Inclusion Compound Design: the Piedfort† Concept

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Two molecules of 2,4,6-tris[4-(2-phenylpropan-2-yl)phenoxy]-1,3,5-triazine **1** undergo self-assembly to produce a composite unit, termed Piedfort unit, which acts as a single hexa-host molecule; the structure of this new host unit, found both in the 1,4-dioxane inclusion compound of **1** and in its unsolvated crystal, has been elucidated by X-ray methods.

Rational host design greatly facilitates the discovery of new classes of host molecule capable of forming crystalline inclusion compounds.[1,2] The value of thinking by analogy is well demonstrated by the hexa-hosts,[1] the genesis of which relied on the recognition of the significance of the hydrogen-bonded hexameric unit in many phenolic hosts.[3] A typical hexa-host, a suitably hexa-substituted benzene, is shown schematically in Fig. 1(*A*), where Z represents a link atom or chain, and ○ and ● outer groups, often enantiomerically related in the crystal,[1] since the host molecule is usually located on a point of $\bar{1}$ or $\bar{3}$ symmetry. We now report the successful use of a new approach, termed the Piedfort concept, which is illustrated in Fig. 1(*B*). As can be seen the Piedfort analogue (*B*), mimicking (*A*), consists of two *tri*-substituted rings, superposed at van der Waals contact, such that the resulting (alternating) disposition of side-chain moieties and overall geometric aspects are similar; however, it should be noted that neighbouring Z atoms (or chains) on separate rings in (*B*), are somewhat further apart than the corresponding neighbouring Z moieties of (*A*). To achieve in reality the self-assembly mode implicit in (*B*), we selected target molecules 2,4,6-tris[4-(2-phenylpropan-2-yl)phenoxy]1,3,5-triazine **1** and 2,4,6-tris[4-(1-naphthyl)phenoxy]1,3,5-triazine **2**, both based on the symmetrical heteroaromatic 1,3,5-triazine ring. Compounds **1** and **2**, new materials, were prepared in good yield employing a general literature method,[4] and have spectroscopic properties (^{1}H, ^{13}C NMR, IR and mass) fully in accord with their formulated structure; **1** has m.p. 178–180 °C, for the unsolvated form (from EtOH–CHCl$_3$). Encouragingly, both **1** and **2** were found to form crystalline adducts. In order to establish whether self-assembly had occurred in the Piedfort mode sought, the triazine **1** was selected for initial X-ray crystal structure analysis. Both the 1,4-dioxane inclusion compound of **1** and, for comparison, the unsolvated molecular crystal of **1** were studied.‡ The 1,4-dioxane adduct has a host–guest ratio 1 : 2, established by ^{1}H NMR spectroscopy (in CDCl$_3$) and by thermogravimmetric analysis.

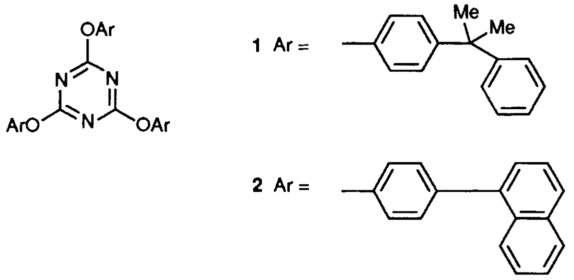

Fig. 2(*a*) gives a general view of the host–guest packing in the 1,4-dioxane adduct of **1**, and Fig. 2(*b*) shows the packing in the molecular crystal of **1**. In the adduct, pairs of host molecules are indeed found to be self-assembled as Piedfort

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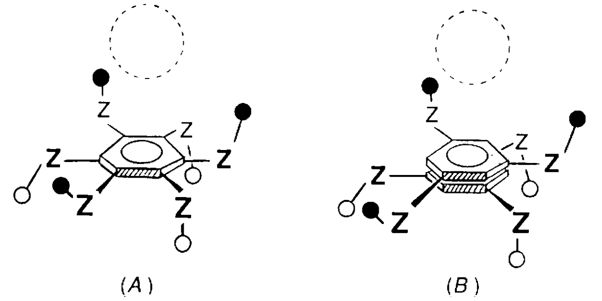
† The numismatic derivation of the name Piedfort, for this idea, comes from special coins struck at double thickness for collectors; here, two aromatic rings at van der Waals contact, which together comprise the central core of (*B*), are in combination about twice as thick as the corresponding central moiety of (*A*).

‡ *Crystal data* for $C_{48}H_{45}N_3O_3$ **1**. $M = 711.9$, triclinic, space group $P\bar{1}$, $a = 13.041(3)$, $b = 13.073(3)$, $c = 13.463(2)$ Å, $\alpha = 71.30(2)$, $\beta = 84.98(2)$, $\gamma = 64.61(2)°$, $U = 1961(1)$ Å^3, $Z = 2$, $D_c = 1.21$ g cm^{-3}. $\lambda(\text{Mo-K}\alpha) = 0.7107$ Å, $\mu = 0.7$ cm^{-1}. $T = 293$ K. Number of independent intensities: 8525 from colourless plate, $0.5 \times 0.5 \times 0.1$ mm. $R = 0.041$, $R_w = 0.043$, for 3503 observed $[I/\sigma(I) > 2.0]$ reflections.

Crystal data for $C_{48}H_{45}N_3O_3$ **1**$\cdot 2C_4H_8O_2$. $M = 888.1$, triclinic, space group $P\bar{1}$, $a = 13.906(3)$, $b = 14.214(3)$, $c = 14.604(2)$ Å, $\alpha = 111.76(1)$, $\beta = 106.82(1)$, $\gamma = 96.25(2)°$, $U = 2489(1)$ Å^3, $Z = 2$, $D_c = 1.19$ g cm^{-3}. $\lambda(\text{Mo-K}\alpha) = 0.7107$ Å, $\mu = 0.7$ cm^{-1}. $T = 293$ K. Number of independent intensities: 10 822 from colourless hexagonal prism, $1.0 \times 0.5 \times 0.5$ mm. $R = 0.087$, $R_w = 0.103$ for 4330 observed $[I/\sigma(I) > 2.0]$ reflections.

For both crystals, X-ray intensity measurements for all possible reflections with $\sin\theta/\lambda < 0.64$ Å^{-1} were made by 2θ–ω scans on a Nonius CAD4 diffractometer. The principal computer programs used in structure solution and refinement are listed in ref. 7. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

units; furthermore, in the unsolvated crystal these units are also present. In each case two superposed molecules of **1**, which are centrosymmetrically related, have their central rings essentially in van der Waals contact (*vide infra*). The Piedfort unit, which possesses exact C_i symmetry, has, it may be noted, the same staggered arrangement of nitrogen atoms as found by calculation[5] for the minimum energy form of the dimer of 1,3,5-triazine itself. The molecular structure of the dimer in the adduct is shown in Fig. 3. In the unsolvated crystal (atom labelling as in Fig. 3) closest intermolecular contacts N(1)···C(4*), N(3)···C(6*), N(5)···C(2*) (asterisks denote neighbouring molecules) are 3.516(3), 3.549(3), and 3.546(3) Å respectively, whilst the corresponding values for the inclusion compound are 3.458(6), 3.416(6) and 3.431(6) Å. These indicate a significantly closer approach of the central rings to exact van der Waals contact on incorporation of the guest. The triazine ring is planar to ±0.01 Å in each case, and the respective C–N–C and N–C–N ring angles have average values of 112.1 and 127.9° for the unsolvated crystal and 111.9 and 128.2° in the adduct. These angles are close to the corresponding unique values of 113.2 and 126.8° found for 1,3,5-triazine itself.[6] Interestingly, the dimeric unit in the adduct possesses approximately trigonal symmetry, a non-exact three-fold proper rotation axis running normal to the central rings. The approach to C_{3i} ($\bar{3}$) symmetry may be appreciated from Fig. 3, and sets of torsion angles for the crystallographically non-equivalent side chains: N(1)–C(2)–O(2)–C(21) (and related) −179, 172, 178°; C(2)–O(2)–C(21)–C(22) −105, −114, −77°; C(23)–C(24)–C(27)–C(30) 59, 54, 57°; C(24)–C(27)–C(30)–C(31) −160, −135, −142°. In contrast the Piedfort unit in the unsolvated crystal is much less symmetrical, although the central region retains some approximate trigonal character. The mean C–N, C–O (inner) and C–O (outer) bond lengths for **1**, unsolvated and solvated respectively, are 1.323(2), 1.338(2), 1.412(2) Å; 1.324(3), 1.338(3), 1.410(3) Å. The C–N bond length may be compared with the unique value of 1.319 Å found for the parent, 1,3,5-triazine.[6]



(*A*) (*B*)

Fig. 1 A comparison of a typical hexa-host (*A*) with its Piedfort analogue (*B*), composed of two trisubstituted (6 π-electron) aromatic rings juxtaposed. The light dotted circle is symbolic of the projected guest region in each case.

The stereoview (Fig. 2*a*) illustrating the host–guest packing in the adduct reveals three crystallographically non-equivalent locations of the 1,4-dioxane guest molecule. All the dioxane guest molecules have a chair conformation; two are situated

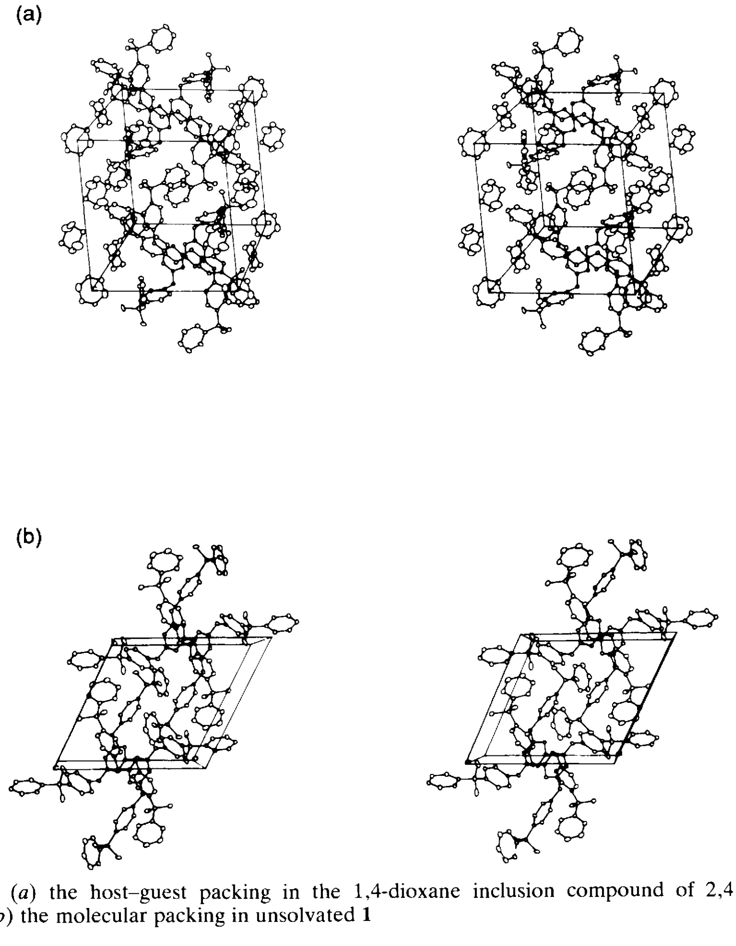


Fig. 2 Stereoviews illustrating (*a*) the host–guest packing in the 1,4-dioxane inclusion compound of 2,4,6-tris[4-(2-phenylpropan-2-yl)-phenoxy]-1,3,5-triazine **1** and (*b*) the molecular packing in unsolvated **1**

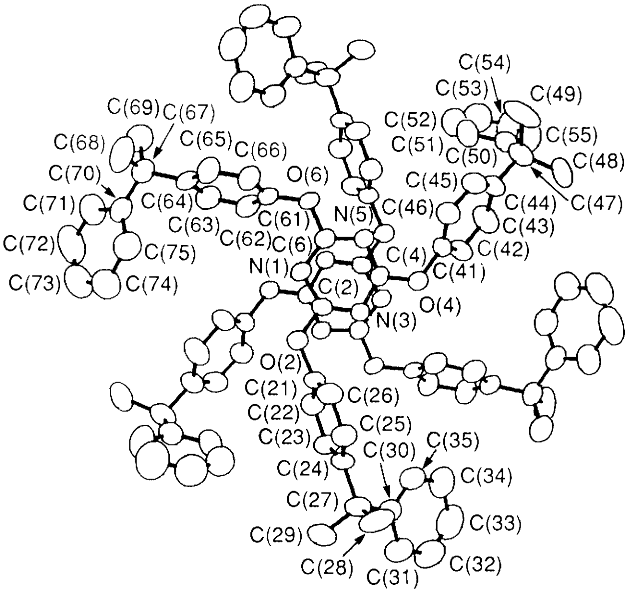


Fig. 3. A view of the Piedfort unit in the 1,4-dioxane inclusion compound of **1**, showing the atomic numbering scheme common to this and unsolvated **1**. The two central 1,3,5-triazine rings are accurately superposed but for clarity the view direction is inclined to the normal of the central ring planes.

on centres of symmetry and the third, occupying a general position, corresponds to the projected guest inclusion region (light dotted circle) in Fig. 1(*B*). The structure exhibits novel void geometry, a network consisting of intersecting channels (running along the *b* and *c* axial directions) providing accommodation for the guest species. In the *c* direction, all dioxane molecules are located on the axis, whereas a zig-zag pattern is found along *b*.

Related host **2**, which incorporates the 4-(1-naphthyl)phenoxy side chain, forms an inclusion compound with a host–guest ratio *ca.* 2 : 1 when recrystallised from propan-2-ol (at *ca.* 100 °C, sealed tube). As a consequence of the modified side-chain composition, this adduct is trigonal rather than triclinic as previously. Preliminary X-ray evidence indicates a rhombohedral lattice with parameters consistent with the presence of Piedfort units which now have attained exact three-fold symmetry.

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