A comparison of the behaviour of (4*R*,5*R*)-bis(diphenylhydroxymethyl)-2-spiro-1'-cyclohexane-1,3-dioxolane in isolated studies and in the presence of water.

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Introduction

Host-guest chemistry is a subset of supramolecular chemistry where the host binds to the guest to produce a host-guest complex.[1] The host is trapped inside cavities that are only form when the guest is present.[1] The types of interactions that take place in complexation events are the non-covalent bonding.[1] The different types of interactions between host and guest include, π···π stacking interactions, X–H···π interactions and hydrogen bonding.[1]

The pyridine guest species all perform important roles in industry[2,3].

- Pyridine (PYR) acts as an acid scavenger in many organic reactions[4,5],
- 2-methylpyridine (2MP) is a precursor for 2-vinylpyridine,
- 3-methylpyridine (3MP) is a precursor to insecticides,
- And 4-methylpyrdine (4MP) is a precursor to the anti-tuberculosis drug, isoniazid.

Therefore, it is important the pyridyls be synthesized with high purity, however synthetic methods often result in mixtures due to their similar boiling points[6].

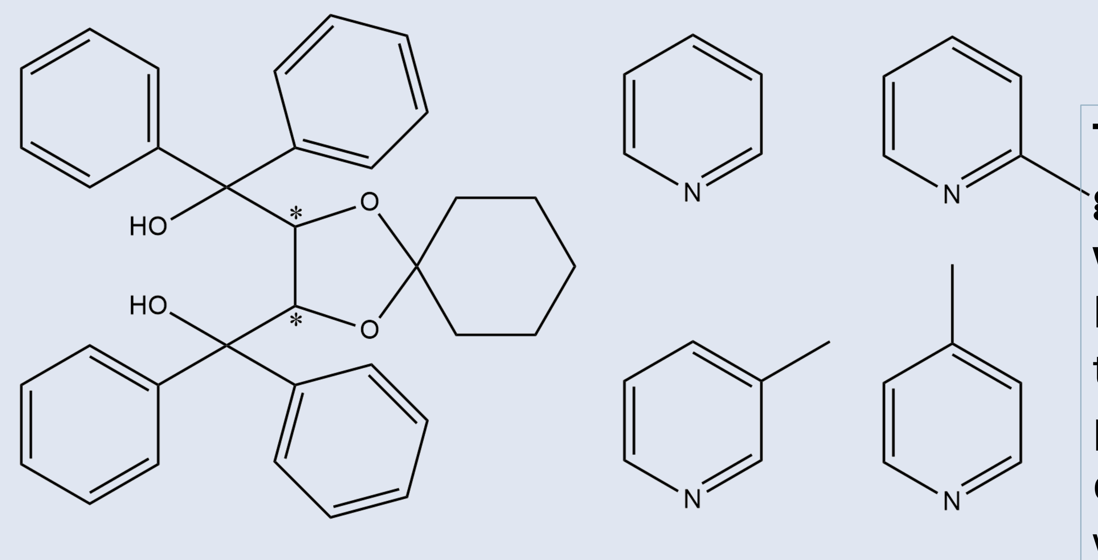


Figure 1 (above): The molecular structures of the host TADDOL6 and the guest series, PYR, 2MP, 3MP and 4MP.

The aim of the present investigation is to test the host ability of TADDOL6 in mixtures of the pyridyls and how the host behaves when exposed to water. As water pollution is a rising concern, methods for insuring clean drinking water are very important fields of study[7,8].

Methodology

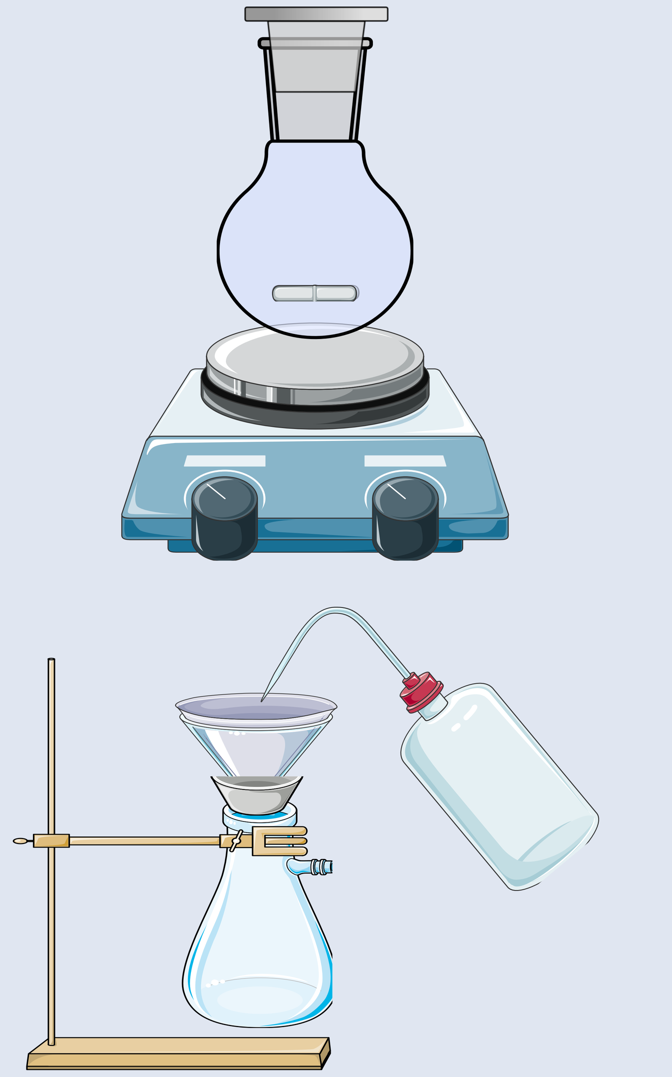
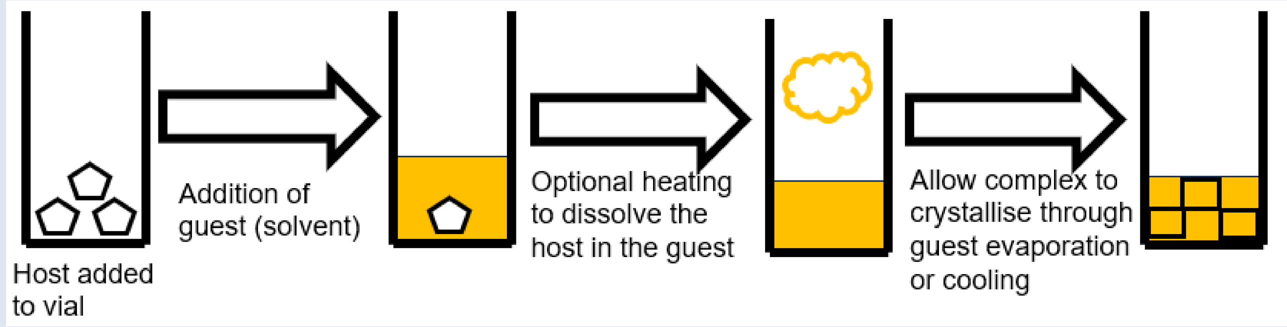


Figure 2 (left): An illustration on how the water studies were conducted[9].

To conduct the water studies, an amount of host, with excess guest were placed in a round bottomed flask and stirred for 2 days. Afterwards host was removed, rinsed and dried. The sample was then analysed by means of SCXRD and TGA.

Figure 3 (below): An illustration on how a host-guest experiment is prepared.

The host is placed in a pill vial and then dissolved by the guest, or mixture of guests. In single solvent experiments, some guest is allowed to evaporate, however in equimolar and selectivity studies, the vial is sealed. Once crystals form they are rinsed and prepared for NMR spectroscopy or GC.



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Results

Guest	H:G ratio	H:G ratio with water
PYR	1:1	2:1
2MP	1:1	1:0
3MP	1:1	1:1
4MP	1:1	2:1

Table 1: Host-guest ratios for each pyridyl guest species alone and when exposed to water.

NMR spectroscopy was used to determine the number of host vs guest molecules present in the crystal structure. It was determined TADDOL6 formed 1:1 H:G ratios with all the pyridyl guests. When water was added, TADDOL6 formed 2:1 H:G inclusion complexes with PYR and 4MP, a 1:1 H:G inclusion with 3MP and no inclusion formed with 2MP. The host was found to be insoluble in water which allowed for easy removal from the water.

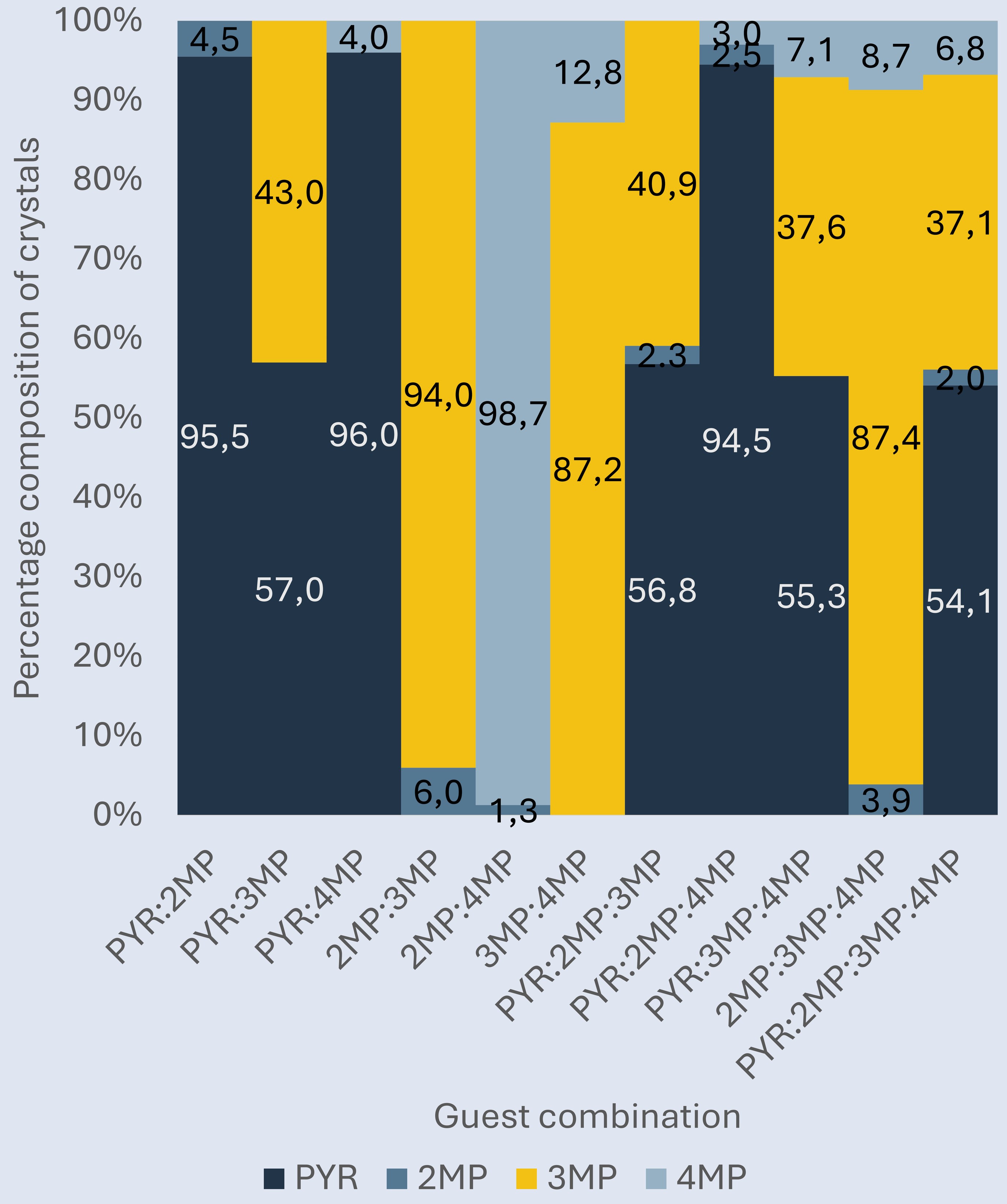

Figure 4: Guest:guest ratios for combinations of the pyridyl series.

The results of the equimolar, binary, ternary and tertiary experiments are summarised here. PYR was highly favoured in all combinations, followed by 3MP, then 4MP and 2MP. In mixtures where PYR was absent, 3MP was next most favoured.

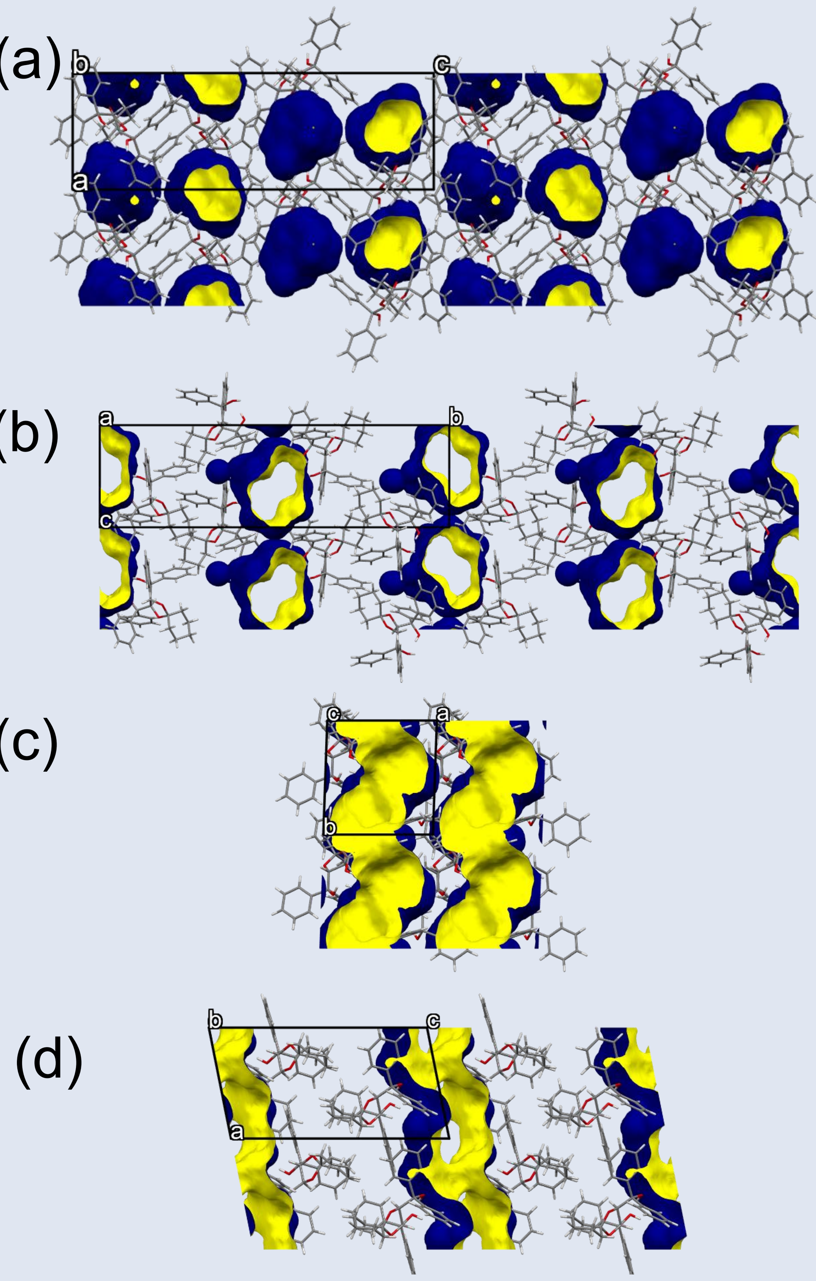

Figure 5 a-d (right): SCXRD results of single solvent experiments indicating the calculated voids for a) TADDOL6·PYR, b) TADDOL6·2MP, c) TADDOL6·3MP and d) TADDOL6·4MP.

It can be noted here that the complexes formed between TADDOL6 and PYR and 3MP, formed discrete cavities where the guest is housed. While TADDOL6 formed endless channels when including 2MP and 4MP. This is often a sign of favourability on a host compound. The tighter the bonds, the stronger the attraction.

Table 3 (below): A summary of the thermogravimetric analyses.

T_{on} is an indicator of when the host first begins to release the guest from the complex. The higher this value, the stronger the intermolecular bonds between them. Therefore, PYR formed the strongest intermolecular bonds, followed by 3MP, 4MP and 2MP.

The water studies were too unstable to calculate the T_{on} value.

Complex	T_{on}/°C	Mass loss expected/%	Mass loss measured/%
TADDOL6·PYR	155.8	13.5	13.7
TADDOL6·2MP	77.8	15.5	15.9
TADDOL6·3MP	92.4	15.5	16.1
TADDOL6·4MP	85.6	15.5	16.1

Table 2 (right): K-values calculated for selectivity profiles.

Selectivity profiles are generated by varying the concentration of the guests. The detected concentrations of the guests are then plotted on a selectivity profile. The K-value which is a measure of the selectivity of the host compound can be calculated using[10]: $K_{G_A:G_B} = Y_{G_A}/Y_{G_B} \times X_{G_B}/X_{G_A}$ $(X_{G_A} + X_{G_b} = 1)$. Low K values (9 or less) indicate low selectivities while values closer to 10 or more allude to the feasibility of employing the host compound for separation purposes[11]. PYR was favoured in all combinations, followed by 3MP, 2MP and 4MP.

Guest percentage in original solution	K-values (in favour of)					
	PYR/2MP	PYR/3MP	PYR/4MP	2MP/3MP	3MP/4MP	2MP/4MP
20	27.9 (PYR)	19.6 (PYR)	88.7 (PYR)	∞ (2MP)	19.1 (3MP)	∞ (2MP)
40	∞ (PYR)	1.1 (PYR)	19.8 (PYR)	∞ (2MP)	11.1 (3MP)	1.0 (2MP)
60	∞ (PYR)	1.9 (PYR)	29.4 (PYR)	∞ (2MP)	∞ (3MP)	1.7 (2MP)
80	∞ (PYR)	2.5 (PYR)	∞ (PYR)	∞ (2MP)	∞ (3MP)	∞ (2MP)

Conclusions

It can be concluded that TADDOL6 can effectively be used as a method of separating the pyridyl series. This is evident by the very high K-values noted in most concentrations, with some even being infinitely high as well as the strong intermolecular forces indicated by the SCXRD and TGA studies. Therefore, proving that PYR followed by 3MP were the most favoured guests. The results of the water studies indicated that TADDOL6 was able to include pyridyl guest species even when present in water. Further studies will need to be made, but it is a promising start as a possible solution to water pollution.

References

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