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COMMUNICATION

Novel Host–Guest Structures of 2,4,6-*Tris*(4-Halophenoxy)-1,3,5-Triazines(XPOT): Inclusion of C_{60} and Pyridine

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Abstract The crystal structures of two halophenoxytriazine host–guest compounds are reported and discussed. They feature inclusion of C_{60} into cages of 2,4,6-tris (4-iodophenoxy)-1,3,5-triazine [IPOT, hexagonal, $P6_3/m$, $a = 16.367(2)$ Å, $c = 20.661(4)$ Å, $V = 4793.1(13)$ Å^3, $Z = 2$] and of pyridine$_6$-clusters into cages of 2,4,6-*tris*(4-bromophenoxy)-1,3,5-triazine (BrPOT, rhombohedral, $R\,\bar{3}$, $a = 15.5186(8)$ Å, $c = 39.521(3)$ Å, $V = 8242.7(8)$ Å^3, $Z = 6$). The stackings of the threefold symmetric layers of XPOT host molecules are different from each other and from those of all previously reported XPOT inclusion compounds (X: Cl, Br, I).

Keywords Inclusion compound · Halophenoxy triazine · Channel/Cage layered structure

Introduction

Depending on halogen substitution, the phenoxy-triazine molecule (Fig. 1) forms a wide variety of crystalline structures. The *para*-substituted 2,4,6-tris(4-halophenoxy)-1,3,5-triazines (4-XPOT, X = Cl, Br, I; or XPOT for short) are known to form many types of host–guest structures which may be classified as either channel or cavity architectures: For co-crystals with ClPOT as host molecule only channels structures are known, IPOT provides cavities and BrPOT forms both channels and cavities. In contrast, the *ortho* and *meta*-substituted analogues form closed packed structures without guests [1]. More recently, the *meta*-fluorination of 4-BrPOT has produced an alternative channel architecture enclosing various guest molecules [2].

Cavity and channel walls in XPOT inclusion compounds are lined with the halogen-substituted phenyl rings. The van der Waals diameter of the voids is 10–12 Å, sufficient to accommodate special guest molecules, such as C_{60}, C_{70} and decamethylmetallocenes. Inclusion compounds with the endohedral C_{60}@N and C_{60}@P molecules are an interesting playground for quantum computing, because of an axial zero-field splitting of the S = 1 state and narrow resonance lines [3]. The inclusion of paramagnetic decamethylmetallocenes is of particular interest for the investigation of magnetically isolated and exchange coupled spin-chains [4].

In this paper we present crystal structure analyses of the 2,4,6-tris(4-iodophenoxy)-1,3,5-triazine-C_{60} inclusion compound IPOT$_3$·C_{60}, and of the 2,4,6-*tris*(4-bromophenoxy)-1,3,5-triazine-pyridine system BrPOT$_2$·py$_3$.

Experimental and Crystal Data

Both compounds were synthesized according to Jetti et al. [5].

IPOT$_3$·C_{60} Co-crystals of IPOT$_3$·C_{60} were obtained by cooling a toluene solution of IPOT and C_{60} from 383 to 297 K at a rate of 1 K/h. Solution ^{1}H NMR data and DTA measurements showed that co-inclusion of solvent was below the detection limit. The dark-red, needle-like hexagonal prisms are stable at room temperature and display

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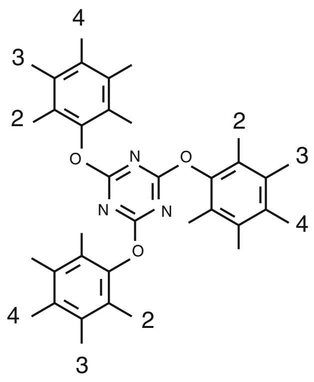


Fig. 1 The phenoxy-triazine molecule (POT). *Labels 2, 3* and *4* indicate the positions occupied by the halogens in various XPOT derivatives

optical dichroism. Extinction was observed perpendicular to the needle axis, whereas no birefringence was noticed for the cross section of prims (uniaxial crystal system). XRD single-crystal measurements were performed with a SMART-CCD diffractometer at $\lambda = 0.31840$ Å on ID11 at ESRF. Crystal dimensions were $0.144 \times 0.135 \times 0.09$ mm^3. The temperature was controlled by means of a Cryostream cooler (Oxford Cryosystems). Reflection intensities were integrated with the SAINT routine (version 6.36a) in the SMART software package (version 5.628) and empirically corrected for absorption by means of the SADABS program (version 2.05, $T_{\min} = 0.6084$, $T_{\max} = 0.8003$).

BrPOT$_2$*·py*$_3$ Co-crystals of BrPOT$_2$·pyridine$_3$ were grown by slow isothermal evaporation of a solution of BrPOT in pyridine at room temperature. Small colourless prismatic crystals were obtained. ^{1}H NMR and TGA analyses confirmed the absence of any impurities. A crystal of BrPOT$_2$·py$_3$ with dimensions of $0.35 \times 0.18 \times 0.13$ mm^3 was mounted on a Stoe Mark II-Imaging Plate Diffractometer System. Data were collected using Mo-Kα radiation ($\lambda = 0.71073$ Å). A numerical absorption correction was applied using 'sphere' (WinGX [6], $T_{\min} = 0.5558$, $T_{\max} = 0.5632$). The temperature was controlled by means of a Cryostream cooler (Oxford Cryosystems).

Both structures were solved by direct methods and refined by full-matrix least squares with the help of SHELXL-97 [7–10]. Hydrogen atoms were placed in calculated idealized positions and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Difference Fourier maps did not show chemically interpretable residual electron density.

IPOT$_3$·C$_{60}$ was refined in space group $P6_3/m$. The threefold molecular axis of the C$_{60}$ molecule coincides with a threefold crystallographic axis. However, the crystallographic mirror plane at (x, y, 1/4) does not coincide with a molecular mirror plane of the C$_{60}$ molecule implying twofold orientational disorder of the C$_{60}$ molecule which seems to be related to a twofold orientational disorder of the iodo-phenoxy groups in general position. During refinement of the twenty crystallographically independent carbon atoms of C$_{60}$ the long bonds were restrained (to 1.45 Å with e.s.d. = 0.001 in DFIX and SADI instructions) to be equal as were the short bonds (1.39 Å) and the distances of the C atoms from the molecular centres [10, 11]. The disorder of the iodo-phenoxy groups is confirmed by a Patterson vector of length 1 Å. Refinement in space group $P6_3$ does not remove disorder nor does it significantly improve agreement factors.

BrPOT$_2$·py$_3$ was refined in space group $R\,\bar{3}$. During refinement the pyridine molecule and the phenoxy group of the BrPOT molecule closer to the equator of the guest cluster acquired large atomic displacement parameters and significant disorder over two positions with populations 56 and 44%.

A summary of crystal data collection and structure refinement parameters is given in Table 1. Crystallographic data for the reported structures have been deposited with the Cambridge Crystallographic Data Centre as CCDC 757514 (IPOT$_3$·C$_{60}$) and CCDC 757515 (BrPOT$_2$·py$_3$). These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.camb.ac.uk; fax: +44(0)1223-336033.

Description of the Crystal Structures

IPOT$_3$·C$_{60}$

The crystal structure is built of trigonal layers of host molecules connected through three I···I contacts. The layers form infinite stacks along the c-axis with the triazine fragments centred at $x = y = 0$ (Fig. 2 left and right).

Three consecutive layers at $z = \sim 0.08$, 1/4 and $\sim$0.42 define a stack of three I$_3$ motifs centred at $\{x, y\} = \{2/3, 1/3\}$ and a cavity centred at $\{x, y\} = \{1/3, 2/3\}$, which is filled with twofold disordered C$_{60}$ molecules. The 6_3 operation relates consecutive triplets of layers and interchanges the location of the stack of three I$_3$ motifs and of the C$_{60}$ cavity in the x and y direction. Figure 2, left, shows the layer at $z = 1/4$ with the centre of the cavity at $\{x, y\} = \{1/3, 2/3\}$ and the centre of an I$_3$ motif at {2/3, 1/3}. Figure 2, right, shows the layers at $z = \sim \pm 0.08$ with an I$_3$ motif at $\{x, y, z\} = \{2/3, 1/3, \sim 0.08\}$, the other at $\{1/3, 2/3, \sim -0.08\}$ and the centre of a cavity at $\{2/3, 1/3, -1/4\}$. The disorder of the iodophenyl groups at $z = \sim \pm 0.08$

Table 1 Crystal data and structure refinement for $IPOT_3 \cdot C_{60}$ and $BrPOT_2 \cdot py_3$

CCDC deposit no.	757514 ($IPOT_3 \cdot C_{60}$)	757515 ($BrPOT_2 \cdot py_3$)
Empirical formula	C123 H36 I9 N9 O9	C57 H39 Br6 N9 O6
Formula weight	2925.71	1425.43
Crystal system	Hexagonal	Rhombohedral
Wavelength (Å)	0.31840	0.71073
Temperature (K)	140	140
Space group	$P\ 6_3/m$	$R\ \bar{3}$
Unit cell dimensions		
a (Å)	16.367(2)	15.5186(8)
b (Å)	16.367(2)	15.5186(8)
c (Å)	20.661(4)	39.5215(25)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
Volume ($Å^3$)	4793.1(13)	8242.7(8)
Z	2	6
Dc (g/cm^3)	2.028	1.723
Absorption coefficient (mm^{-1})	1.9	4.444
F(000)	2,772	4,212
Crystal size (mm^3)	0.144 × 0.135 × 0.090	0.35 × 0.18 × 0.13
θ range (°)	1.20–13.16	1.83–30.65
Reflections collected	84676	27943
Observed reflections [$I > 2\sigma(I)$]	4351	3285
Independent reflections/R_{int}	4,985/0.0625	5,463/0.1212
Parameters	391	220
Goodness-of-fit on F^2	1.075	1.037
R_1, wR_2 [$I > 2\sigma(I)$]	0.0558, 0.1719	0.0765, 0.1527
R_1, wR_2 (all data)	0.0618, 0.1789	0.1320, 0.1719
Residual electron densities ($e^-/Å^3$)	1.85 and −0.99	1.171 and −0.916

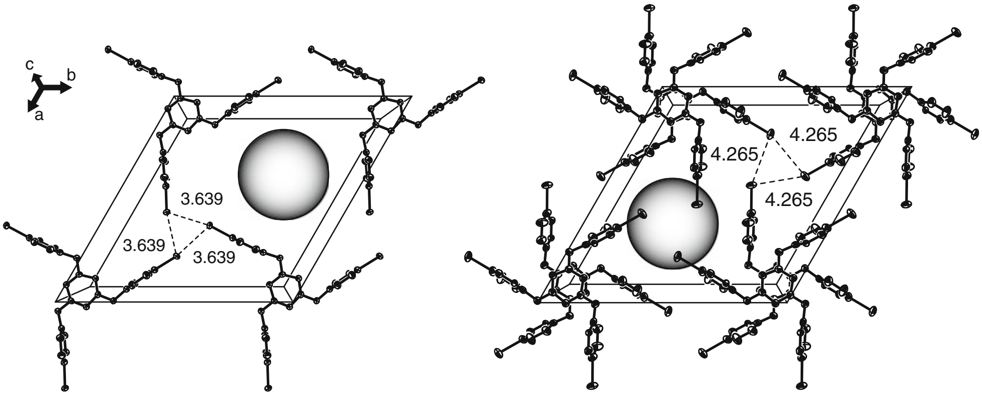


Fig. 2 *Left* Layer of IPOT molecules in the crystallographic mirror plane, $z = 1/4$, with the phenyl groups embracing the equator of C_{60} at$\{x, y, z\} = \{1/3, 2/3, 1/4\}$. *Right* Two layers of IPOT molecules in general position. The lower layer embraces the upper hemisphere of the C_{60} molecule at $z = -1/4$, and forms an I_3 motif at $\{x, y, z\} = \{1/3, 2/3, \sim -0.08\}$. The I_3 motif of the upper layer [d(I···I) = 4.265 Å] is above the C_{60} molecule and completes a cavity at $\{x, y, z\} = \{2/3, 1/3, \sim +0.08\}$

over two sites with populations 0.5 is probably due to the disorder of the C60 molecules.

Of the three layers in a triplet two are crystallographically independent: the layer at $z = 1/4$ coincides with a crystallographic mirror plane which relates the layer in general position at $z = \sim 0.08$ to the one at ~ 0.42. There are two independent interlayer distances along the c axis: 3.496(1) Å between the triazine plane of the molecule at

$z = \sim 0.08$ and that at $z = 1/4$, and 3.338(1) Å between the centroids of the two triazine fragments at $z = \sim \pm 0.08$ in general position. A weak C–H···O interaction is observed between the ortho hydrogen of the phenyl group at $z = \sim 0.08$ and the oxygen atom of the triazine at $z = 1/4$ [2.662(4) Å, 152.5(3)°].

The interactions between iodines within the IPOT layers in both special and general position are of type II [12–14] (i.e. $\theta 1$(C–I···I′) ~ 180°, $\theta 2$(I···I′–C′) ~ 120°). The I(31)···I(31) distance of the I_3 unit in the mirror plane is 3.6394(5) Å (Fig. 2 left), is small compared to the sum of the van der Waals radii for iodines (3.96 Å). The shortest distance between the disordered iodine atoms of the I_3 unit in general position, I(21)···I(21), is 4.2705(6) Å (Fig. 2 right). The difference in I···I distances implies a difference in the cavity diameter: it is larger in the plane of the $I(31)_3$ unit than in the one of the $\{I(21)/I(11)\}_3$ units thus allowing a snuggly fit of the phenyl rings to the equatorial and northern/southern regions of C_{60}, respectively.

The C_{60} ball is surrounded by nine phenoxy rings at the vertices of a tricapped trigonal prism, three each in the northern and southern hemispheres and three in the equator. The iodophenoxy-groups are approximately tangential to the surface of the C_{60} molecules implying a tilt of the phenoxygroups in the northern and southern hemispheres. The largest principal components of the anisotropic displacement parameters belonging to the disordered iodine atoms are also tangential to the C_{60} molecule suggesting a correlation with C_{60} disorder. The poles of the C_{60} molecules are capped by I_3-motifs. The distance between the centres of C_{60} molecules is ~16.4 Å in the *a,b*-plane and 14.0 Å between the layers. Additional information regarding molecular interactions is listed in Table 2.

$BrPOT_2 \cdot py_3$

Again the crystal structure of $BrPOT_2 \cdot py_3$ is built of trigonal layers of host molecules connected through Br···Br contacts in the shape of equilateral triangles (Br_3 motif, Fig. 3).

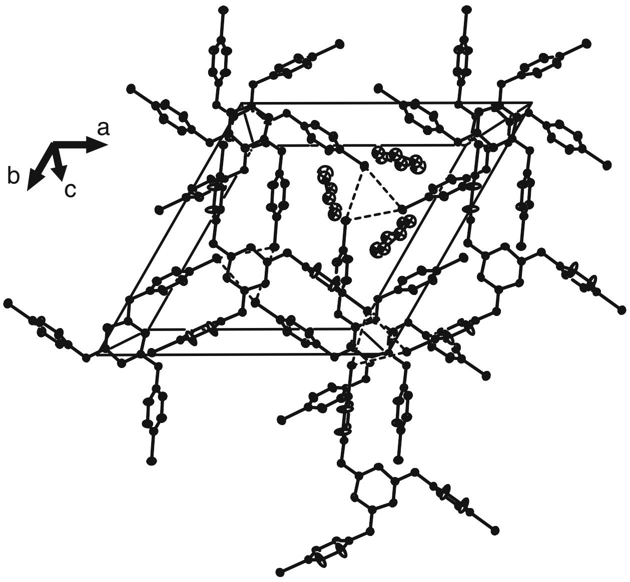


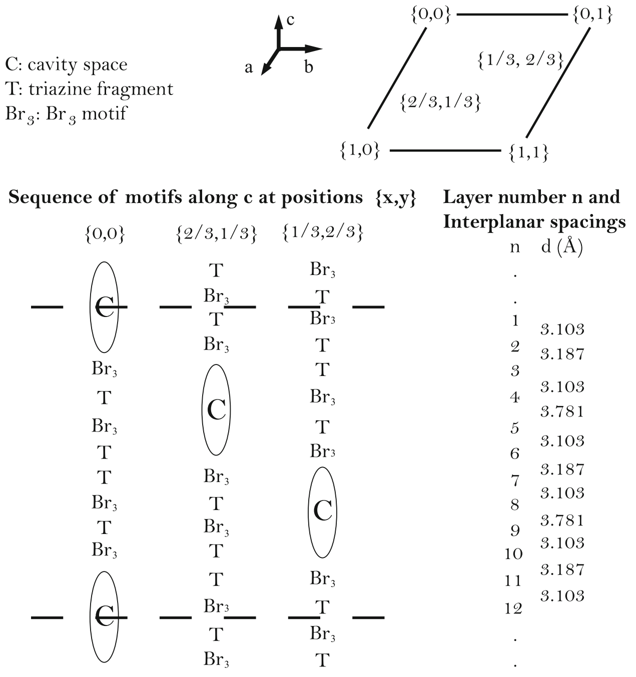
Fig. 3 Projection of the crystal structure of $BrPOT_2 \cdot py_3$ along *c*. Three BrPOT layers and three pyridine molecules are shown: layer 7 at $z \sim 0.54$ with the capping Br_3 triangle at $\{x, y\} = \{1/3, 2/3\}$ is lowest [d(Br···Br) = 3.689 Å]; layer 6 at $z \sim 0.46$ with the Br_3 unit at $\{x, y\} = \{2/3, 1/3\}$ is in the middle [d(Br···Br) = 3.689 Å]; it contains the tilted phenoxy groups closer to the poles of the pyridine-containing cavity; layer 5 at $z \sim 0.38$ with the Br_3 *triangle* shown at $\{x, y\} = \{1, 1\}$is highest [d(Br···Br) = 3.456 Å] and contains the upright phenoxy groups closer to the equator of the cavity

Table 2 Selected interactions for $IPOT_3 \cdot C_{60}$ and $BrPOT_2 \cdot py_3$

Structure	Atoms	H···A distance	Halogen contacts	Angle
$IPOT_3 \cdot C_{60}$				
	C(33)–H···O(20)#10	2.662(4)		152.5(3)
	C(23)–H···N(30)#11	2.757(9)		152.4(6)
	C(31)–I(31)···I(31)#11		3.6394(5)	169.22(1)
	C(31)#11–I(31)#11···I(31)		3.6394(5)	109.22(1)
	C(21)–I(21)···I(21)#11		4.2705(6)	107.78(1)
	C(21)#11–I(21)#11···I(21)		4.2705(6)	167.18(1)
$BrPOT_2 \cdot py_3$				
	C(43)–H···Br(2)#4	3.047(9)		166.9(8)
	C(12a)–H···N(21)#5	2.695(3)		151.1(3)
	C(12b)–H···O(21)#6	2.690(5)		155.2(4)
	C(11)–Br(1)···Br(1)#2		3.4558(2)	109.91(1)
	C(11)#2–Br(1)#2···Br(1)		3.4558(2)	169.56(1)
	C(21)–Br(2)···Br(2)#3		3.6888(2)	164.54(1)
	C(21)#3–Br(2)#3···Br(2)		3.6888(2)	105.49(1)

Symmetry codes: IPOT #10: $-Y, X - Y - 1, Z$. #11: $-Y + 1, X - Y, Z$

Symmetry codes: BrPOT #2: $-X + Y, -X + 1, Z$. #3: $-Y + 1, X - Y, Z$. #4: $1/3 + X - 1, 2/3 + Y - 1, 2/3 + Z - 1$. #5: $X - 1, Y, Z$. #6: $-Y + 1, X - Y, Z$



Scheme 1 Idealized representation of the layered packing occurring in the $BrPOT_2 \cdot py_3$ compound

Although individual layers are similar to those in $IPOT_3 \cdot C_{60}$, their stacking is much more complicated and we have introduced a schematic description (Scheme 1) of the $BrPOT_2 \cdot py_3$ layered architecture in order to facilitate the discussion.

The Scheme 1 shows the sequence of structural elements along the *c*-axis ($0 < z < 0.5$) at $\{x, y\} = \{0,0\}$, $\{2/3,1/3\}$ and $\{1/3,2/3\}$. T stands for the triazine unit, Br_3 for the triangular Br-motif and C for cavity space. The sequence of layers 1–4 is repeated two times by the centering translations (2/3, 1/3, 1/3) and (1/3, 2/3, 2/3) of the R-centred hexagonal unit cell, e.g. layers 5 and 9 are generated from layer 1, etc. There are three independent interlayer distances defined by triazine mean planes, 3.103, 3.187, 3.781 Å, two of them rather short compared to the smallest distance found for $IPOT_3 \cdot C_{60}$ (3.338 Å). One of them is associated with C–H···O/N interactions between the phenyl and oxy-triazine parts of the symmetrically independent layers 9 and 10 or 11 and 12, the other with hydrogen bonds C–H···Br2 (3.047(9) Å, 166.9(8)°) between pyridine guests and bromide atoms pertaining to layers with superimposed triazine motifs (e.g. layers 10 and 11).

Additional information regarding molecular interactions is listed in Table 2.

The cavities extend over four BrPOT layers (e.g. layers 3, 4, 5, 6 or 7, 8, 9, 10) and are filled with an ellipsoidal cluster of six pyridine molecules related by a $\bar{3}$ symmetry operation. The cavities are capped with Br_3 units (e.g. layers 2 and 7 or 6 and 11) and embraced by 12 bromophenoxy groups from the four BrPOT layers 3, 4, 5, 6 or 7, 8, 9, 10. Three bromophenoxy groups are close to each of the two poles (e.g. layers 3 and 6 or 7 and 10) and three each are north and south of the equator (e.g. layers 4 and 5 or 8 and 9). The centres of the bromophenoxy groups occupy the corners of three face-sharing, flattened octahedra (Fig. 4). The bromophenoxy groups in layers 3 and 6 (or 7 and 10) are slightly tilted and thus approximately tangential to the surface of the pyridine cluster.

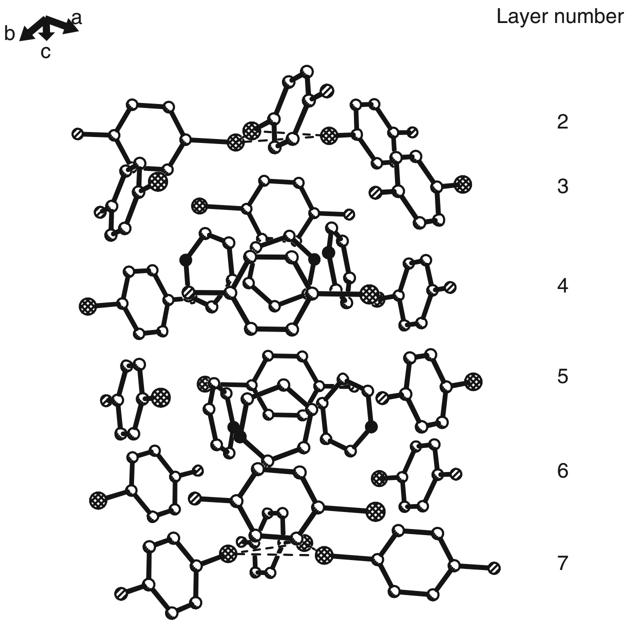


Fig. 4 Structural cavity containing six pyridine molecules (*black dots* nitrogen atoms). The cavity is delineated by two Br_3 units at the poles (layers 2 and 7) by three tilted bromophenoxy groups (layers 3 and 6) and by three upright ones (layers 4 and 5; *hatched circles* oxygen atoms, *crossed hatched circles* bromine atoms)

The interactions between bromines within the layers are of type II [12–14] (with $\theta1(C\text{–}Br\cdots Br') \sim 180°$ and $\theta2(Br\cdots Br'\text{–}C') \sim 120°$). The Br(1)···Br(1) distance of the Br_3 unit near the equatorial plane of the cavity (e.g. layers 4 and 5) is smallest (3.456(1) Å, $\theta1 = 169.6(1)°$, $\theta2 = 109.9(1)°$) and, as a consequence, the cavity diameter is largest. The Br(2)···Br(2) distance in the upper/lower hemisphere position (e.g. layers 3 and 6) is larger (3.689(1) Å, $\theta1 = 164.5(1)°$, $\theta2 = 105.5(1)°$) thus bringing the tilted phenyl rings closer to the northern and southern hemispheres of the pyridine assembly.

Conclusion

The crystal structures of two new inclusion compounds, $IPOT_3 \cdot C_{60}$ and $BrPOT_2 \cdot py_3$, represent new structure types in the family of threefold symmetric XPOT inclusion compounds (X = Cl, Br, I, CN, NO_2, CHO). $IPOT \cdot C_{60}$

represents the first cage structure featuring continuous stacks of triazine moieties surrounded by columns in which a sequence of three I_3-motifs alternates with one C_{60} guest molecule (also extending over three layers). $BrPOT_2{\cdot}py_3$ belongs to the family of rhombohedral cage structures. The number of stacked layers in the translational repeat along the hexagonal *c*-axis is twelve, larger than that in any of the already known structures (six or nine) with such simple planar guest molecule [15, 16].

The two structures described here represent novel stacking patterns in the $P6_3/m$ and $R\,\bar{3}$ families of triazine host/guest compounds. The singular packing patterns adopted by $IPOT{\cdot}C_{60}$, and above all by BrPOT·py, have led us to a new shorthand (viz. Scheme 1) which allows to classify the structural complexity of all known phenoxy-triazine host–guest structures in terms of a few simple rules. This formalism will be described in a forthcoming review.

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