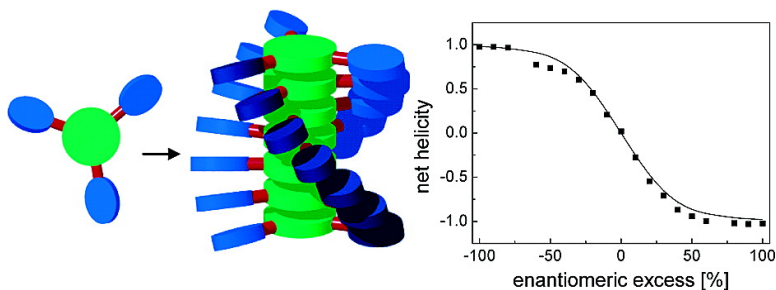


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“Majority-Rules” Operative in Chiral Columnar Stacks of C_3 -Symmetrical Molecules

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Abstract: C_3 -symmetrical disks **1**, preorganized by acylated 2,2'-bipyridine-3,3'-diamine moieties and decorated with nine identical chiral, lipophilic tails, aggregate into a dynamic helix in apolar solvents. The aggregates, previously shown to be governed by the “sergeants-and-soldiers” principle when mixed with achiral analogues, are now also revealed to obey the “majority-rules” effect, a phenomenon not earlier observed in nonpolymers. Our experimental circular dichroism data can be accurately described with a recently developed theory. A fit of the theory to the experimental results shows that the mismatch penalty, i.e., the free energy of a monomer present in a helix of its nonpreferred screw sense (0.94 kJ/mol), is about 8 times lower than the penalty for a helix reversal (7.8 kJ/mol). This corresponds well to our vision of the supramolecular architecture of the disks.

Introduction

Amplification of chirality is a well-known phenomenon in solutions of (stiff) helical polymers.¹ Pioneering studies by Green and co-workers distinguished two effects that influence the amplification of chirality and referred to them as the “sergeants-and-soldiers” principle and “majority-rules” effect.² The sergeants-and-soldiers principle implies the control of the movements of large numbers of cooperative achiral units (the soldiers) by a few chiral units (the sergeants), whereas in the majority-rules effect, a slight excess of one enantiomer leads

to a strong bias toward the helical sense preferred by the enantiomer that is present in majority.

Over the past few years, several examples have been presented showing that the sergeants-and-soldiers principle is also operational in noncovalently bound, low molecular weight systems.³ Notably, C_3 -symmetrical disk-shaped compounds forming helical columnar stacks as a result of cooperative π - π -stacking and intermolecular H-bonding interactions (Figure 1) were found to show strong sergeants-and-soldiers effects both in polar and apolar solvents.^{3a,b} These effects could be accurately described in terms of a one-dimensional two-component Ising model.⁴

Although the majority-rules effect was found to be operational in polymeric systems, such as polyisocyanates and polythiophenes, examples employing noncovalently bound helical aggregates are to the best of our knowledge nonexistent.^{1e,2b-f} Here, we describe the majority-rules effect in chiral columnar stacks of compound **1** (Figure 2). To quantify this effect, a recently described predictive model is applied.⁵ Finally, the

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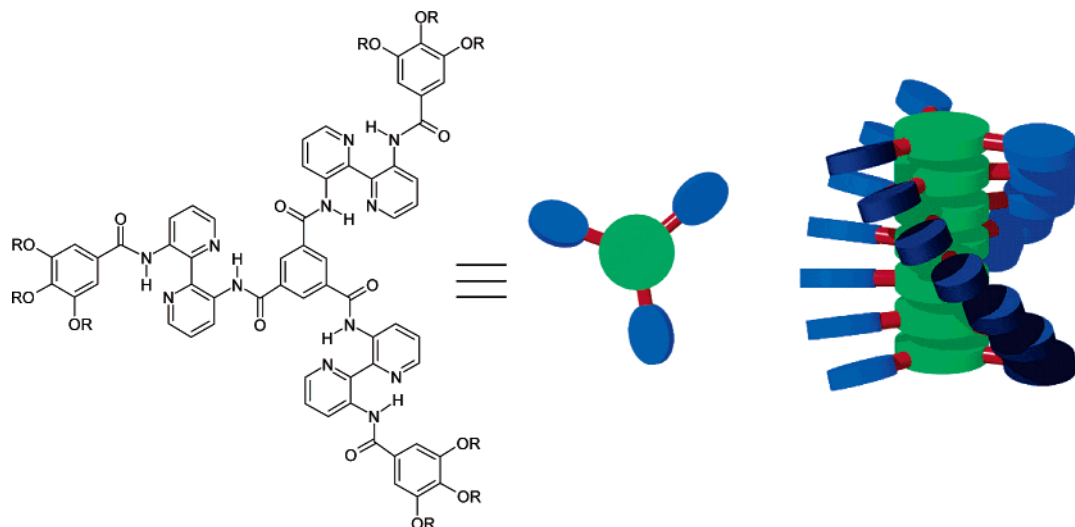


Figure 1. Self-assembled helical aggregates of C_3 -symmetrical disks based on 3,3'-diamino-2,2'-bipyridine.

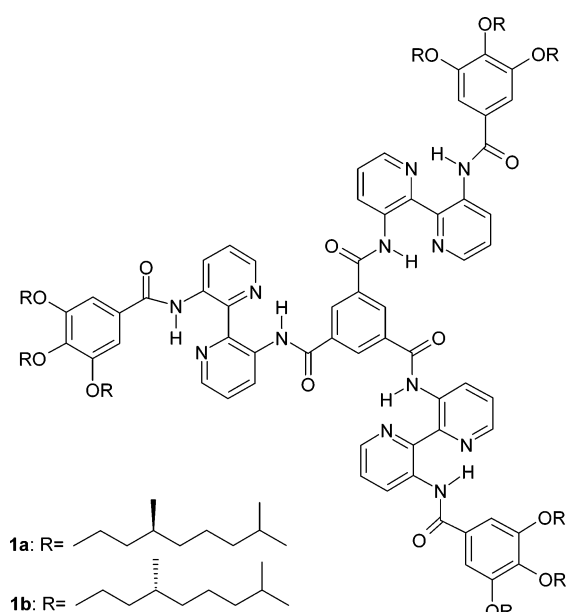


Figure 2. C_3 -symmetrical disk-shaped compound **1**; **1a** = all *S*-configuration and **1b** = all *R*-configuration in the side chains.

rationale behind the expression of the principles of sergeants-and-soldiers and majority-rules effects in the C_3 -symmetrical compounds shall be addressed.

Results and Discussion

Compounds (*S*)-**1a** and (*R*)-**1b** only differ in the stereoconfiguration at C-3 of the nine aliphatic side chains (see Figure 2). Both compounds were synthesized according to a previously described procedure for **1a** starting from (*S*)- or (*R*)-citronellol to introduce the chiral side chains, resulting in (*S*)-**1a** and (*R*)-**1b**, respectively.⁶ Optical rotation measurements showed opposite signs for the optical rotation of (*S*)-**1a** and (*R*)-**1b** of -8.23° and $+7.70^\circ$, respectively. Stock solutions of (*S*)-**1a** and (*R*)-**1b** were prepared in octane ($c = 2.49 \times 10^{-5}$ M) to perform UV and CD measurements. The UV spectra of both compounds were identical while the CD spectra showed the expected mirror

image relationship with strong Cotton effects in the bipyridine transitions at $\lambda = 387$ and 369 nm (Figure 3a).⁷ The $\Delta\epsilon$ values at $\lambda = 387$ nm amount to -33.9 and $+32.6$ L/mol cm for pure (*S*)-**1a** and (*R*)-**1b**, respectively. The small deviations in the Cotton effect are in correspondence with the deviation in optical rotation, suggesting that the (*R*)-enantiomer is less optically pure. This may reflect the small difference in optical purity of the commercially available citronellol enantiomers: $[\alpha]_D$ (*S*)-citronellol = -4.60 and $[\alpha]_D$ (*R*)-citronellol = $+4.46$.

Subsequently, stock solutions of (*S*)-**1a** and (*R*)-**1b** were mixed in different volumetric ratios. Assuming that each stock solution contains an enantiomeric excess (ee) of 100% for (*S*)-**1a** and (*R*)-**1b**, respectively, the ee's of the mixtures were calculated from the volumes of each identically concentrated stock solution. At $\lambda = 387$ nm, the anisotropy factor, *g*, was determined as a function of the ee, and the results are summarized in Figure 3b. This figure clearly shows the nonlinear dependence of the anisotropy factor on the ee, suggesting that a "majority-rules" effect is operational indeed. Upon increasing the temperature to 50°C , the effect is retained, although, as expected, the absolute values of *g* are smaller than at 20°C .⁸ This decrease of the Cotton effect with increasing temperature has been observed repeatedly and is ascribed to deaggregation.^{3a} Nonetheless, the majority-rules effect remains present also at 50°C .

To gain a deeper insight into the dependence of the Cotton effect on the enantiomeric excess, we have compared our results to a recently published theory.⁵ While this theory is not the first to deal with the majority-rules effect,⁹ it is the only one that is applicable to self-assembled aggregates, at least in principle.^{4,5} The model we applied captures the details of the chemical architecture of the aggregates in two free-energy penalties.⁵ The

(7) Concentration-dependent UV measurements in the range from 10^{-3} to 10^{-6} mol/L of compound **1a** in hexane showed spectra with identical shapes. This suggests that also at 10^{-6} mol/L all molecules are in an aggregated state. The corresponding CD spectra show Cotton effects of similar size, suggesting that also at 10^{-6} mol/L the aggregates are long. See ref 3a for details.

(8) Temperature-dependent UV and CD measurements of **1a** in dodecane show a steady decrease of the CD effect and a shift to lower wavelength in the UV. This is consistent with a decreased aggregation length. At 100°C in dodecane, the UV spectrum of **1a** resembles the UV spectrum of **1a** in CHCl_3 , a solvent in which **1a** is molecularly dissolved. The CD effect at 100°C is, as expected, close to zero. See ref 3a for details.

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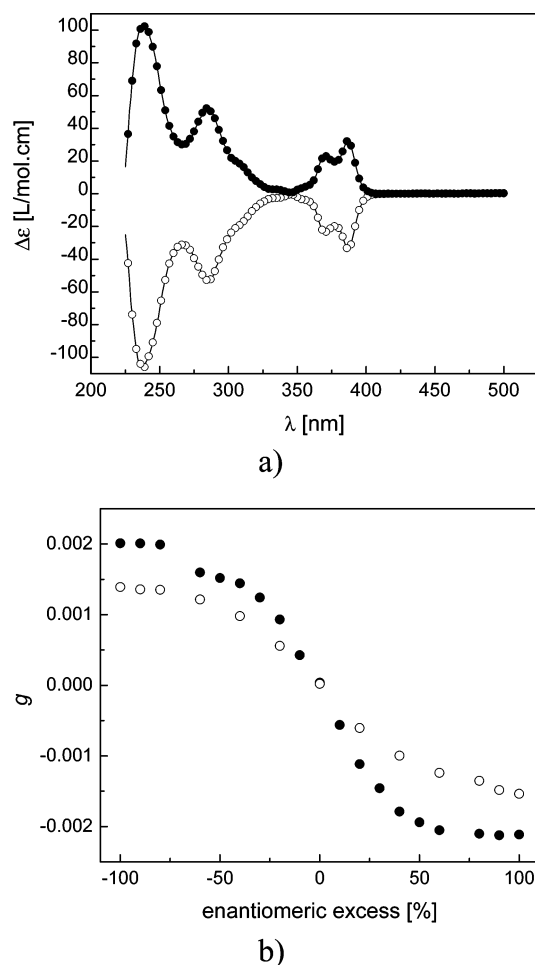


Figure 3. (a) CD spectra in *n*-octane of compounds (*S*)-**1a** (open circles) and (*R*)-**1b** (closed circles); $c = 2.49 \times 10^{-5}$ M. (b) Anisotropy factor g as a function of the enantiomeric excess for mixtures of (*S*)-**1a** and (*R*)-**1b** at 20 °C (closed circles) and 50 °C (open circles).

first (denoted R) penalizes reversals in the helical screw sense along the chain, and the second arises when a monomer is present in a helix of its nonpreferred screw sense. The latter is referred to as the mismatch penalty and is denoted M . By comparing theory and experiment, values may be extracted for these free-energy penalties. Note that, in doing so, we implicitly assumed that the aggregates are relatively long, compared to the correlation length of their right- and left-handed helical regions, i.e., the number of monomers that any one monomer influences. This is justified, because for the concentration at which the measurements were performed ($\sim 10^{-5}$ M), the Cotton effect was found to be virtually concentration-independent,^{3a} which implies that the aggregates are indeed long.⁴ Note, however, that the concentration dependence becomes more pronounced with increasing temperature.^{3a} Therefore, we compared the theory only with the results of the measurements performed at the lowest temperature, i.e., 20 °C, where the concentration dependence is minimal.

To compare theory and experiment, we connect the experimentally measured Cotton effect to the net helicity of the chains (i.e., the fraction of right-handed helical material minus that of left-handed material). For this, we renormalized the experimental anisotropy factor g to equal unity at its maximum. (Note that, since the magnitude of the Cotton effect of **1a** differs somewhat from that of **1b**, we used the mean of these two values to

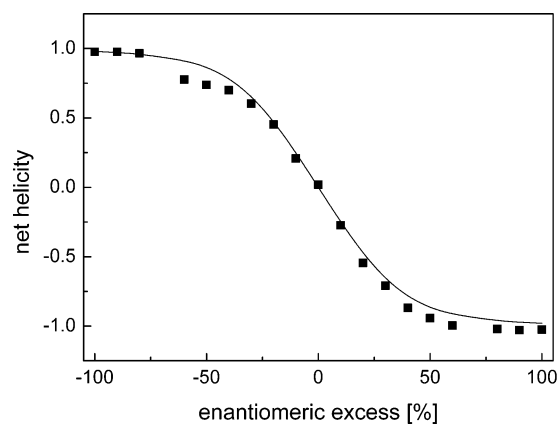


Figure 4. Net helicity as a function of enantiomeric excess. Symbols indicate CD results for mixtures of (*S*)-**1a** and (*R*)-**1b** in *n*-octane at 20 °C. The line indicates the theoretical result that gives the closest agreement with the experiment.

renormalize the curve.) This renormalization means that we assume that the chains are fully right-handed or fully left-handed helical when only one type of enantiomer is used. This assumption seems valid since the CD curve approaches its maximum value before the enantiomeric excess equals unity.¹⁰ The theoretical enantiomeric excess is defined as the fraction of **1a** minus that of **1b**, expressed in percentiles.

From the renormalized CD results (Figure 4) we extracted the enantiomeric excess required to achieve 50% of the maximum net helicity at 20 °C. This value (averaged for the case where an excess of right-handed and that where an excess of left-handed monomers is used) lies at an ee of ± 0.2 . Comparison of this value with results previously described⁵ gives limits for the values of R and M : R must lie above $3.1k_B T$ (7.5 kJ/mol), and M must be smaller than $1.1k_B T$ (2.7 kJ/mol), with T being the absolute temperature and k_B being Boltzmann's constant. To determine the exact values of M and R best describing the experiments, we applied a least-squares-type fitting procedure. For this, we calculated the net helicity at the values of the enantiomeric excesses investigated in this experiment and subtracted the experimental net helicity from the theoretical one at each of these values. The sum over all data points of the square of these differences then gives a measure of the quality of the curve fit. The value of M that minimizes this sum of squares for several fixed values of R was then determined. The lowest of these minimum values was selected, and then the values of both R and M were varied until the overall best agreement was found. In this way, we obtained optimal values of $M = 0.39k_B T$ (0.94 kJ/mol) and $R = 3.2k_B T$ (7.8 kJ/mol). The theoretical curve that corresponds to these values is depicted in Figure 4 and exhibits a good agreement with the experimental results. The values of the free-energy penalties indicate that a helix reversal is much more unfavorable than a mismatch, a result which mirrors that for polyisocyanate copolymers.^{2b,c,9} There, a comparison between experiment and theory yielded values of $R = 6.1k_B T$ and $M = 0.1k_B T$.⁵ The discotic monomers seem to form helix reversals more readily than the polyisocyanates do, but their mismatch penalty is somewhat higher.

When one considers the architecture of the disk-shaped molecules **1**, it makes sense that the helix reversal should be

(10) For a more in-depth discussion about the translation from optical results to a net helicity, see ref 5.

much more unfavorable than a mismatch, since these individual molecules are preorganized to form a helix, even when no chirality is present at the periphery. The observation of chirality amplification in the context of molecular architecture for C_3 -symmetrical disks is discussed in more detail below.

In C_3 -symmetrical molecules **1**, a strong tendency exists to aggregate in apolar solvents.^{3a} A first consideration to rationalize this behavior is the propensity of the mesogenic peripheral groups and the huge central core to undergo phase separation in the bulk, also in the case of nonchiral analogues. X-ray diffraction reveals an ordered hexagonal columnar LC-phase in which the cofacial interdisk distance amounts to ~ 3.4 Å, while the lateral interactions of the mesogenic groups give rise to the hexagonal arrangement of the columns and a quadruplet splitting at ~ 17.5 Å assigned to the pitch of the helix.⁶ Polarization microscopy on dilute solutions in alkanes revealed that the lateral interactions are easily lost, but UV spectroscopy showed that the cofacial interactions survive even below 10^{-6} M.^{3a} Therefore, it seems justified to consider the intervention of π - π -interactions as a driving force for aggregation. A second consideration is the presence of three amide bonds at the central benzene core capable of intermolecular hydrogen bonding of the α -helix type.¹¹ In similar systems these 3-fold hydrogen bonds were found to lock the molecules together and are the driving force for the expression of chirality.¹² In the system described here, the consequence of a combination of π - π -stacking between the central trimesic units and 3-fold intermolecular hydrogen bonding of the α -helix type is that the amide bonds are significantly tilted with respect to the helical axis to reconcile the 5.5 Å distance between two superimposed hydrogen bonds ($H\cdots O=C-N-H$) with the 3.4 Å cofacial interdisk distance. This implies a rotation of superimposed bipyridine units to construct a strongly bound propeller-shaped structure (see Figure 1), presumably accompanied by a deviation from coplanarity within a bipyridine moiety. The latter may render this chromophore chiral, as measured by CD spectroscopy when homochiral peripheral information is present. In line with the red shift in UV that accompanies aggregation,^{3a} superimposed bipyridine moieties in the ordered stacks are subject to strong translation.¹³ Molecular models clearly indicate that in order to keep the distance between the trimesic and the bipyridine moieties of superposed molecules at ~ 3.4 Å distance, a tilt of the amides and a strong rotation and translation of the bipyridine moieties are necessary. A result of the enforced propeller shape of the molecules is that stacking inevitably leads to a helical superstructure and, if homochiral peripheral information is present, a preferred helical sense will result.

If at the periphery contradictory chiral information is present, as is the case in the majority-rules experiments, it is plausible that the energy gained by aggregation is still larger than the energy lost by a mismatch. After all, in the system discussed here, the "wrong" enantiomer has a different orientation of a methyl group in the disordered aliphatic part of the molecule. If present in small amounts, this minor enantiomer is unlikely to strongly affect the helicity of the aggregate and will act in accordance with the helical sense preferred by the majority.

Indeed, the values obtained by fitting the experimental data with the model discussed above confirm this: the mismatch penalty (0.94 kJ/mol) is about 8 times lower than the penalty for a helix reversal (7.8 kJ/mol).

We now take a closer look at the intriguing question why the C_3 -symmetrical disk-shaped molecules **1a** and **1b** obey the sergeants-and-soldiers principle and the majority-rules effect.^{3a} Most probably, the C_3 -symmetry present in compound **1**, in combination with a subtle matching of the π - π -stacking interactions and the α -helix-type hydrogen bonding, guarantees a highly dynamic nature of the aggregation process. The C_3 -symmetry inevitably generates a void space, which is an element of instability in crystals, rationalizing the scarcity of C_3 -symmetrical crystals.¹⁴ However, this void space, in combination with delicately tuned secondary interactions, allows for adaptive docking and dedocking of molecules during the aggregation process in solution. The importance of the careful matching of secondary interactions in the aggregation process is illustrated by the aggregation behavior of analogous C_3 -symmetrical molecules provided with additional methoxy substituents on the bipyridine units or C_3 -symmetrical molecules containing diphenylpyrazine moieties. These molecules were shown to give rise to stronger aggregation as expected in view of their stronger π - π -interaction but lack any expression of the sergeants-and-soldiers principle.¹⁵

Conclusions

In summary, we have shown that C_3 -discotic molecules such as **1a** and **1b** are equipped with a combination of features that guarantees highly ordered hierarchical growth. Phase separation between periphery and core and a balanced interplay between π - π -stacking and 3-fold intermolecular hydrogen bonding allows for the construction of highly ordered helical stacks. These aggregates, previously shown to be governed by the sergeants-and-soldiers principle, are now also revealed to obey the majority-rules effect, a phenomenon not earlier observed in nonpolymers. A recently developed theory is found to accurately describe the majority-rules principle in these aggregates and yields a mismatch penalty, i.e., a free energy penalty on a monomer present in a helix of its nonpreferred screw sense (0.94 kJ/mol), that is approximately a factor of 8 lower than the penalty on a helix reversal (7.8 kJ/mol). This is in good agreement with our understanding of the molecular architecture of the aggregates. We believe that the combination of majority-rules experiments and theory may be of general application in appropriate helical aggregates and can give more insight in the details of the aggregation behavior.

Experimental Procedures

UV spectra were taken on a Perkin-Elmer Lambda 3B UV-vis spectrophotometer. CD measurements were recorded on a Jasco J-600 spectropolarimeter. All experiments were conducted using *n*-octane pro analysis (p.a.) as the solvent. The anisotropy value was calculated from $\Delta\epsilon$ and ϵ : $g = \Delta\epsilon/\epsilon$. Optical rotations were recorded at room temperature on a Jasco DIP-370 polarimeter at a wavelength of 589 nm (Na_D -line). (*S*)-Citronellol was purchased from Takasago ($[\alpha]_D = -4.60$) and (*R*)-citronellol from Aldrich ($[\alpha]_D = +4.46$). Efforts to distinguish the commercially available (*R*)- and (*S*)-citronellol analyti-

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cally or by derivatization failed. Compounds **1a/b** were prepared as previously described.⁶ Analytical data for **1b**: $[\alpha]_D = +7.70$ (CHCl₃, $c = 0.51$ g/dL). ¹H NMR (CDCl₃): δ 15.52 (s, 3H, NHCO), 14.40 (s, 3H, NH'CO), 9.60 (dd, 3H, H-4), 9.40 (dd, 3H, H-4'), 9.25 (s, 3H, H-ortho), 9.05 (d, 3H, H-6'), 8.44 (d, 3H, H-6), 7.54 (m, 6H, H-5 and H-5'), 7.32 (s, 6H, H-ortho'), 4.07 (m, 18H, OCH₂), 1.88 (m, 9H, OCH₂CH), 1.75 (bs, 9H, OCH₂CH), 1.55 (m, 18H, C*HCH₃CH₂), 1.33 (m, 27H, C*H and C*HCH₃CH₂CH₂), 1.15 (m, 27H, CH(CH₃)₂ and CH₂CH(CH₃)₂), 0.95 (m, 27H, C*CH₃), 0.88 (dd, 54H, CH₃). Anal. Calcd for C₁₅₀H₂₂₂N₁₂O₁₅ (2433.47): C, 74.03; H, 9.19; N, 6.91. Found: C, 73.4; H, 9.2; N, 6.9.

Preparation of the Stock Solutions. **1a** and **1b** (6.06 mg, 2.49×10^{-3} mmol) were (separately) weighed into 100 mL volumetric flasks and around 50 mL of *n*-octane p.a. was added. The solution was sonicated for 30 min. After cooling, the volume was adjusted with

octane to 100 mL. UV measurement of both solutions confirmed that the concentrations were identical. Mixtures of **1a** and **1b** were prepared by adding to a 10 mL volumetric flask a defined volume of solution containing **1a** and filling the volumetric flask with the stock solution containing **1b** up to the 10 mL volume. The flasks were well-shaken before measuring the UV and CD spectra, ensuring complete mixing of the stock solutions. The enantiomeric excesses of the mixtures were calculated as follows: $ee = (V_{1a} - V_{1b}) / (V_{1a} + V_{1b})$ in which V_{1a} and V_{1b} represent the volumes of the stock solutions used of **1a** and **1b**, respectively.

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