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# 2,4,6-Tris[4-(1-naphthyl)phenoxy]-1,3,5-triazine: formation of a unique piedfort-based host lattice with trigonal symmetry

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**X-Ray crystal structure analysis of the isopropanol clathrate of the title compound 1 has revealed a trigonal lattice, space group $R\bar{3}c$ with $a$=24.760(3), $c$=87.644(14)Å, Z=48 (host), in which self-assembly of host molecules, in the form of three crystallographically independent Piedfort units of symmetry $C_{3i}$, $C_3$ and $D_3$ located along $c$, has led to the formation of two types of trigonal cage, each occupied by an isopropanol guest molecule.**

## INTRODUCTION

As part of a systematic study of the rational design of new classes of crystalline inclusion compound[1], we have recently introduced the Piedfort concept[2] in which two tri-substituted aromatic molecules, arranged back-to-back, successfully mimic a single hexahost molecule[3]. In the 1,4-dioxane inclusion compound of 2,4,6-tris[4-(2-phenylpropan-2-yl)phenoxy]-1,3,5-triazine, previously reported[2], the Piedfort host unit has symmetry approximating to $C_{3i}$, though its exact symmetry is only $C_i$. We now report results from a single-crystal X-ray analysis of the novel trigonal clathrate formed between 2,4,6-tris[4-(naphthyl)phenoxy]-1,3,5-triazine (**1**) and isopropanol.

## EXPERIMENTAL

This inclusion compound was formed by recrystallisation of **1** from isopropanol at *ca.* 100°C in a sealed tube. The adduct, obtained as very squat hexagonal prisms, had a host-guest ratio of *ca.* 2:1 as determined by $^1$HNMR analysis, and also by thermogravimetric analysis, TGA, which indicated tight retention of guest up to *ca.* 190°C, the main weight loss occurring in the range 220–240°C ($N_2$ atmosphere, heating rate 10°C/min). The m.p. of the adduct, observed on the hot-stage microscope, is *ca.* 220–230°C. The preparation and initial spectroscopic characterisation of host **1** were as previously described[2].

*Crystal data* for $C_{51}H_{33}N_3O_3 \cdot \frac{1}{2}C_3H_8O$. $M$=765.4, rhombohedral, space group $R\bar{3}c$, $a$=24.760(3), $c$=87.644(12)Å, $U$=46540(12)Å$^3$, $Z$=48(4/3 host molecules per asymmetric unit). $D_c$=1.311gcm$^{-3}$, λ(Mo-Kα)=0.7107Å, μ=0.082mm$^{-1}$. T=123K. Number of independent intensities 10488 from colourless hexagonal prism, 0.3×0.3×0.1mm. $R$=0.0749, $R_w$=0.2127 for 4523 observed reflections ($I/\sigma(I)$>2.0). X-ray intensity measurements for all possible reflections with sinθ/λ <0.64Å$^{-1}$ were made by 2θ-ω scans on a Nonius CAD4 diffractometer. However, even at the experimental temperature of 123 K, the crystal scattered weakly. Only *ca.* 25 % of reflections with sin θ/λ >0.4 Å$^{-1}$ were observed. The principal computer programs used in structure solution and refinement are listed in ref 4. Atomic coordinates, and selected bond lengths and angles are given in Tables 1 and 2. Phenyl rings were treated as rigid groups during refinement, but all other non-hydrogen atoms of the host were refined free. Hydrogen atoms were added by geometric construction. Difference maps indicated guest molecules on the crystallographic 3-fold axis, and a model of the guest was refined at full occupancy, in one of the two cavities. The second guest (in a cavity with site occupancy factor apparently less than unity) gave diffuse electron density, and was modelled in terms of two carbon atom positions.

## RESULTS AND DISCUSSION

As illustrated in Fig. 1, (a)-(c), there are three different types of Piedfort unit comprising the host component in the isopropanol adduct of 2,4,6,-tris[4-(1-naphthyl)-

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**Table 1** Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (A^2 × 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

| | *x* | *y* | *z* | *U(eq)* |
|---|---|---|---|---|
| O(1A) | -1039(1) | 27(1) | 3610(1) | 49(1) |
| N(1A) | -551(2) | -557(2) | 3612(1) | 37(1) |
| C(1A) | -523(2) | -13(2) | 3612(1) | 39(1) |
| C(2A) | -1624(1) | -511(1) | 3623(1) | 44(1) |
| C(3A) | -1842(1) | -783(1) | 3765(1) | 49(1) |
| C(4A) | -2454(1) | -1264(1) | 3781(1) | 48(1) |
| C(5A) | -2849(1) | -1471(1) | 3655(1) | 41(1) |
| C(6A) | -2632(1) | -1199(1) | 3513(1) | 61(2) |
| C(7A) | -2019(1) | -718(1) | 3497(1) | 55(1) |
| C(8A) | -3531(1) | -1968(1) | 3677(1) | 42(1) |
| C(9A) | -3875(1) | -1775(1) | 3763(1) | 49(1) |
| C(10A) | -4513(1) | -2168(2) | 3781(1) | 54(1) |
| C(11A) | -4807(3) | -2739(3) | 3712(1) | 63(2) |
| C(12A) | -4460(2) | -2941(2) | 3622(1) | 52(1) |
| C(17A) | -3808(2) | -2535(2) | 3605(1) | 40(1) |
| C(16A) | -3461(2) | -2758(2) | 3527(1) | 58(2) |
| C(15A) | -3751(2) | -3346(2) | 3461(1) | 70(2) |
| C(14A) | -4402(4) | -3737(3) | 3481(1) | 80(2) |
| C(13A) | -4742(3) | -3537(3) | 3556(1) | 76(2) |
| O(1B) | -744(1) | 464(1) | 4021(1) | 50(1) |
| N(1B) | -637(2) | -377(2) | 4019(1) | 41(1) |
| C(1B) | -347(2) | 247(2) | 4020(1) | 37(1) |
| C(2B) | -517(1) | 1097(1) | 4000(1) | 42(1) |
| C(3B) | -340(1) | 1498(1) | 4125(1) | 44(1) |
| C(4B) | -184(1) | 2116(1) | 4104(1) | 47(1) |
| C(5B) | -206(1) | 2332(1) | 3959(1) | 35(1) |
| C(6B) | -383(1) | 1931(1) | 3835(1) | 41(1) |
| C(7B) | -539(1) | 1313(1) | 3855(1) | 45(1) |
| C(8B) | -59(1) | 3003(1) | 3937(1) | 39(1) |
| C(9B) | 531(1) | 3456(1) | 3985(1) | 45(1) |
| C(10B) | 720(2) | 4084(1) | 3968(1) | 52(1) |
| C(11B) | 331(2) | 4258(2) | 3899(1) | 51(1) |
| C(12B) | -270(2) | 3807(2) | 3849(1) | 44(1) |
| C(17B) | -460(2) | 3165(2) | 3867(1) | 37(1) |
| C(16B) | -1068(2) | 2725(2) | 3820(1) | 44(1) |
| C(15B) | -1469(2) | 2899(2) | 3755(1) | 50(1) |
| C(14B) | -1265(3) | 3536(3) | 3738(1) | 53(1) |
| C(13B) | -688(3) | 3972(2) | 3783(1) | 49(1) |
| O(1C) | 635(2) | 1220(2) | 207(1) | 57(1) |
| N(1C) | 642(2) | 295(2) | 202(1) | 53(1) |
| C(1C) | 319(2) | 592(2) | 202(1) | 54(1) |
| C(2C) | 1272(1) | 1532(1) | 185(1) | 48(1) |
| C(3C) | 1512(1) | 1709(1) | 38(1) | 45(1) |
| C(4C) | 2153(1) | 2018(1) | 15(1) | 45(1) |
| C(5C) | 2554(1) | 2150(1) | 138(1) | 41(1) |
| C(6C) | 2314(1) | 1973(1) | 284(1) | 46(1) |
| C(7C) | 1673(1) | 1664(1) | 308(1) | 48(1) |
| C(8C) | 3253(1) | 2466(1) | 107(1) | 38(1) |
| C(9C) | 3620(1) | 3019(1) | 186(1) | 49(1) |
| C(10C) | 4260(1) | 3354(1) | 162(1) | 52(1) |
| C(11C) | 4530(2) | 3141(3) | 58(1) | 53(1) |
| C(12C) | 4167(2) | 2586(2) | -24(1) | 44(1) |
| C(17C) | 3507(2) | 2237(2) | 2(1) | 37(1) |
| C(16C) | 3156(2) | 1678(2) | -78(1) | 41(1) |
| C(15C) | 3428(2) | 1458(2) | -181(1) | 46(1C) |
| C(14C) | 4073(2) | 1796(3) | −204(1) | 51(1) |
| C(13C) | 4430(2) | 2347(3) | -128(1) | 51(1) |
| O(1D) | 1153(1) | 902(1) | 2689(1) | 47(1) |
| N(1D) | 467(2) | -152(2) | 2693(1) | 35(1) |
| C(1D) | 566(2) | 424(2) | 2694(1) | 33(1) |
| C(2D) | 1658(1) | 801(1) | 2674(1) | 39(1) |
| C(3D) | 1963(1) | 949(1) | 2534(1) | 41(1) |
| C(4D) | 2538(1) | 982(1) | 2520(1) | 43(1) |
| C(5D) | 2808(1) | 866(1) | 2645(1) | 37(1) |
| C(6D) | 2503(1) | 718(1) | 2785(1) | 39(1) |
| C(7D) | 1929(1) | 686(1) | 2799(1) | 40(1) |
| C(8D) | 3473(1) | 978(1) | 2628(1) | 40(1) |
| C(9D) | 3903(1) | 1567(1) | 2574(1) | 44(1) |
| C(10D) | 4527(1) | 1735(2) | 2560(1) | 55(1) |

**Table 1** (Continued)

| | *x* | *y* | *z* | *U(eq)* |
|---|---|---|---|---|
| C(11D) | 4721(2) | 1309(3) | 2597(1) | 54(1) |
| C(12D) | 4284(2) | 717(3) | 2653(1) | 45(1) |
| C(17D) | 3649(2) | 550(2) | 2670(1) | 39(1) |
| C(16D) | 3213(2) | -58(2) | 2720(1) | 41(1) |
| C(15D) | 3400(2) | -484(2) | 2759(1) | 56(1) |
| C(14D) | 4036(3) | -307(3) | 2742(1) | 64(2) |
| C(13D) | 4454(3) | 269(3) | 2693(1) | 60(2) |
| CX1 | -3519(4) | 3393(4) | 1510(1) | 73(6) |
| CX2 | -3821(4) | 3462(4) | 1378(1) | 70(3) |
| CX3 | -3650(8) | 2713(5) | 1524(1) | 82(6) |
| CX4 | -2839(4) | 3888(7) | 1508(1) | 77(6) |
| CQ1 | 107(16) | 76(15) | 5584(1) | 541(29) |
| CQ2 | 182(13) | -464(14) | 5580(2) | 207(14) |

phenoxy]-1,3,5,-triazine (**1**). All three Piedfortunits, located on the crystallographic *c*-axis, are constrained to have exact trigonal symmetry. Unit (b) has $C_3$ symmetry; whilst (a), located on a point of inversion, possesses $C_{3i}$ symmetry; and unit (c), also located on the crystallographic two-fold axis at $z=\frac{1}{4}$, has exact $D_3$ symmetry. The relative dispositions of the two halves of units (a),(b), and (c) are described by the magnitudes of the respective pseudo torsion angles, 60°, 21° and 24°, which correspond to the *c*-axis and the closest oxygen atoms in the adjacent triazines. The corresponding pseudo torsion angles for the closest oxygen atoms in *neighbouring* Piedfort units along *c* are 6°, between units (a) and (b), and 10°, between units (b) and (c). All the triazine rings are accurately planar; and for unit (b), atoms O(1A) and O(1B) are close to their respective triazine ring planes, magnitudes of displacements .013(5) and .015(9)Å, respectively. For units (a) and (b), however, atoms O(1C) and O(1D) are more displaced, by 0.045(6) and 0.037(5)Å, from their respective triazine ring planes. The bond lengths and angles closely parallel those reported previously[2] for 2,4,6-tris[4-(2-phenylprop-2-yl)phenoxy]-1,3,5-triazine. Interestingly, the N-C-O angles for a given oxygen atom are markedly unequal, mean angles corresponding respectively to *cisoid* and *transoid* side-chain dispositions being 119.6° and 112.6°. The inter-triazine plane distances for Piedfort units (a),(b), and (c) are 3.544(8), 3.574(5), and 3.390(6)Å, respectively.

**Table 2** Selected bond lengths [Å] and angles [deg] for 1

| | |
|---|---|
| O(1A)-C(1A) | 1.331(5) |
| O(1A)-C(2A) | 1.397(3) |
| N(1A)-C(1A) | 1.313(5) |
| N(1A)-C(1A)#1 | 1.343(5) |
| O(1B)-C(1B) | 1.335(5) |
| O(1B)-C(2B) | 1.388(3) |
| N(1B)-C(1B)#1 | 1.319(6) |
| N(1B)-C(1B) | 1.340(5) |
| O(1C)-C(1C) | 1.347(5) |
| O(1C)-C(2C) | 1.381(4) |
| N(1C)-C(1C)#2 | 1.325(6) |
| N(1C)-C(1C) | 1.331(6) |
| O(1D)-C(1D) | 1.340(5) |
| O(1D)-C(2D) | 1.401(3) |
| N(1D)-C(1D) | 1.320(5) |
| N(1D)-C(1D)#2 | 1.334(5) |
| C(1A)-O(1A)-C(2A) | 120.3(3) |
| C(1A)-N(1A)-C(1A)#1 | 113.0(5) |
| N(1A)-C(1A)-O(1A) | 121.0(4) |
| N(1A)-C(1A)-N(1A)#2 | 127.0(5) |
| O(1A)-C(1A)-N(1A)#2 | 112.0(4) |
| C(1B)-O(1B)-C(2B) | 119.4(3) |
| C(1B)#1-N(1B)-C(1B) | 112.9(4) |
| N(1B)#2-C(1B)-O(1B) | 120.2(4) |
| N(1B)#2-C(1B)-N(1B) | 127.1(4) |
| O(1B)-C(1B)-N(1B) | 112.7(4) |
| C(1C)-O(1C)-C(2C) | 118.9(4) |
| C(1C)#2-N(1C)-C(1C) | 111.9(5) |
| N(1C)#1-C(1C)-N(1C) | 128.1(5) |
| N(1C)#1-C(1C)-O(1C) | 113.5(5) |
| N(1C)-C(1C)-O(1C) | 118.4(5) |
| C(1D)-O(1D)-C(2D) | 121.1(3) |
| C(1D)-N(1D)-C(1D)#2 | 111.1(4) |
| N(1D)-C(1D)-N(1D)#1 | 128.9(4) |
| N(1D)-C(1D)-O(1D) | 119.3(4) |
| N(1D)#1-C(1D)-O(1D) | 111.8(4) |

Symmetry transformations used to generate equivalent atoms: #1 -y,x-y,z #2 -x+y, -x,z

The intricate host-guest packing in the isopropanol adduct of **1** is illustrated in Fig. 2. There are two types of crystallographically distinct void, and these are located along the *c*-axial direction which is vertical in the view shown. Both cavities have exact $C_3$ symmetry and each is occupied by an isopropanol guest molecule, although one of these is highly disordered and could not be located unambiguously. Only the better ordered isopropanol guest is shown in Fig. 2. The ends of the cavity containing the better ordered guest are bounded by Piedfort units, (b) and (c), with $C_3$ and $D_3$ symmetry, whilst its walls are formed by three symmetry related $C_{3i}$, (a) units and three $C_3$, (b) units. The cavity containing the highly disordered guest has ends comprised of (a) and (b) Piedfort units, and walls comprised of three (b) units and three (c) units. Computed van der Waals sections at 1Å spacing along *c* show that both cavities are of the completely closed cage type (in keeping with the extremely tight guest retention found by TGA), estab-

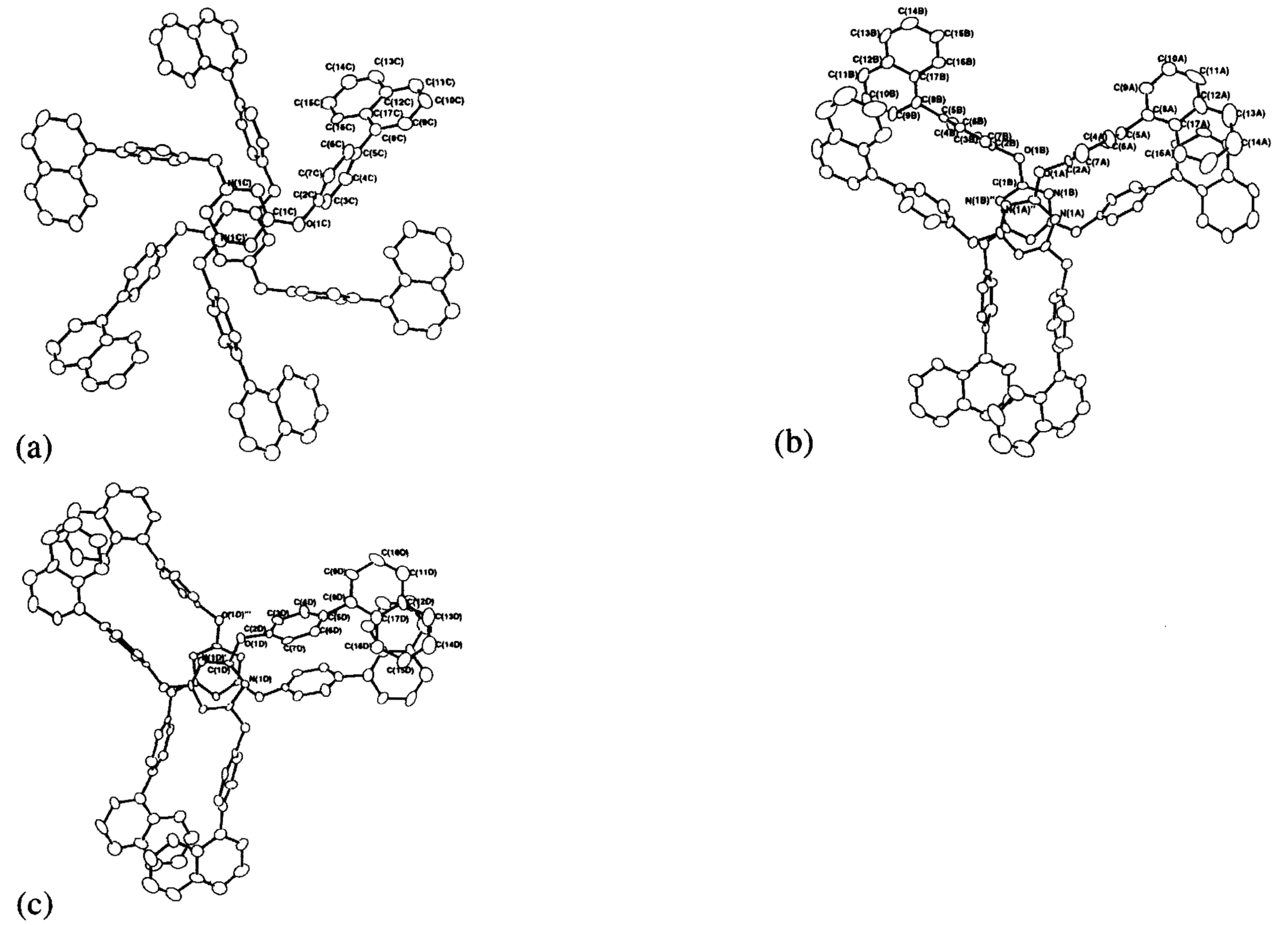

**Figure 1** An illustration of the three distinct types of Piedfort unit present in the isopropanol clathrate of 2,4,6-tris[4-(1-naphthyl)phenoxy]-1,3,5-triazine **1**; the three units, viewed at a narrow angle to the crystallographic *c*-axis, have exact respective symmetres $C_{3i}$, $C_3$, and $D_3$. The disposition of the side-chain in unit (a) is described by torsion angles N(1C)-C(1C)-O(1C)-C(2C), -11.5(7)°, and C(1C)-O(1C)-C(2C)-C(7C),89.2(4)°; whilst corresponding torsion angles for unit(b) are N(1A)-C(1A)-O(1A)-C(2A), and N(1B)"-C(1B)-O(1B)-C(2B),6.1(7)° and 9.0(6)°; C(1A)-O(1A)-C(2A)-C(7A), and C(1B)-O(1B)-C(2B)-C(7B), -110.0(7)° and 96.6(4)°; and for unit(c), N(1D)-C(1D)-O(1D)-C(2D), and C(1D)-O(1D)-C(2D)-C(7D), are 4.4(6)° and -85.7(4)°, respectively.

lishing the true classical clathrate character of this adduct of **1**. The potential storage of gaseous guest species in Piedfort-based rhombohedral host latticies of this type is currently under consideration.

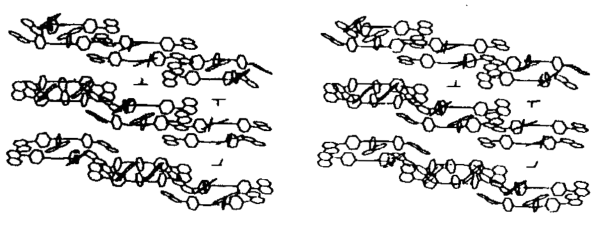

**Figure 2** A stereoview, looking normal to the *c*-axis, showing the host-guest packing in the isopropanol clathrate of **1**. There are two types of crystallographically independent trigonal cage; each is occupied by an isopropanol guest molecule, but only the better ordered guest (representative orientation) is shown.

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