

Inclusion of tetramethylpyrazine in channels of the organic zeolite 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine

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Abstract 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine (BrPOT) features a channel size (11–12 Å) allowing the inclusion of large guest molecules such as tetramethylpyrazine (TMPZ). TMPZ forms π -stacks (d: 3.5 Å) along channels of BrPOT and shows rotational disorder for methyl positions. Co-inclusions of I₂ resulted in a doped state where I₂ molecules are oriented perpendicular to the channel axis with positional disorder as well. The particular orientation of I₂ molecules is evident from the observed dichroism.

Keywords Host–guest systems · Inclusion compounds · Organic zeolites

The triazine family [1] of channel inclusion compounds is of particular interest, because a channel size of about 10–12 Å opens up opportunities for hosting guest molecules of a much larger diameter than possible for the 4–5 Å class of many other host compounds [2]. Given the large diameter, an intuitive view might assume that elongated prolate type molecules based on trans disubstituted benzene rings (biphenyls, stilbenes, etc...) would enter the channel by a packing mode with overlapping guest species. However, this seems not to be the case, because it was found that this functional class of molecules might only be included in the

presence of fitting solvent molecules. This applies as well to C₆₀ and C₇₀ [3] for which no solvent free inclusions in e.g. 2,4,6-tris(4-bromo-phenoxy)-1,3,5-triazine (BrPOT) and 2,4,6-tris(4-bromo-3,5-difluorophenoxy)-1,3,5-triazine (Br-3,5-DFPOT) could be prepared so far. The more interesting is the fact that cylindrical types of molecules, such as decamethyl-bis-cyclopentadienyl-metallate (M(cp*)₂) molecules enter the channels without necessity of a solvent co-inclusion. And most surprisingly the combination of M(cp*)₂ and C₆₀, C₇₀ does it as well, whereas C₆₀(CH₃)₅-Fecp [3] requires again solvent co-inclusion. So, these triazine channels obviously provide sites, where optimally (length) cylindrical molecules may allow 1D close packing being interesting for physical property generation (charge transport, magnetism).

Here, we present the inclusion of tetramethylpyrazine (TMPZ), which represents a further guest, although not of a proper symmetry in respect to a trigonal or hexagonal channel, which enters by a stacking of aromatic rings. Attempts were made to intersect this 1D stack with I₂, showing, however, that only a low level I₂ may substitute TMPZ entering the channel with the molecular axis at I₂ perpendicular to c.

Preparation of crystals: Needle-shaped crystals (size: 1.2 × 0.2 × 0.2 mm³) were obtained by slow cooling (1 °C/h) of a toluene solution containing a mixture of BrPOT and TMPZ. The nature of solvent and the quantity of TMPZ engaged in preparation were of crucial importance: Butanone, mesitylene, and carbon disulfide did not yield crystals being stable against a loss of guests after getting out of the nutrient. Presumably, in the case of toluene we were obtaining a solvent free inclusion for TMPZ. Attempts to obtain a mixed chain of TMPZ and I₂ or at least a doped TMPZ chain were using particular relative amounts in the nutrient (see Table 1).

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Samples A, B, D, and E were stable at long term and thus used for the analysis (DSC: decomposition above ~ 120 °C). C and F probably were co-inclusions with toluene accepting more iodine than others. Solution $^1\text{H-NMR}$ showed for A, B, D, and E a molar ratio of 1.0(1):1.0(1) for BrPOT/TMPZ and no presence of toluene. Thermogravimetry confirmed these results (Fig. 1). The mass loss corresponded to a ratio of 1.0(1):1.0(1) and no significant amount of I_2 was detected.

The small concentration of I_2 inside channels was measured by ICP-MS: A few mg of crystals (B, D, E) were destroyed in HNO_3 (68%) and finally diluted in water to 1:10 for being measured by an ICP-MS Varian 820 MS. The found concentrations for I_2 of 320 ppm (B), 80 ppm (D), and 50 ppm (E) scale well with the decreasing color intensity of crystals. A blank test for A showed no I_2 . To demonstrate that I_2 is really present within *channels*, the pronounced dichroism was used for confirmation. In Fig. 2, the maximum absorption is obtained for a polarization *perpendicular* to the channels. The optical absorption for a polarization along *c* was not significant. Because of I_2 perpendicular to *c*, a rotation of the needle around *c* might show an extinction of color or not. In the first case, this would indicate ordering in the (*a*,*b*) plan. However, the overall hexagonal symmetry of the inclusion (Table 2) would not support this. From observation of a crystal rotated around the *c*-axis, we can conclude

Table 1 Conditions and results of crystallization (1 ml solution of toluene, cooling rate of 1 °C/h starting from 70 °C to room temperature)

Sample no.	BrPOT/TMPZ / Iodine (molar ratio)	Color	Remarks
A	1/13.3/0	Colorless	Stable in air
B	1/70.40/4.53	Yellow	Stable in air
C	1/3.25/0.96	Yellow	Not stable in air
D	1/34.11/1.59	Light yellow	Stable in air
E	1/4.19/1.14	Slight yellow	Stable in air
F	1/1.12/0.92	Orange	Not stable in air

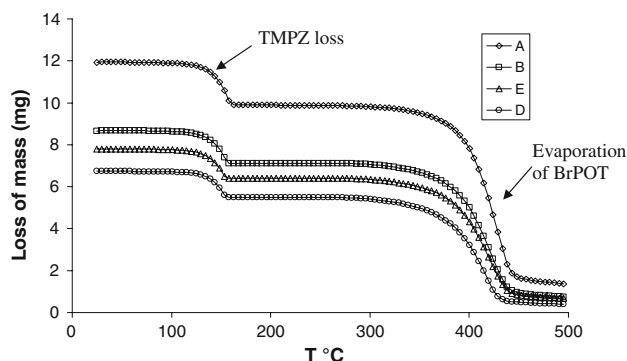


Fig. 1 Thermogravimetry for samples A, B, E, and D showing a loss of TMPZ

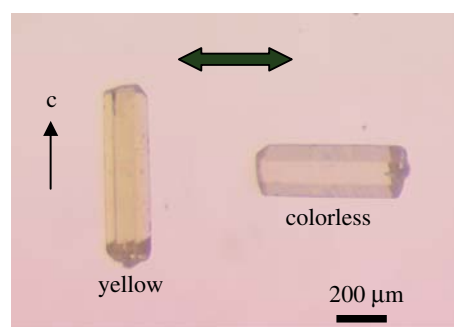


Fig. 2 Dichroism of a crystal of type B BrPOT(TMPZ)(I_2)_x (*x*: 320 ppm). The arrow shows the direction of polarization. (Color picture available on the web)

Table 2 Crystal data

	A	B
Crystallization method	Slow cooling	Slow cooling
Empirical formula	$\text{C}_{21}\text{H}_{12}\text{Br}_3\text{N}_3\text{O}_3$ $\text{C}_8\text{H}_{12}\text{N}_2$	$\text{C}_{21}\text{H}_{12}\text{Br}_3\text{N}_3\text{O}_3$ $\text{C}_8\text{H}_{12}\text{N}_2$
Formula wt. (g mol^{-1})	730.26	730.26
Crystal color	Colorless	Yellow
Crystal shape	Prism	Prism
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal size (mm^3)	$0.20 \times 0.18 \times 0.16$	$0.51 \times 0.17 \times 0.13$
Crystal system	Hexagonal	Hexagonal
Space group	$\text{P6}_3/\text{m}$	$\text{P6}_3/\text{m}$
<i>a</i> (Å)	15.695(2)	15.669(2)
<i>b</i> (Å)	15.695(2)	15.669(2)
<i>c</i> (Å)	7.1085(14)	7.1052(14)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
<i>V</i> (Å ³)	1516.4(4)	1510.7(4)
<i>Z</i>	2	2
ρ (g cm^{-3})	1.599	1.605
2θ max (°)	63.89	58.71
μ ($\text{MoK}\alpha/\text{mm}^{-1}$)	4.03	4.04
Measured reflect	18474	14630
Independent reflect	1876/ $I > 2\sigma(I)$ 1383	1479/ $I > 2\sigma(I)$ 1250
R_{int}	0.0519	0.0394
R_1	$I > 2\sigma(I)$ 0.0523/ 0.0780	$I > 2\sigma(I)$ 0.0444/ 0.0542
wR_2	0.1398	0.1243
CCDC η°	667809	667810

Note: Cambridge Crystallographic Data Centre (CCDC) contains the supplementary data for this paper. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif

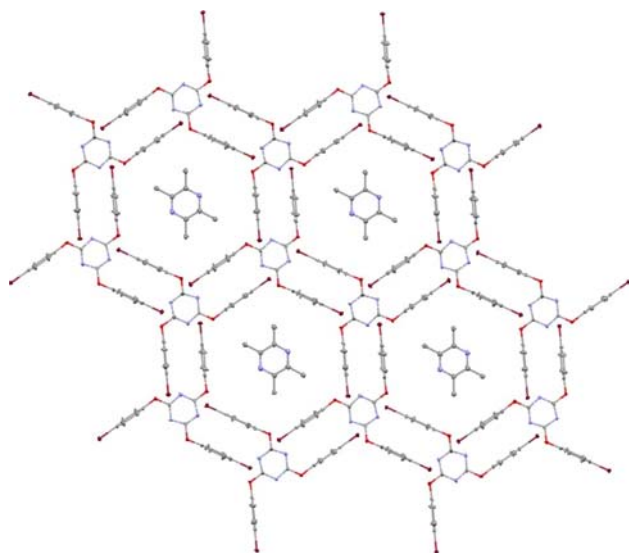


Fig. 3 Typical hexagonal packing layer of BrPOT(TMPZ). For clarity only one possible orientation of three of the pyrazine guest molecules is shown

that no preferred I_2 orientation in the (a, b) plane is evident for sample B.

For a structural analysis, crystals of sample A, B, and D were mounted on a Stoe Mark II-imaging plate diffractometer system [4] equipped with a graphite monochromator. Data collection, using Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$), was performed at $-100 \text{ }^\circ\text{C}$ for sample B and room temperature for sample A. Exposures were obtained at an image plate distance of 80 mm with $\varphi = 0^\circ$ and $0 < \omega < 180^\circ$ for the crystal oscillating through 1° in ω . The structure was solved by direct methods using the program SHELXS-92 [5] and refined by full matrix least squares on F^2 with SHELXL-97 [6]. The hydrogen atoms were included in calculated positions and treated as riding atoms. The diameter of the channel was estimated by using the Mercury visualization software [7]. The crystallographic data are reported in Table 2.

Both types of crystals, A, B (see Table 2) crystallize in the hexagonal space group $P6_3/m$, typical for many triazine inclusion compounds. As the two-fold molecular symmetry of the TMPZ is incompatible with the 3-fold channel symmetry (Fig. 3), rotational disorder is present. Three TMPZ's share one site, each of them rotated by 120° . The main feature of the structural analysis reveals a stacking of pyrazine moieties (stacking: 3.5 \AA) along the channels. There, the pyrazine is located at the center of the cavity formed by 3 bromo-phenoxy groups of host molecules. Obviously, this system is not adapting a mixed stack of

TMPZ and I_2 as found in pyrazine $\cdots I_2$ on pure crystals [8] and in the channels of tris(*o*-phenylenedioxy)cyclotriphosphazene (TPP), where pyrazine and I_2 form an alternate pyrazine $\cdots I_2\cdots$ pyrazine $\cdots I_2$ packing [9].

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