of the $Mo_6Cl_{14}^{2-}$ anion[14] and formed as a result of addition of $MoCl^+$ to the $Mo_4Cl_{12}^{3-}$ cluster unit. The structural relationships noted here indicate the possibility of rational syntheses of both homonuclear and heteronuclear clusters containing four, five, or six metal atoms. Such chemistry is under active investigation in this laboratory.

Acknowledgment. This work was supported by NSF Grant CHE-8406822. We thank Professor Robert Shelton for help with magnetic susceptibility measurements.

Supplementary Material Available: Complete listings of positional parameters, anisotropic thermal parameters, and bond distances and angles for $(Ph_4As)_2(Et_4N)Mo_4Cl_{12}\cdot 2CH_2Cl_2$ and $(Et_4N)_3Mo_4Cl_{12}$ (14 pages). Ordering information is given on any current masthead page.

Asymmetric Synthesis of Premonensin, a Potential Intermediate in the Biosynthesis of Monensin

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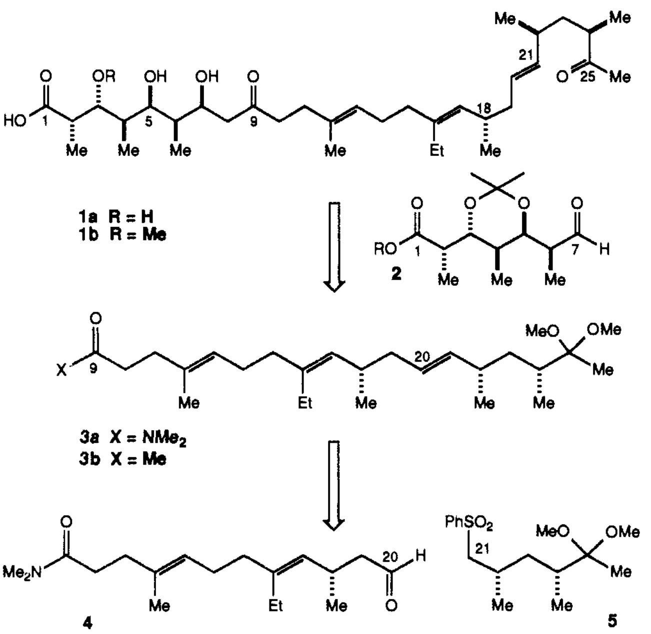
Received December 3, 1985

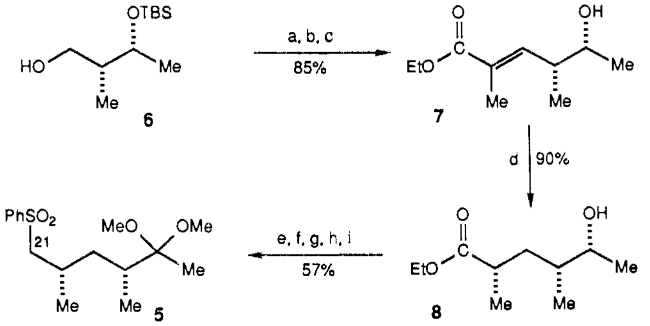
The Cane, Celmer, and Westley hypothesis on the biosynthesis of polyether antibiotics is an innovative contribution to the field of natural products chemistry.[1] Although the assemblage of the carbon skeleton of this class of compounds generally mimics fatty acid biosynthesis,[2] the construction of the polyether portion of these structures is without precedent. In 1982, Cane and co-workers proposed a mechanism for the formation of this structural element of monensin A.[3] Their isotopic labeling experiments, combined with projections provided by Westley,[4] implicated the triene **1a**, premonensin triene, as a probable intermediate in the biosynthesis of monensin. Recently, a synthesis of premonensin methyl ether (**1b**) has been reported;[5] however, indirect evidence implicates **1a** as a more likely intermediate in the biosynthesis.[6] In conjunction with projected studies which might illuminate the later events in the biosynthesis of monensin A, we have completed an asymmetric synthesis of premonensin (**1a**). The obvious disconnection strategy for the structure is illustrated in Scheme I.

The asymmetric synthesis of the C_{21}–C_{26} synthon **5** (Scheme II) evolved from the monoprotected diol **6** which was efficiently constructed via the asymmetric aldol reactions reported earlier.[7]

Scheme I

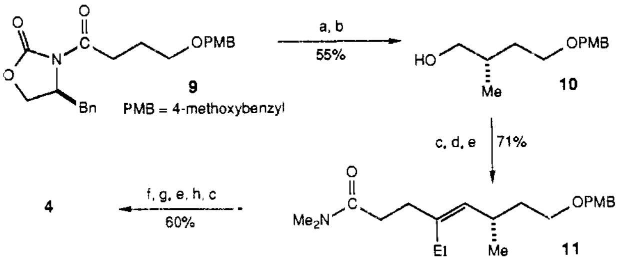


Scheme II[a]



[a] (a) $(COCl)_2$, DMSO, CH_2Cl_2, −78 °C; Et_3N; (b) (carboethoxyethylidene)triphenylphosphorane, toluene, 50 °C; (c) HF, CH_3CN; (d) $[Rh(NBD)(+)\text{-}BINAP]BF_4$, H_2, 1000 psi, CH_2Cl_2; (e) TBSCl, imidazole, DMF; (f) DIBAL, CH_2Cl_2, −78 °C; (g) $(PhS)_2$, n-Bu_3P, CH_2Cl_2; Oxone, MeOH, H_2O; (h) pyr·SO_3, Me_2SO, Et_3N; (i) $HC(OMe)_3$, PPTS, MeOH.

Scheme III[a]



[a] (a) $NaN(TMS)_2$, THF, −78 °C; MeI; (b) LAH, Et_2O, −30 °C; (c) $(COCl)_2$, Me_2SO, CH_2Cl_2, −78 °C; Et_3N; (d) 2-lithiobutene, THF, −78 °C; (e) $Me_2NC(OMe)_2Me$, cyclohexane, 80 °C; (f) $Li(EtO)_3AlH$, Et_2O, −30 °C; (g) 2-lithiopropene, THF, −78 °C; (h) DDQ, CH_2Cl_2, H_2O.

Successive oxidation[8] of **6** and subsequent Wittig reaction of the resultant aldehyde with the illustrated phosphorane (toluene, 70 °C, 12 h) afforded exclusively the derived E-α,β-unsaturated ester which was disilylated (HF, MeCN, 25 °C, 1 h)[9] to hydroxy ester **7** (85% overall). Recent results from this laboratory have doc-

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[7] **6** was prepared as follows: (1) (S)-3-(1-oxopropyl)-4-(phenylmethyl)-2-oxazolidinone, n-Bu_2BOTf, Et_3N, 0 °C; −78 °C, CH_3CHO; 0 °C, H_2O_2, MeOH, pH 7 buffer; (2) TBS-Cl, imidazole, DMF (85% overall); (3) $C_6H_5CH_2OLi$, THF, 0 °C (75%); (4) DIBAL, CH_2Cl_2, −78 °C (75%). 61% overall yield. For chiral aldol methodology, see: Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127. Full details are included in the supplementary material.

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