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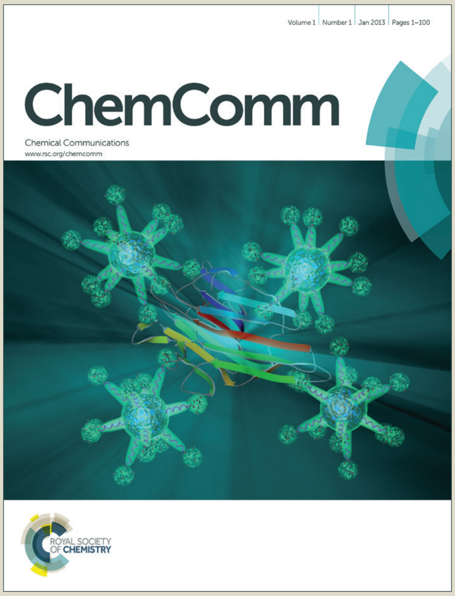

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ARTICLE TYPE

# Separation of xylenes by enclathration

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**The isomers of xylene have been separated by enclathration using three host compounds: 9,9'-bianthryl (H1), 9,9'-spirobifluorene (H2) and *trans*-2,3-dibenzoylspiro[cyclopropane-1,9-fluorene] (H3). The structures of each host with a single xylene isomer have been elucidated and, for H1, the relative lattice energies of the clathrates with *ortho*-and *para*-xylene have been evaluated.**

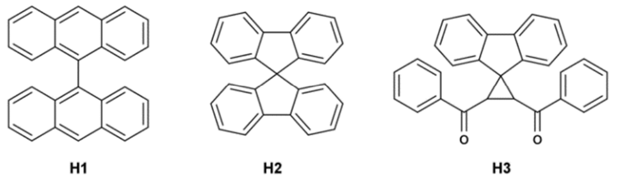
The three isomers of xylene; *ortho*-xylene (**ox**), *meta*-xylene (**mx**) and *para*-xylene (**px**) are obtained by the catalytic process of naphtha reforming.[1,2] The isomers are important raw materials for the manufacture of a variety of products.[3] *Para*–xylene is converted into terephthalic acid and dimethylterephthalate and subsequently to poly(ethyleneterephthalate). *Ortho*-xylene is converted to phthalic anhydride, used in plasticisers and *meta*-xylene is used to obtain isophthalic acid and isophthalic nitrite. The xylene isomers have similar boiling points but different melting points, (Table 1) thus the separation of the isomers by distillation is difficult.

**Table 1** Normal boiling and melting points of xylenes

| | *ortho*-xylene | *meta*-xylene | *para*-xylene |
|---|---|---|---|
| Boiling point/ °C | 144.4 | 139.1 | 138.3 |
| Melting point/ °C | -25.2 | -47.9 | +13.4 |

Fractional crystallisation has been employed to separate *para*-xylene from the other two isomers because of its higher melting point. The process is however rendered inefficient by the formation of an eutectic mixture of components. Most industrial separations currently use selective adsorption on zeolites and these processes have been reviewed.[4,5] The separation of xylene isomers by metal organic frameworks and by Host-Guest chemistry techniques have been studied.[6,7] Lusi and Barbour[8] utlilized the Werner host [Ni(NCS)$_2$(para-phenylpyridine)$_4$] to selectively enclathrate **ox** over **mx** and **px** from an equimolar ternary mixture and **mx** over **px** from a binary mixture of the xylene vapours.

We present the results of enclathration experiments by three different hosts: 9,9-bianthryl (**H1**), 9,9'-spirobifluorene (**H2**) and *trans*-2,3-dibenzoylspiro[cyclopropane-1,9'- fluorene] (**H3**). The structures of the three host compounds are shown in Scheme 1.



**Scheme 1** Schematic diagram of hosts: (H1) 9,9'-bianthryl (H2) 9,9'spirobifluorene and (H3) *trans*-2,3-dibenzoylspiro[cyclopropane-1,9'-fluorene]

The enclathration capabilities of these host molecules with a variety of hydrocarbons and simple heterocyclic guests have been studied.[9,10] The bianthryl host **H1** exhibits two polymorphic structures[11,12] and its inclusion compounds with benzene, α-ionone[13] and chlorocyclohexane[14] have been elucidated. The bifluorene host **H2** also manifests two different solid forms of the apohost[15,16] and its clathrates with benzene and biphenyl have been characterised. Only one crystal structure of the host **H3** has been published, that of its inclusion compound with toluene.[17]

In this work, the procedure employed for each host was to dissolve it in the pure xylene isomer, the binary equimolar mixtures of two isomers and the tertiary equimolar mixture of all three isomers. The resulting crystalline products were analysed by singe crystal X-ray diffraction, NMR spectroscopy and thermal gravimetry (TG). The enclathration results are summarised in Table 2. This shows that **H1** does not enclathrate **mx** and selects **ox** over **px**. **H2** is selective towards **px** and **H3** is selective towards **ox**. The thermal gravimetry results are in good agreement with the calculated values of the stoichiometry derived from the crystal structures.

The structure of **H1•0.5ox** crystallises in *P*-1 with Z=8. The **ox** guest molecules are located in the channels running along [1-10]. The packing is shown in Fig1a. In order to further understand the non-bonded interactions between the host and guest molecules in this structure and the related structure with **px**, we employed the program Crystal Explorer which calculates the Hirshfeld surfaces of a target molecule and depicts all the interactions with its neighbours.[18]

The structure of **H1•0.5px** crystallises in $P2_1/c$ with Z=4. The **px** guest is located in the channels running along [010] at centres of inversion at Wykcoff position *c*. the packing and corresponding fingerprint plot are shown in Fig 2b.

**Table 2** Enclathration results

| *Host* | *Starting solvent* | *Resulting crystal* | *TG % mass loss found (calc)* |
|---|---|---|---|
| **H1** | ox | H1•0.5ox | 12.9 (13.0) |
| | mx | H1 apohost | - |
| | px | H1•0.5px | 12.6 (13.0) |
| Equimolar | ox/mx | H1•0.5ox | 12.7 (13.0) |
| | ox/px | H1•0.5ox | 12.8 (13.0) |
| | mx/px | H1•0.5px | 12.8 (13.0) |
| | ox/mx/px | H1•0.5ox | 12.7 (13.0) |
| **H2** | ox | H2 apohost | - |
| | mx | H2 apohost | - |
| | px | H2•0.5px | 13.6 (14.4) |
| Equimolar | ox/mx | H2 apohost | - |
| | ox/px | H2•0.5px | 13.6 (14.4) |
| | mx/px | H2•0.5px | 12.8 (14.4) |
| | ox/mx/px | H2•0.5px | 14.0 (14.4) |
| **H3** | ox | H3•ox | 21.0 (20.9) |
| | mx | H3 apohost | - |
| | px | H3 apohost | - |
| Equimolar | ox/mx | H3•ox | 21.2 (20.9) |
| | ox/px | H3•ox | 20.8 (20.9) |
| | mx/px | H3 apohost | - |
| | ox/mx/px | H3•ox | 20.9 (20.9) |

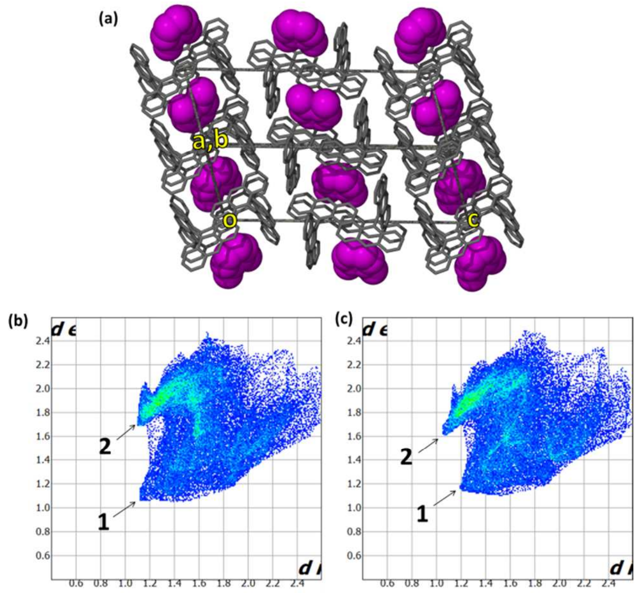


**Fig 1.** (a) Packing diagram for H1•0.5ox and Hirshfeld plots for H1•0.5ox (b: molecule A, c: molecule B)

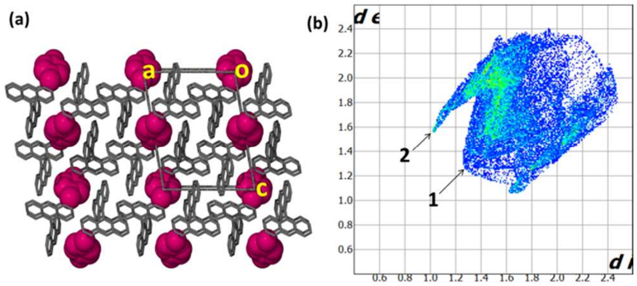


**Fig 2.** (a) Packing diagram and (b) Hirshfeld plot for H1•0.5px

Analysis of the fingerprint plots for these two structures explains the selectivity of **H1** for **ox** versus **px**. In the **H1•0.5ox** structure there are two crystallographically independent **ox** molecules with corresponding fingerprints shown in Fig 1b and Fig 1c. The peaks labelled 1 correspond to H•••H interactions and give the shortest internal (Guest) versus the external (Host) distances. The sum of these is 2.20 Å (Fig 1b, **ox** guest A) and 2.33 Å (Fig 1c, **ox** guest B). Both these are shorter than the corresponding H•••H contacts in the **H1•0.5px** structure, which shows peak 1 at 2.60 Å (Fig 2b). This is the most important interaction between the host and guest molecules. The peak labelled 2 in all the threes figures are associated with (Guest)H•••C(Host) interactions, and their interatomic distances are similar at ≈ 2.65 Å. We surmise that the dominant H•••H interactions, being shorter in the **H1•0.5ox** structure drive the selectivity to *ortho*-xylene. The density of the **H1•0.5ox** crystal (1.239 $g.cm^{-3}$) is also higher than that of the **H1•0.5px** crystals (1.222 $g.cm^{-3}$). The secondary interactions between the methyl hydrogens of the xylene guests and the host molecules for all structures have been deposited in the ESI.

Lattice energy calculations were performed with the program OPIX.[19] The functional form for the i-j atom-atom potential used is $E_{ij}= A \exp(BR_{ij})-C/R^{6}_{ij}$ where $R_{ij}$ is the interatomic distance and the coefficients A, B and C have been normalised against the known sublimation energies of organic compounds. The result yielded lattice energies of -186.3 $kJmol^{-1}$ and -184.9 $kJmol^{-1}$ for the **H1•0.5ox** and **H1•0.5px** compounds respectively, which conforms the result found in the competition experiments. The small difference of 1.4 kJ is in keeping with the trend in the lattice energies of organic polymorphs, where the values are often in a small range of a few kJ.[20]

The **H2•0.5px** structure crystallises in $P2_1/c$ with Z=4. The **px** guest molecules are located in centres of inversion at Wyckoff position *c*. The packing of this structure is shown in Fig 3 and is characterised by several edge-to-face π-π contacts.[2121]

**H3•ox** crystallises in C2/c with Z=4 and the host is located in a diad at Wykcoff position *e* and the two **ox** guests are disordered and lie at the centre of inversion at Wyckoff position *c*. The packing is shown in Fig 4.

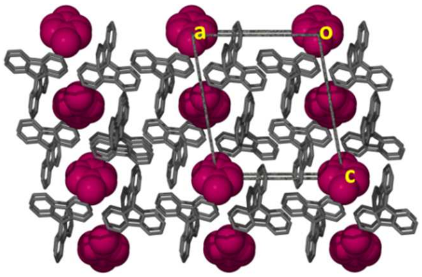


**Fig 3.** Packing diagram for H2•0.5px

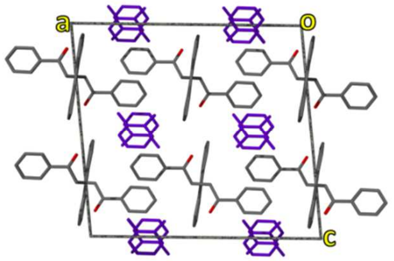


**Fig 4.** Packing diagram for H3•ox

## Conclusions

The three hydrocarbon host compounds **H1**, **H2** and **H3** can efficiently discriminate between the isomers of xylene by forming inclusion compounds. **H1** enclathrates both **ox** and **px** but prefers the former. **H2** and **H3** only enclathrate **px** and **ox** respectively.

## Notes and references

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‡ Crystal data for **H1•0.5ox**: $C_{64}H_{46}$, M = 815.01 g/mol$^{-1}$, triclinic, *P*-1, a=11.346(4) Å, b=14.634(5) Å, c=27.361(9) Å, α=101.652 (2)º, β=99.918(2)º, γ=92.534(2)º, V=4368.17(3) Å$^3$, T=173(2) K, Z=4 out of 13331 reflections with I>2σ(I), R1=0.0534, wR2= 0.1339. Crystal data for **H1•0.5px**: $C_{32}H_{23}$, M = 407.50 g/mol$^{-1}$, monoclinic, $P2_1/c$, a=14.1541(3) Å, b=9.1925(18) Å, c=17.3072(4) Å, α= 90º, β=100.42(19)º, γ=90º, V=2214.7(8) Å$^3$, T=173(2) K, Z=4 out of 3301 reflections with I>2σ(I), R1=0.0497, wR2= 0.1304. Crystal data for **H2•0.5px:** $C_{29}H_{21}$, M= 369.46 g/mol$^{-1}$, monoclinic, $P2_1/c$, a=13.911(3) Å, b=9.1555(18) Å, c=16.101(3) Å, α=90º, β=99.76(3)º, γ=90º, V=2021.0(7) Å$^3$, T=173(2) K, Z=4 out of 3796 reflections with I>2σ(I), R1=0.0451, wR2= 0.1539. Crystal data for **H3•0.5ox**: $C_{37}H_{30}O_2$, M = 506.61 g/mol$^{-1}$, monoclinic, *C2/c*, a=18.733(4) Å, b=8.5251(17) Å, c=17.4063(4) Å, α=90º, β=95.92(3)º, γ=90º, V=2764.9(10) Å$^3$, T=173(2) K, Z=4 out of 2654 reflections with I>2σ(I), R1=0.0450, wR2= 0.1222.

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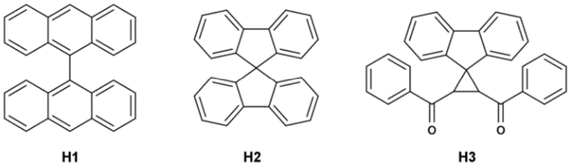

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