

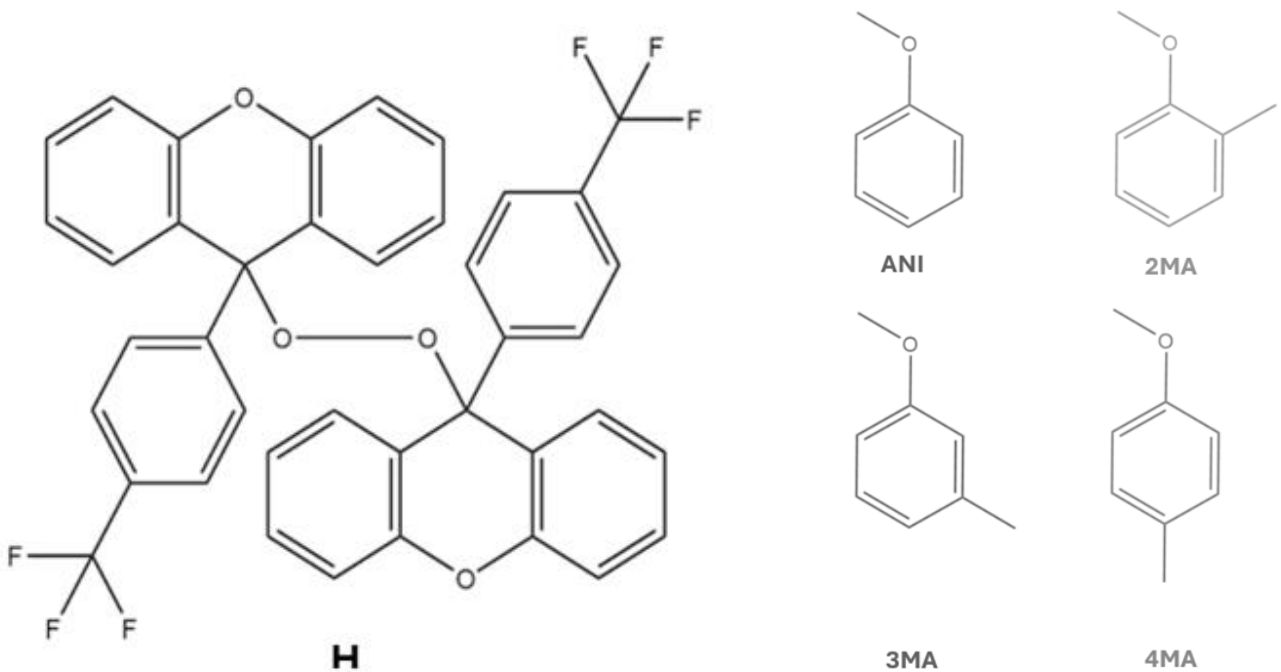
Peroxides as Host Compounds: An Investigation of the Host Ability and Selectivity of Di-9-(*p*-trifluoromethylphenyl)xanthen-9-yl) Peroxide in Anisole/Methylanisole Mixtures

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Introduction

Supramolecular chemistry has very many applications including the separation of positional isomers. In the present work , a peroxide host compound **H** was used to determine whether it has the ability to separate mixtures of anisole and methylanisoles (Scheme 1). Any successfully formed complexes in the present work were analysed by means of single crystal X-ray diffraction (SCXRD) and thermal experiments. Furthermore, extensive guest/guest competition experiments were carried out, involving both equimolar and non-equimolar anisole mixtures, and the results from all of these investigations are contained herein. Our interest in these anisole and methylanisole guest compounds is the challenge that they present when their separation is required: conventional fractional distillation procedures are laborious and costly (with respect to both economics and energy) owing to their narrow boiling range, more especially that of the methylated isomers (2MA, 3MA, 4MA, 170–176 °C; Ani boils at 154°C).^{1–3}



Scheme 1: Structures of host compounds **H** and anisole and methylanisole guest compounds

Experimental

Synthesis of 1,4-bis(diphenylhydroxymethyl)benzene (H). The proposed host compound, di(9-(*p*-trifluoromethylphenyl)- xanthen-9-yl) peroxide (**H**), was prepared as reported previously by Taljaard.^{4–5}

Single solvent complexes: The study investigated the formation of **H** complexes with ANI, 2MA, 3MA and 4MA by dissolving the host compound in these guest solvents. Crystals that formed were isolated (depicted in Figure 1), washed, and analyzed using 1H-NMR spectroscopy, revealing the inclusion success and H:G ratio.

Equimolar mixed guest competition experiments. The study investigated the selectivity of **H** in mixed anisoles by dissolving the host compound in various mixtures, analysing so-formed crystals using GC, and providing overall H:G ratios through 1H-NMR spectroscopy. All experiments were conducted in duplicate and percentage standard deviations are provided in each case.

Binary guest competition experiments in which the quantity of each guest was varied. The study involved dissolving **H** in binary anisole mixtures with varying molar ratios of Guest A and Guest B, analyzing resultant crystals by GC, and creating selectivity plots using the equation by Pivovar et al.⁶

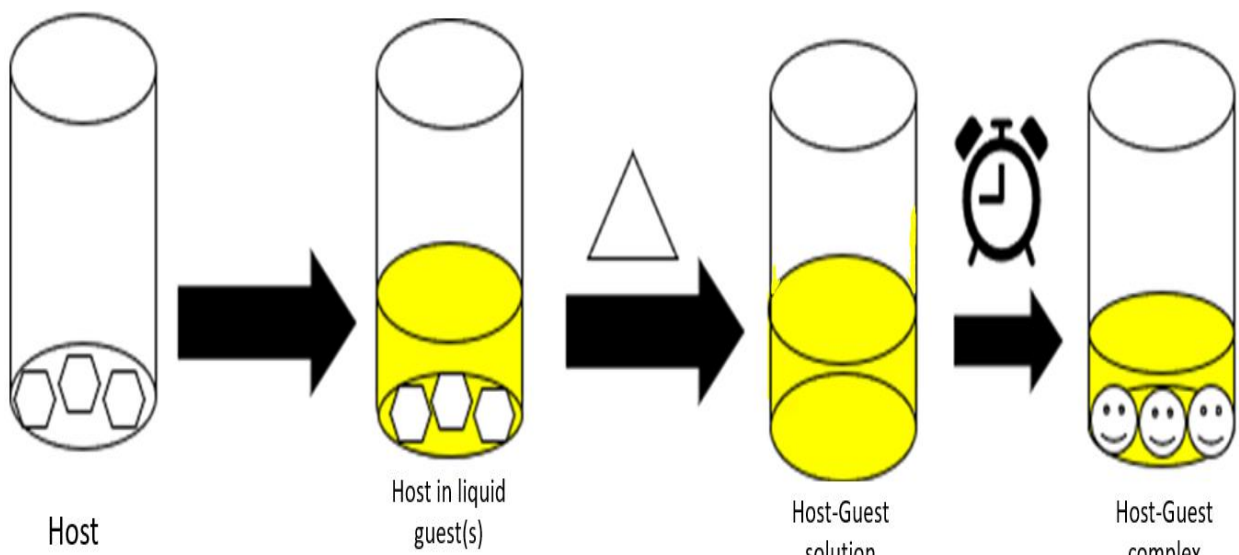


Figure 1. Experimental procedure for host-guest complex formation.

Results

The equimolar mixture experiments revealed high selectivity of the host (**H**) for **ANI** whenever it was present in the guest mixture. In binary equimolar experiments , crystals obtained from ANI/2MA and ANI/4MA mixtures showed high selectivity towards ANI (85.2% and 82.5%, respectively). However when ANI/3MA were present, the result was not as extreme, and only 52.4% of ANI was measured in the crystals in this experiment. When ANI was absent, inclusion was much more limited. For example, 2MA/3MA and 3MA/4MA afforded no inclusion, while the 2MA/4MA mixture resulted in high preference towards 4MA(92.4%).

In ternary mixtures, selectivity depended on the guest combination. The ANI/2MA/3MA mixture unexpectedly favored 2MA (42.0%), while both ANI/2MA/4MA and ANI/3MA/4MA showed high selectivity for ANI (73.3% and 73.5%). For the 2MA/3MA/4MA mixture, where ANI was absent, 4MA was again the preferred guest (38.0%). The quaternary mixture further confirmed strong selectivity of the host toward ANI, with 65.6% of this guest incorporated into the complex.

Overall, these results establish a clear order of selectivity: **ANI is most strongly preferred, followed by 4MA, whereas 2MA and 3MA are generally excluded.** This trend is consistent with single-guest experiments, where 2MA and 3MA did not form inclusion complexes at all.

Table 1: Results from the equimolar mixed anisole guest experiments with H .						
ANI	2MA	3MA	4MA	Guest ratios	Overall H:G ratios	% e.s.d.s
X	X			85.2 : 14.8	2 : 1	0.7
X		X		52.4 : 47.6	5 : 2	2.3
X			X	82.5 : 17.5	3 : 1	0.0
	X	X		"	"	"
	X		X	7.6 : 92.4	3 : 1	2.6
		X	X	"	"	"
X	X	X		24.7 : 42.0 : 33.3	5 : 1	3.8 : 3.2 : 0.6
X	X		X	73.3 : 13.9 : 12.8	4 : 1	0.2 : 0.1 : 0.1
X		X	X	73.5 : 11.3 : 15.2	7 : 2	0.8 : 1.3 : 0.5
	X	X	X	28.6 : 33.4 : 38.0	4 : 1	2.2 : 0.5 : 1.7
X	X	X	X	65.6 : 15.7 : 9.9 : 8.8	5 : 1	4.1 : 3.8 : 0.2 : 0.1

^aNo inclusion occurred.

Table 2. Selectivity Coefficients for the Data Points Contained in the Selectivity Profiles ^a				
Binary solution	20:80	40:60	60:40	80:20
ANI/2MA	10.3 (ANI)	6.7 (ANI)	3.5 (ANI)	2.0 (ANI)
ANI/3MA	1.2 (ANI)	1.2 (3MA)	1.2 (3MA)	2.2 (3MA)
ANI/4MA	5.1 (4MA)	4.5 (ANI)	3.2 (ANI)	2.6 (ANI)
2MA/4MA	4.3 (4MA)	10.1 (4MA)	1.2 (4MA)	1.2 (4MA)

^aGuests in brackets after the *K* values are those preferred in that particular experiment.

Results continued

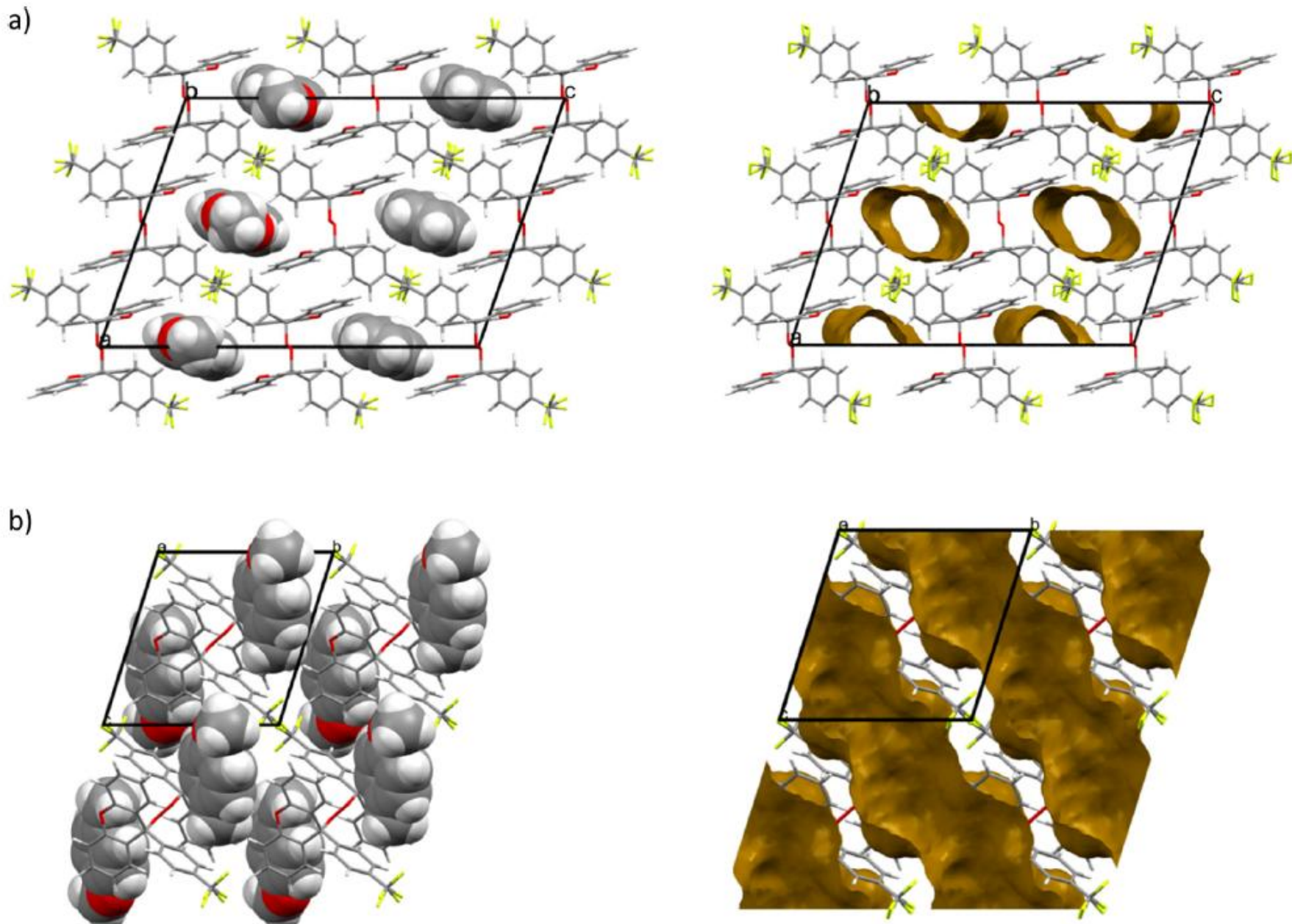


Figure 2. Unit cell and host-guest packing (left) and void (right) diagrams in (a) **H** · ANI ([010]) and (b) **H** · 2(4MA) ([100]).

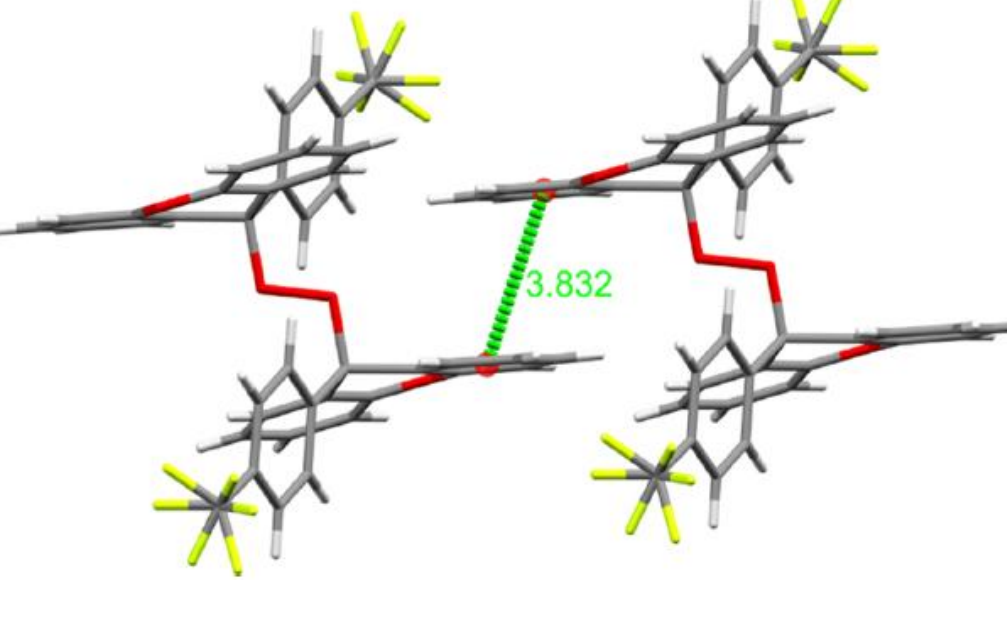


Figure 3. (host)π · · · π(host) interaction (green) observed in **H** · ANI).

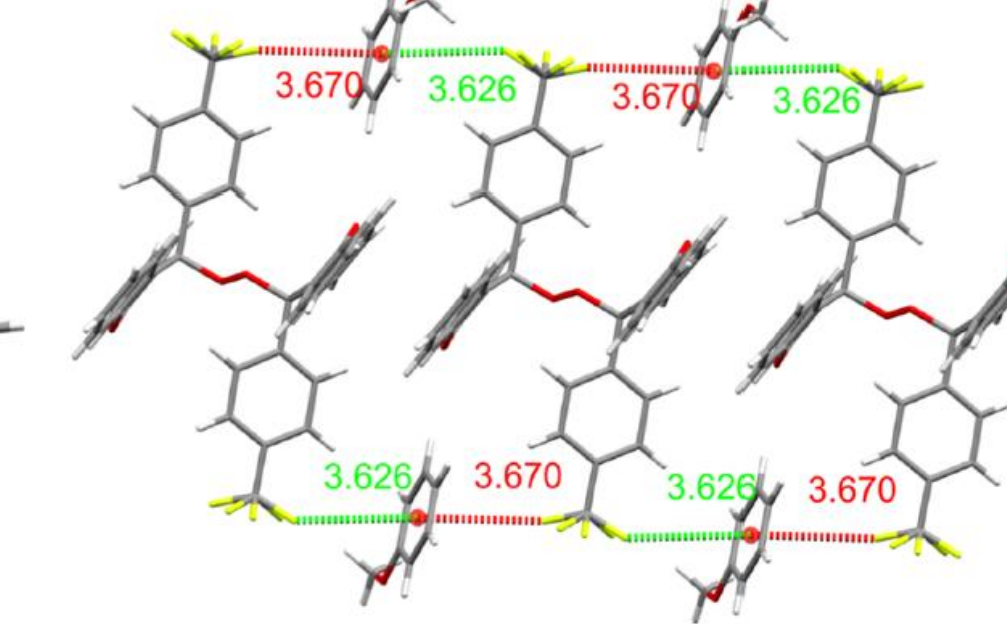


Figure 4. (host)C-F · · · π(guest) (green and red) interactions in **H** · ANI.

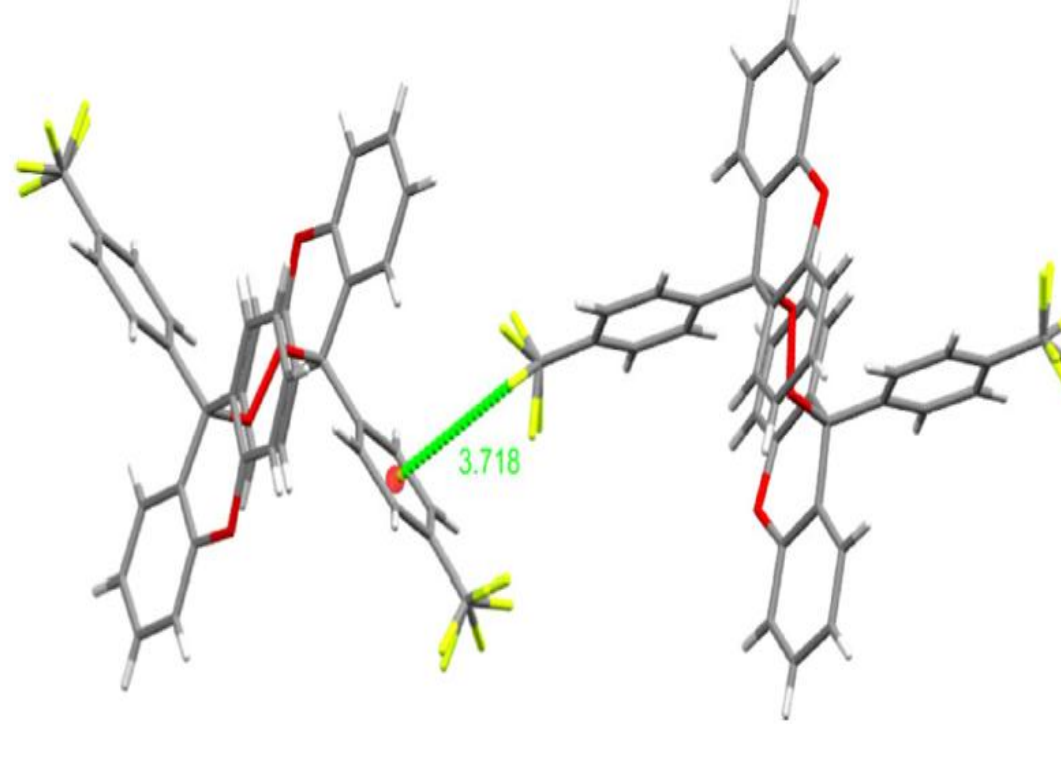


Figure 5. (host)C-F · · · π(host) interaction present in **H** · ANI.

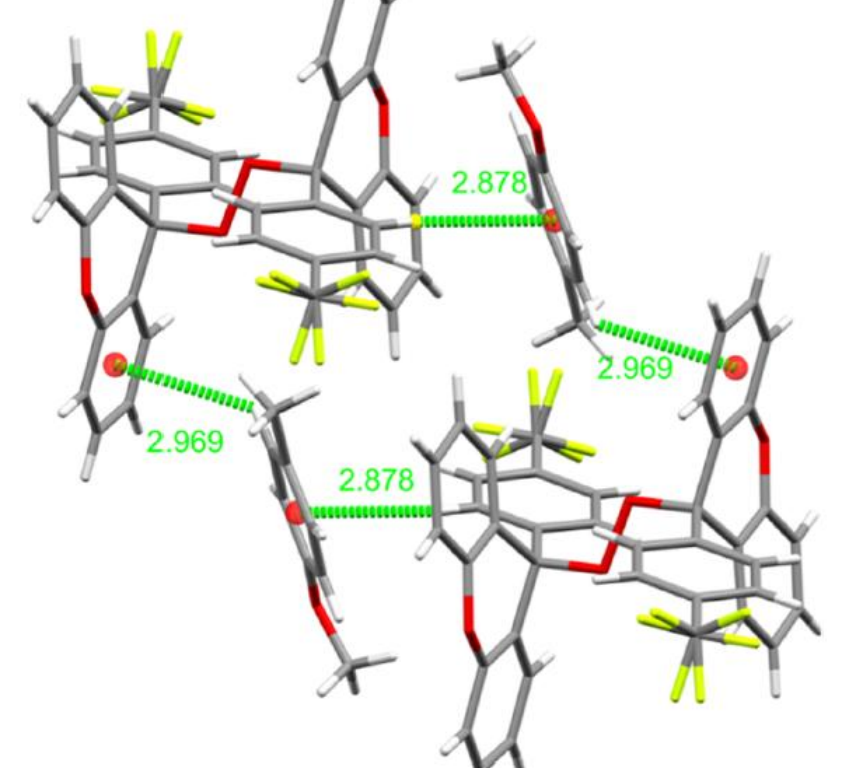


Figure 6. (host)C-H · · · π(guest) and (guest)C-H · · · π(host) interactions (green) in **H** · 2(4MA).

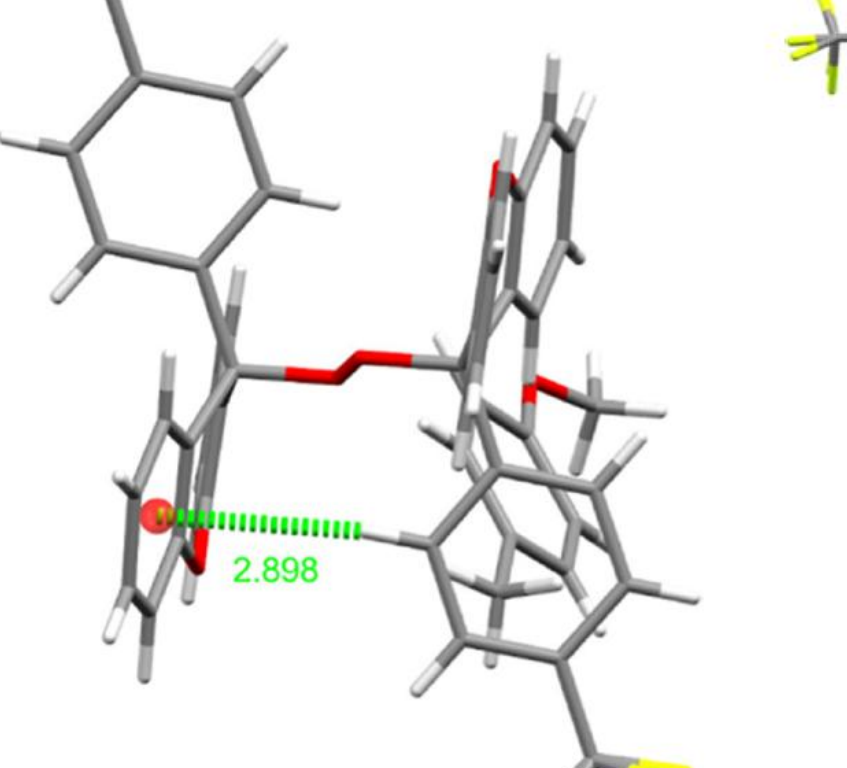


Figure 7. An intramolecular (host)C-H · · · π(host) interaction in **H** · 2(4MA).

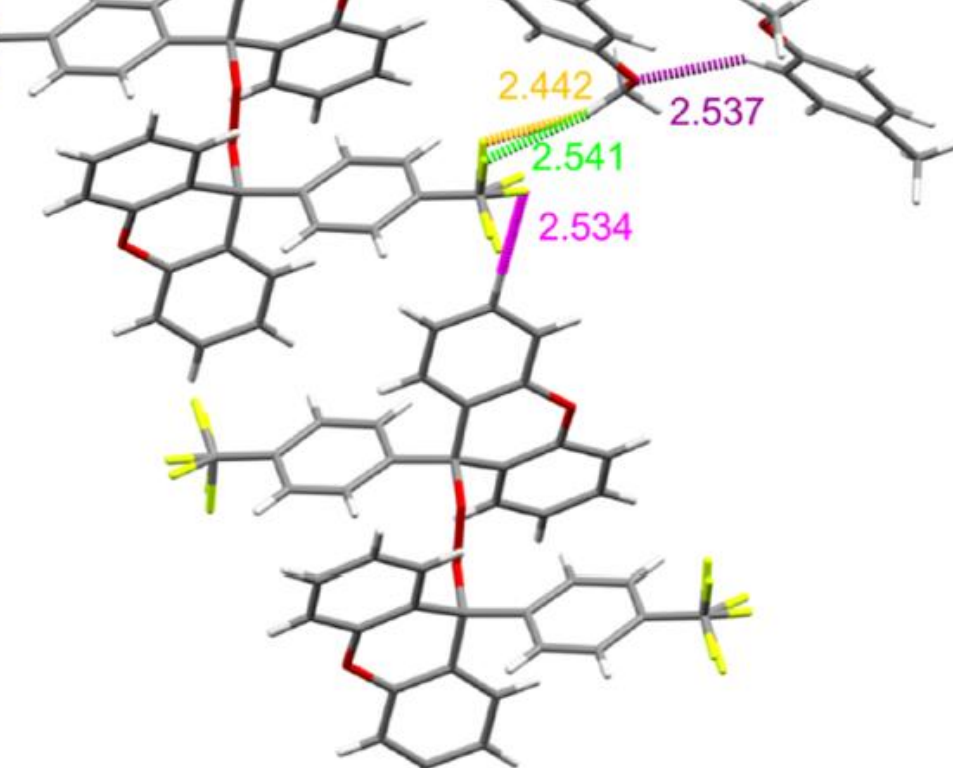


Figure 8. (guest)C-H · · · F(host) (yellow, green and magenta) and a (guest)C-H · · · O(guest) (purple) close contacts.

Results continued

The guest release event for the ANI-containing inclusion compound occurred in two steps and over a wide temperature range, and decomposition of the complex initiated at 56.1 °C (Figure 9a). The expected and measured mass losses were in reasonable agreement for this complex (Table 3). The inclusion compound containing 4MA, on the other hand, appeared to be unstable even at ambient conditions (illustrated by the downward trend of the TG curve right from the outset of the experiment and the lower-than-expected experimental mass loss observed). For this reason, it is difficult to speculate as to the nature of the guest release process; however, it is clear that this event took place over a broad temperature range (Figure 9b). The stability difference between the two complexes explains the affinity of **H** for ANI in the mixed guest competition experiments. Since the 4MA-containing complex is unstable at room temperature and pressure, it remained difficult to confirm the H/G ratio (which differed in the 1H NMR experiment and the SCXRD analysis) from this thermal experiment. Finally, since the peak relating to **H** was an exotherm, this host compound decomposed rather than melted (melting is always endothermic). The decomposition peak temperatures were 212.0 and 214.9 °C. This feature of these stable peroxides has previously been reported by Taljaard.^{3–4}

Table 3. Thermal Parameters Obtained From the Thermal Traces

complex	<i>T</i> _{on} /°C ^a	<i>T</i> _p /°C ^b	measured mass loss/%	expected mass loss/%
H·ANI	56.1	212.0	15.3	13.7
H·4MA	^b	214.9	13.2	15.2

^a*T*_{on} is the temperature at which the guest release process commenced and represents the relative thermal stability of the complex, while *T*_p is the endotherm peak temperature representing the host decomposition event. ^bThis complex was unstable at ambient conditions.

Conclusion

In this investigation, di(9-(*p*-trifluoromethylphenyl)xanthen-9-yl) peroxide (**H**) was revealed to be an effective host compound when crystallized from both ANI and 4MA; 1H NMR experiments on the resultant complexes showed that the H/G ratio was 1:1 in both instances. 2MA and 3MA, on the other hand, failed to form complexes with this host species. In the guest competition experiments, ANI and then 4MA were most readily selected by **H**, while 2MA and 3MA were less favored. In fact, it was shown that **H** is able to separate 20:80 ANI/2MA and 60:40 4MA/2MA mixtures, in favour of ANI and 4MA, respectively, since these experiments furnished high selectivity coefficients. **H**, therefore, is a highly competent host molecule for these separations through host-guest chemistry strategies, a much greener alternative separation strategy compared with current methods, largely owing to the recyclability of the host compound in this process. The SCXRD results showed 4MA to experience one (host)C-H · · · π(guest) and also one (guest)C-H · · · π(host) interaction with **H**. However, no (host)C-F · · · π(guest) bonds were evident in this complex, two of which were identified to each ANI molecule in **H** · ANI, explaining the selectivity behaviour of **H** for ANI. This latter guest also formed a more stable complex with **H** than 4MA did, as observed from their respective *T*_{on} temperatures during thermal analyses; this observation therefore also corresponded with the affinity of **H** for the ANI guest solvent.

References

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