Pseudo-polymorphism in the toluene solvate of *p-tert*-butylcalix[5]arene: structural and gas sorption investigation†

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Crystallisation of the host molecule *p-tert*-butylcalix[5]arene from toluene affords three pseudo-polymorphs, two of which can be isolated on a large scale and used to form 'frustrated' organic solids that are capable of gas sorption. The structures of these three polymorphs are compared, and the gas sorption capabilities of the two phases that can be isolated in bulk form are described.

Introduction

The tailored synthesis of, and gas sorption in, metal–organic frameworks (MOFs), covalent–organic frameworks (COFs) and coordination networks/polymers is being actively pursued.[1] These materials can offer rigidity that presents pores for gas sorption upon solvent removal for example, rendering them useful for gas storage. Organic solids have received significantly less attention with respect to gas storage and application. One organic solid, *p*-^{t}Bu-calix[4]arene, has displayed remarkable properties with regard to this function.[2] When sublimed, a low density kinetic form of the material can be isolated in bulk, and this allows for the passage of gas through seemingly nonporous crystals to the resulting void space generated. To date, this form has shown the ability to sorb carbon dioxide (while also separating the gas from a CO_2–H_2 mixture),[2a] methane,[2b,c] acetylene[2e] and hydrogen[2d] (at high pressure) to varied extents. With respect to porous organic solids, we have recently shown that calix[5]arene can be sublimed to afford an interesting arrangement of self-included and back-to-back helices, the latter of which possesses suitable channels for the inclusion of gas molecules.[3] We also recently discovered that slow removal of solvent from one form of the crystalline toluene solvate of *p*-^{t}Bu-calix[5]-arene (**TBC5**, Fig. 1A) afforded a 'frustrated' porous organic solid that is capable of sorbing various gases to different extents (form **TBC5·Tol I**).[4]

In this new type of sorbant, the concept of 'frustration' relates not to magnetism, but rather to the fact that the material collapses to a 'dead' phase (which can also be obtained by sublimation) upon removal of the few residual toluene molecules in the crystal lattice. Crystals of the 2 : 1 Tol : **TBC5** solvate (that are used to generate the original 'frustrated solid' by controlled desolvation) are of parallelogram like morphology, and grow from a toluene solution of **TBC5** at a point approaching dryness. In this form of the toluene solvate, the crystals are very large and can easily be separated and studied as reported.[4] That structure showed solvent molecules to occupy both *endo* and *exo* cavity positions within the crystal lattice, and the crystals were found to be stable towards solvent loss, thereby allowing for relatively controllable de-solvation of the crystalline material.

The phenomenon of polymorphism is becoming increasingly important in the chemical and pharmaceutical industries alike for various reasons.[5] The phenomenon is also evident in the pure form of the related *p*-^{t}Bu-calix[4]arene, which has been shown to display polymorphic behaviour under thermal stimuli.[6] Herein we report two additional pseudo-polymorphic forms of the toluene solvate of **TBC5** that are isolated when the toluene solution of **TBC5** approaches dryness during the crystallisation process. These forms, **TBC5·Tol II** and **TBC5·Tol III**, crystallise as hexagonal plates and cubic shaped crystals respectively, and we also show that the former is capable of gas sorption when partially de-solvated. Although previously described, general (and previously unhighlighted) features of the structure of form **I** are described below for useful comparison with forms **II** and **III**.

Prior to the description of each crystal structure in detail, it is important to note that all three have a common structural entity, a base-to-base dimerisation around the 'lower-rim' hydroxyl groups with the **TBC5** molecules oriented in a staggered fashion (Fig. 1B and C). In **TBC5·Tol I** and **TBC5·Tol II**, additional **TBC5** molecules are also present in other motifs within these structures, while in **TBC5·Tol III**, this base-to-base dimer is the only major building block elucidated (other than solvent molecules).

Results and discussion

To aid clarity, each structure has been described separately below, prior to studies of gas storage capabilities for forms **TBC5·Tol I** and **TBC5·Tol II**. The calixarenes have been coloured blue and red in selected diagrams to aid visualisation of the motifs found in each of the three pseudo-polymorphs.

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† Electronic supplementary information (ESI) available: Revised crystal details for **TBC5** and **TBC5·Tol II**. CCDC 698672 (**TBC5·Tol II**) and 698673 (**TBC5·Tol III**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b809457h

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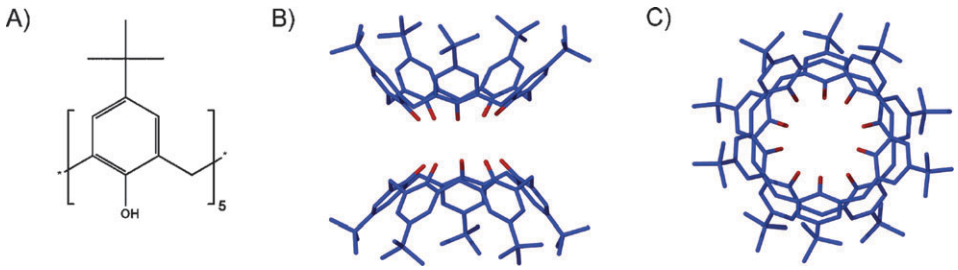

Fig. 1 (A) Schematic of *p-tert*-butylcalix[5]arene. (B) The base-to-base dimer formed between the hydroxyl rich regions of neighbouring calixarenes. (C) An orthogonal view of B showing the staggered arrangement at the 'lower rim'.[4]

In this regard, the common base-to-base calixarenes are coloured blue.

TBC5·Tol I: Form **I** crystallises in a triclinic cell with dimensions a = 17.127(3), b = 18.127(3), c = 22.045(3) Å, α = 87.057(3), β = 67.666(3), γ = 70.904(3)°, U = 5961.6(16) Å^3, and the structural solution was performed in space group $P\bar{1}$.[4] The asymmetric unit comprises two calixarenes, two *endo*-cavity (one in each **TBC5**) and two disordered *exo*-cavity toluene molecules that reside in interstitial spaces between calixarenes. Symmetry expansion around each **TBC5**, without considering toluene molecules, shows the presence of the base-to-base dimer, and a partly offset head-to-head dimer (coloured blue and red respectively in Fig. 2A and B).

Within the extended structure, these dimers pack in a near-orthogonal fashion to generate the layers shown in the bc plane, as shown in Fig. 2C. These layers pack in an offset manner along the a axis through another offset head-to-head dimerisation (between nieghbouring blue base-to-base dimers, Fig. 2D and E), and one crystallographically unique CH···π interaction (3.09 Å) from a **TBC5** methylene bridge to an aryl ring (between neighbouring red head-to-head dimers, Fig. 2D and F).

As described in our previous report, toluene molecules reside in the cavity of the host, as well as in the interstitial voids generated between neighbouring calixarenes.[4] The *endo*-cavity toluene molecules form (some strong[7]) CH···π interactions (five interactions with CH···aromatic centroid distances in the range of 2.57–2.89 Å) with the aryl rings of the calixarenes, and we believe that this lends stability to the frustrated phase prior to removal of these strongly bound guest molecules from the crystal lattice, which results in structural collapse to the self-included chain form. With respect to the *exo*-cavity toluene molecules, both of which are disordered, one resides in a region generated by the packing of neighbouring *tert*-butyl groups. The remaining molecule resides on an inversion centre and is sandwiched between the aryl rings of two symmetry equivalent molecules of **TBC5**, forming four equivalent π-stacking interactions (due to symmetry and disorder) with an aromatic centroid···centroid distance of 3.698 Å.

TBC5·Tol II: Form **II** crystallises as thin hexagonal plates that are in a triclinic cell with dimensions a = 17.986(3), b = 18.145(3), c = 20.583(4) Å, α = 83.817(3), β = 64.575(3), γ = 76.418(3)°, U = 5897.1(17) Å^3. Structural solution was performed in space group $P\bar{1}$, and the asymmetric unit was found to be similar to that of **TBC5·Tol I** in that it comprises two calixarenes, two *endo*-cavity toluene molecules, and additional disordered *exo*-cavity toluene molecules. In order to confirm the stoichiometry, TGA analysis was performed and showed the **TBC5** : Tol ratio to be approximately 1 : 2.

Examination of the extended structure shows the presence of the common base-to-base dimer (Fig. 3A) and another different offset head-to-head dimeric arrangement (Fig. 3B). The packing of the base-to-base and head-to-head dimeric arrangements is markedly different to those in **TBC5·Tol I**.[4] Each type of dimer in the present structure is isolated from symmetry equivalent arrangements (Fig. 3C and D) such that there is no additional dimer formation between layers, as is the case in **TBC5·Tol I** (Fig. 2D). Although this is the case, the location of, and intermolecular interactions associated with the co-crystallised toluene molecules show some similarities with those found in **TBC5·Tol I**.[4] For the two *endo*-cavity toluene molecules, one of which is disordered over two positions,[8] there are a total of six CH···π interactions with CH···aromatic centroid distances in the range of 2.60–2.91 Å, thereby indicating that as is the case for **TBC5·Tol I**. the guest molecules are strongly bound in the host cavity.[7] One *exo*-cavity toluene molecule occupies a position generated by the packing of neighbouring *tert*-butyl groups of **TBC5** molecules in a similar way to that found in **TBC5·Tol I**.[4] Also in a similar manner, the second toluene molecule, which displays limited disorder, resides on an inversion centre and is sandwiched between aryl rings of neighbouring **TBC5** molecules, forming four symmetry equivalent π-stacking interactions with an aromatic centroid···centroid distance of 3.798 Å.

TBC5·Tol III: During the crystallisation process, only a small number of crystals containing form **TBC5·Tol III** are identifiable with a microscope. The small cubic shaped crystals are in a triclinic cell with dimensions a = 13.392(3), b = 13.860(3), c = 18.433(4) Å, α = 92.014(4), β = 108.769(4), γ = 107.867(4)°, U = 3049.1(12) Å^3, and the structural solution was performed in space group $P\bar{1}$. The asymmetric unit was found to be different to those of forms **I** and **II**, comprising only one crystallographically unique **TBC5** and two co-crystallised toluene molecules. As the crystals were sensitive to solvent loss, and given that it was not possible to obtain this form on a scale large enough for TGA or NMR analysis for example, we have modelled the calixarene : toluene ratio as 1 : 2.

When considering only the calixarene, the structure is simpler than those of forms **I** and **II**. Both *endo* and *exo*-cavity toluene molecules are present but there is only one crystallographically unique **TBC5** in the asymmetric unit. Symmetry expansion at the base of this molecule affords the

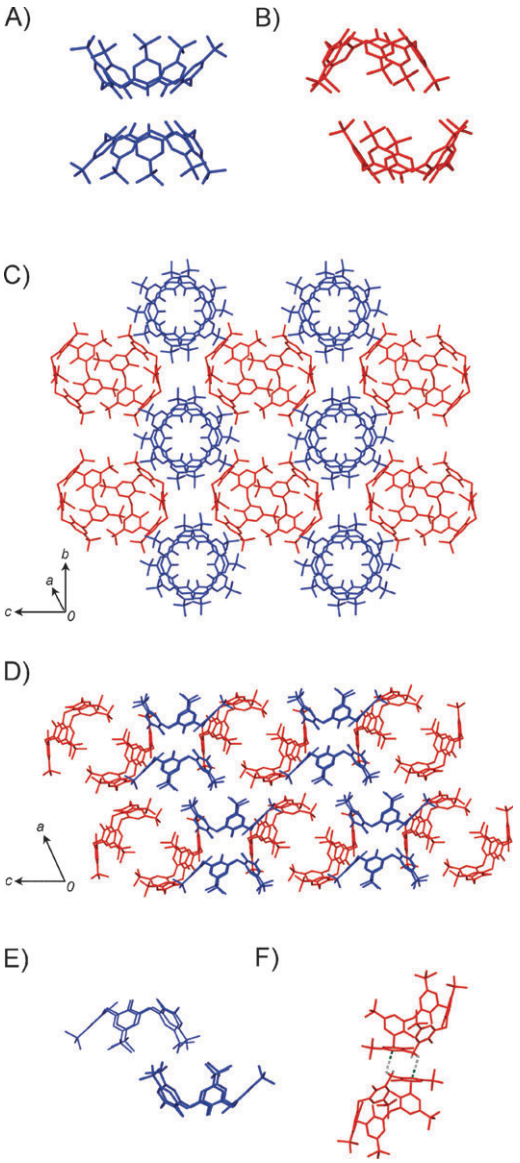

Fig. 2 Structural features of **TBC5·Tol I**.[4] (A) The common base-to-base dimer. (B) The intra-layer offset-dimer. The extended structure showing (C) the arrangement of base-to-base and head-to-head dimers (blue and red respectively) and (D) an orthogonal view of (C) showing the offset nature of each dimer type between layers in the extended structure. (E) The offset head-to-head arrangement found between neighbouring base-to-base dimers. (F) The CH···π interactions found between neighbouring pairs of head-to-head dimers shown as dashed lines. Toluene molecules and hydrogen atoms have been omitted from all views to aid clarity, with the exception of (F). Figures not to scale.

common base-to-base dimer shown in Fig. 4A. The simplest way to view the extended structure is that these dimers form skewed head-to-head arrangements within a theoretical sheet or cross-section (Fig. 4B). Upon further examination, base-to-base dimers form pseudo-columnar arrangements looking down an orthogonal axis (Fig. 4C) although these contain interstitial spaces that are occupied by solvent molecules (Fig. 4B, although solvent molecules not shown). The other major difference in **TBC5·Tol III** relative to **TBC5·Tol I** and **TBC5·Tol II** is that the *endo* toluene molecule is inverted such that the methyl group is inserted into the calixarene cavity

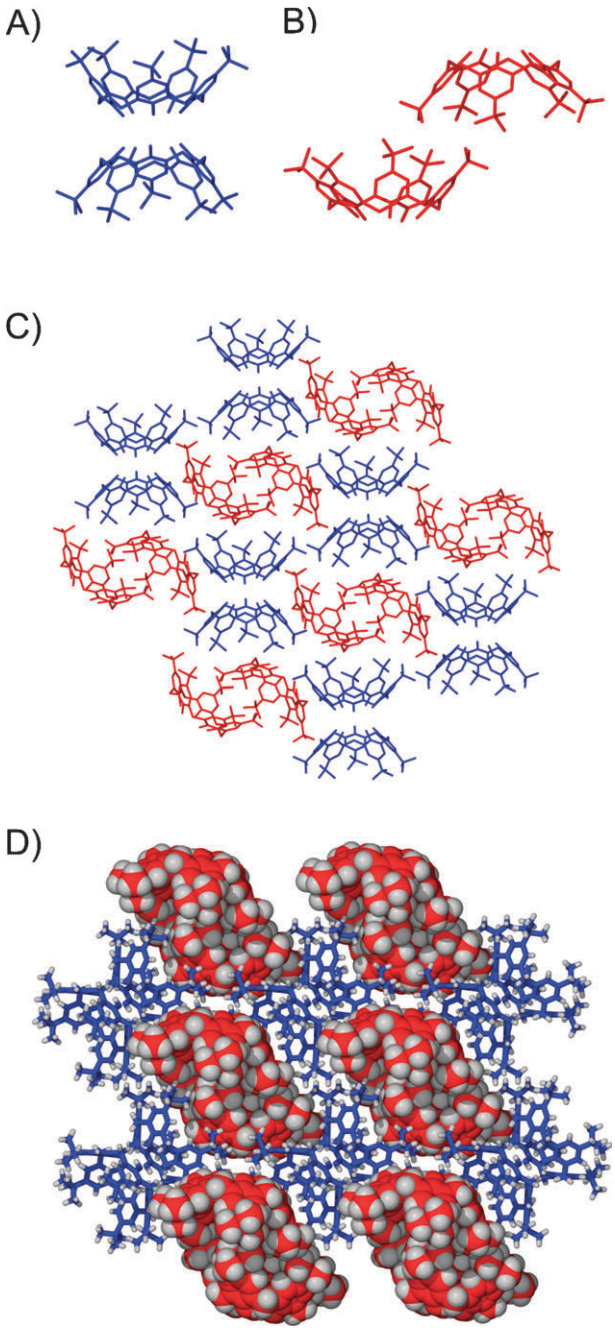

Fig. 3 Structural features of **TBC5·Tol II**. (A) The common base-to-base dimer. (B) The offset head-to-head dimer. The extended structure showing (C) the arrangement of base-to-base and head-to-head dimers (blue and red respectively) and (D) an alternative partial space filling representation of the extended structure showing that each type of dimeric arrangement is well separated from symmetry equivalents, precluding the formation of additional head-to-head dimers. Figures not to scale.

(Fig. 5). This occurs with one significant CH···π interaction (*ortho* relative to toluene methyl group) with an Ar-H···aromatic centroid distance of 2.83 Å.[7]

Gas sorption in forms **TBC5·Tol I** and **TBC5·Tol II**: As mentioned in the introductory section, we found that slow de-solvation of **TBC5·Tol I** affords a material (or phase) that we believe contains a 'frustrated' form of **TBC5·Tol** that was

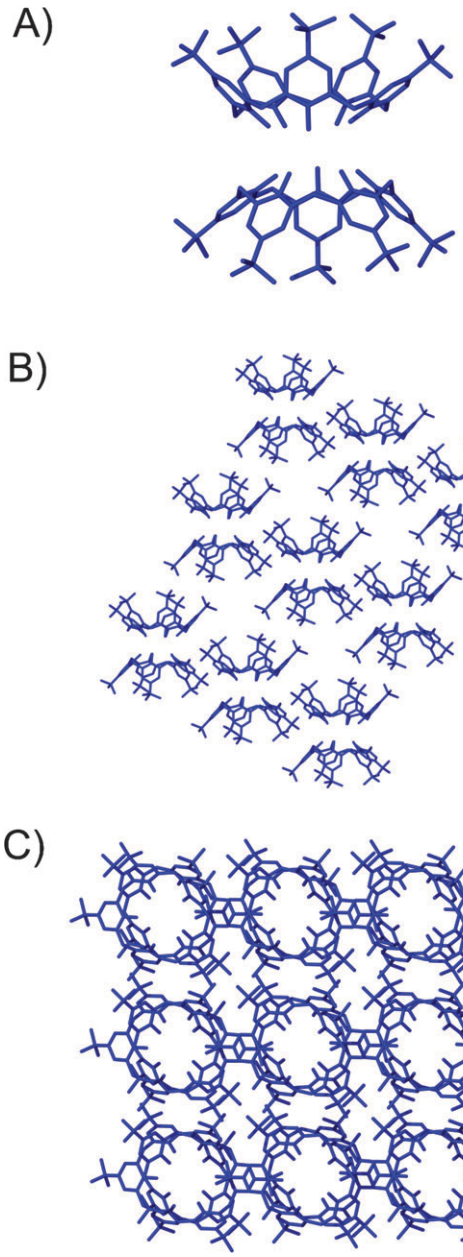

Fig. 4 Structural features of **TBC5·Tol III**. (A) The common base-to-base dimer. The extended structure showing (B) the head-to-head arrangements of base-to-base dimers (running diagonally from lower left to upper right) within a 'sheet' and (C) a perpendicular view of the 'sheet' in (B) sandwiched between two neighbouring 'sheets' (image in B running left to right as central layer in C). Figures not to scale.

subsequently found to rapidly sorb a number of different gases to varied extents.[4] Thorough de-solvation of this material results in the conversion of the 'frustrated' phase to a sorptively dead phase comprising self-included chains of **TBC5** that are non-porous.

In the above comparison of all three forms, the toluene molecules occupy both *endo* and *exo*-cavity positions in each case. Given that it was possible to isolate **TBC5·Tol II** in bulk by repeated crystallisation and crystal separation, the material was harvested, checked for purity by X-ray powder diffraction, and was examined for sorption properties *via* the same

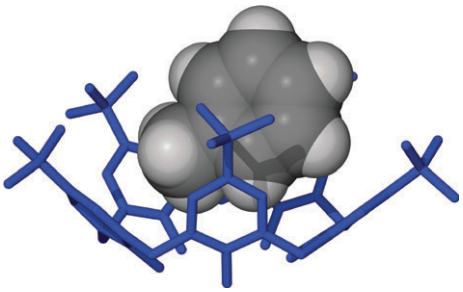

Fig. 5 Partial space filling representation of the *endo*-cavity toluene molecule in **TBC5·Tol III** that is inverted relative to the analogous toluene molecules in **TBC5·Tol I** and **TBC5·Tol II**.

desolvation process performed for **TBC5·Tol I** on the reasoning that it would be possible to remove some but not all of the *exo*-cavity toluene molecules. The result of this treatment was the isolation of a frustrated phase, that when studied for sorption capability, showed similar properties to the original frustrated phase *i.e.* with respect to porosity (Fig. 6). This suggests that a number of such phases could exist based on a number of different solvates, as long as there are weakly bound *exo*-cavity solvent molecules that can be removed incrementally, an avenue we are currently exploring.

Experimental

The *p-tert*-butylcalix[5]arene was synthesised according to literature procedures, and purity was checked *via* ^{1}H NMR prior to use in crystallisation.[9] Recrystallisation was performed by heating a toluene suspension of **TBC5** until dissolution was achieved. Evaporation while hot (80 °C), with monitoring of crystallisation near dryness, afforded colourless single crystals that could be separated. Thermogravimetric analysis on **TBC5·Tol II** afforded a **TBC5** : toluene ratio of 1 : 2 that was used to model solvent occupancy in the single-crystal structure. X-Ray data were collected on a Bruker SMART 1000 CCD diffractometer. The structures possess disorder in *exo*-cavity toluene molecules, *endo*-cavity toluene molecules (**TBC5·Tol II** only) and *tert*-butyl groups. As this was the case, a number of restraints were applied to these

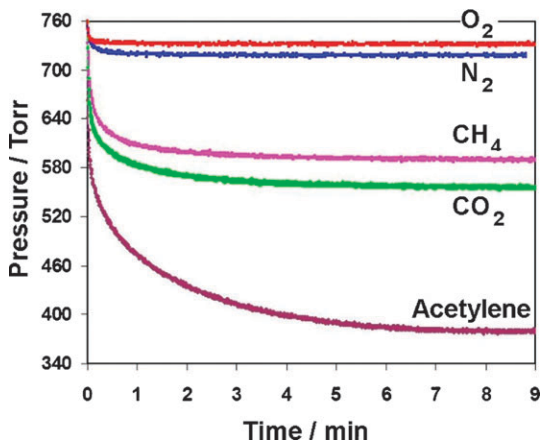

Fig. 6 Gas sorption isotherms for gases sorbed by frustrated **TBC5·Tol II** over a nine minute period at room temperature and pressure.

molecules and groups. Crystals of **TBC5·Tol III** were very small and were weakly diffracting.

Crystal data for TBC5·Tol II

Large hexagonal plates: $C_{134.5}H_{168}O_{10}$, M = 1944.69, triclinic, space group $P\bar{1}$, a = 17.986(3), b = 18.145(3), c = 20.583(4) Å, α = 83.817(3), β = 64.575(3), γ = 76.418(3)°, U = 5897.1(17) Å^3, T = 173(2) K, Z = 2, Mo-Kα radiation (wavelength, λ = 0.71073 Å), GOF = 1.052, agreement index R_1 = 0.0931, 42 265 reflections measured, 25 456 unique (R_{int} = 0.0309) which were used in all calculations. The final $wR(F^2)$ was 0.2916 (all data).

Crystal data for TBC5·Tol III

Small cubic crystals: $C_{69}H_{86}O_5$, M = 995.38, triclinic, space group $P\bar{1}$, a = 13.392(3), b = 13.860(3), c = 18.433(4) Å, α = 92.014(4), β = 108.769(4), γ = 107.867(4)°, U = 3049.1(12) Å^3, T = 173(2) K, Z = 2, Mo-Kα radiation (wavelength, λ = 0.71073 Å), GOF = 1.046, agreement index R_1 = 0.1150, 21 492 reflections measured, 13 038 unique (R_{int} = 0.1048) which were used in all calculations. The final $wR(F^2)$ was 0.2927 (all data).

Conclusions

To conclude, we have shown that solvent removal in two forms of the **TBC5** toluene solvate affords two different frustrated materials that have similar properties with regard to porosity and the ability to sorb gases. We have also shown that three polymorphs of the solvate exist, two of which are in abundance. We are currently investigating other calixarenes for similar behaviour, and different solvent systems to gain maximum control over the frustration prior to conversion to non-porous phases.

Notes and references

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