Letter

1,3,5-Triaroylbenzenes as versatile inclusion hosts *via* C–H···O hydrogen bonding

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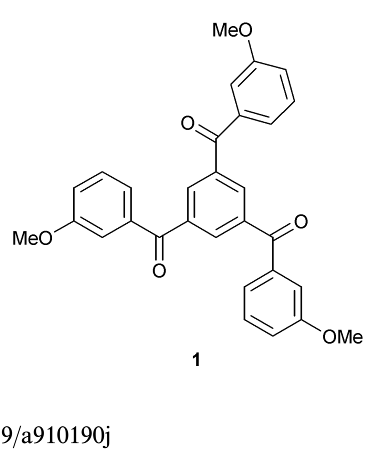
1,3,5-Tris(4-nitrobenzoyl)benzene was prepared by cyclotrimerization of (4-nitrobenzoyl)acetylene. This material was found to form 1 : 1 crystalline inclusion complexes with CH$_2$Cl$_2$ and DMSO as revealed by X-ray crystallography. These inclusion complexes are mediated by C–H···O hydrogen bonding.

The study of crystalline inclusion compounds continues to attract the attention of chemists across several subdisciplines.[1] An understanding of the forces responsible for inclusion complex formation has important implications for the design of new solid state materials possessing desirable chemical and physical properties.[2] It is now recognized that certain structural features embodied in putative inclusion hosts can maximize opportunities for inclusion complex formation.[3] Among these important structural features are the topology of the host framework, the presence of symmetry elements, and functional groups capable of engaging in strong hydrogen bonding interactions (such as O–H and N–H). Examples of inclusion hosts incorporating these structural elements include certain alicyclic diols,[4] diarylmethanol derivatives,[5] "scissors" shaped hosts,[6] "roof" shaped hosts[7] and thienothiophene derivatives.[8]

In recent years much attention has been focused on the nature of inclusion complexes formed by hosts devoid of traditional H-bonding functional groups. In these complexes much weaker interactions, such as C–H···O hydrogen bonds, acquire increased significance.[9] Indeed, in certain instances numerous C–H···O hydrogen bonds can override the effects of stronger O–H···O and N–H···O bonding motifs. It is generally regarded as much more difficult to predict (and subsequently design) the structures of solid state networks assembled *via* C–H···O hydrogen bonds as compared to supramolecular assemblies incorporating polar (and stronger) hydrogen bonding patterns. Consequently, the identification and preparation of new inclusion hosts that utilize weak C–H···O interactions constitutes a worthwhile synthetic objective and may provide valuable insight relevant to the design of future solid state supramolecular complexes.[10]

A recent report from this laboratory communicated the preparation and characterization of a 1 : 1 inclusion complex formed between benzene and the new inclusion host **1** exhibiting the 1,3,5-triaroylbenzene framework.[11] The inclusion complex displayed perfect C_3 symmetry, presumably as a consequence of the host structure, and the included benzene guests were held in place solely *via* three C–H···O hydrogen bonds. Recognizing that **1** may constitute the first member of a new family of inclusion hosts, a trinitro analog **2** was prepared [eqn. (1)] and screened for the ability to form crystalline inclusion complexes.†[12] Gratifyingly, triaroylbenzene **2** was found to form C–H···O hydrogen bond mediated inclusion complexes with two guests, DMSO and CH$_2$Cl$_2$,[13] and these 1 : 1 complexes have been characterized by X-ray crystallography.‡



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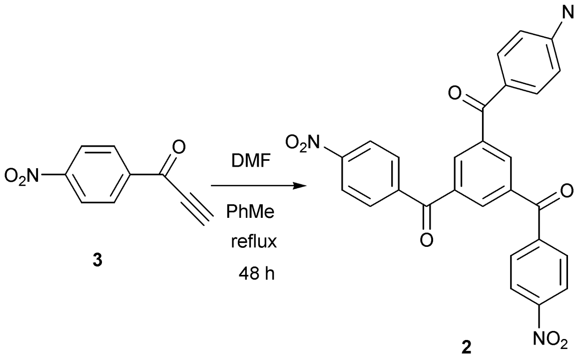

3 **2** (1)

The packing diagram of $\mathbf{2}\cdot CH_2Cl_2$ (down *b*) is shown in Fig. 1. While the specific intermolecular interactions are difficult to discern it is clear that the 3-fold symmetry encountered in the benzene complex of **1**[11] is completely absent and each molecule of **2** adopts an unsymmetrical conformation. The CH$_2$Cl$_2$ guest molecules appear to be acting as hydrogen bond donors to carbonyl groups present in the host (Fig. 2). The H···O distance in this interaction was found to be 2.577 Å. The C–H···O angle deviates substantially from linearity (135.6°), but the C=O···H angle of 116.8° is nearly exactly what one expects for a carbonyl H-bond acceptor.[9] The host molecules **2** crystallize as "dimers" held together by two apparent hydrogen bonds between aromatic C–H groups *ortho* to an NO$_2$ moiety and carbonyl oxygen atoms (Fig. 2, H···O distance = 2.654 Å, C–H···O angle = 135.8°, C=O···H angle = 97.2°). It is interesting to note that this H-bond mediated "dimerization" generates a 20-membered ring. The three nitro groups in **2** also interact with three adjacent host molecules, again *via* apparent C–H···O hydrogen bonding (Fig. 3). These interactions are of two types. One hydrogen bond is formed from an aromatic C–H group *ortho* to nitro (H···O distance = 2.465 Å, C–H···O angle = 141.7°, N–O···H angle = 145.2°) while the remaining two interactions involve aromatic C–H groups *meta* to nitro. Of these two interactions, one exhibits a relatively short H···O distance of 2.449 Å and nearly linear angles about both the hydrogen and oxygen participants (164.7 and 166.9°,

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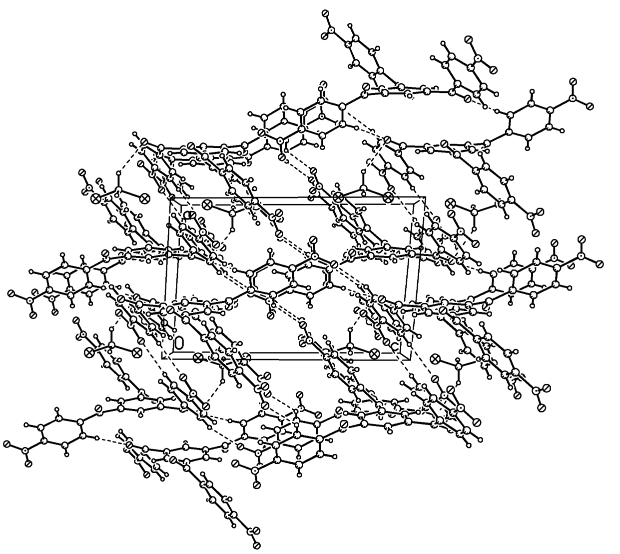

Fig. 1 Packing diagram of $2 \cdot CH_2Cl_2$ down *b*. Hydrogen bonds are indicated by dashed lines.

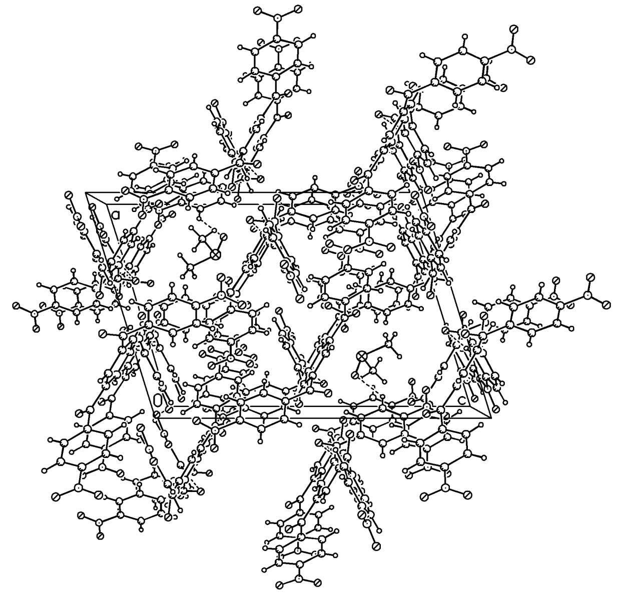

Fig. 4 Packing diagram of $2 \cdot DMSO$ down *b*. Hydrogen bonds are indicated by dashed lines.

respectively) while the other displays a slightly longer H···O distance (2.555 Å) and a more bent geometry (C–H···O angle = 141.3°, N–O···H angle = 152.9°).[14]

Triaroylbenzene **2** also forms a stable inclusion complex with DMSO, however the molecular arrangement in this complex is much different than that described above. This is perhaps not surprising given that DMSO serves as an H-bond acceptor while CH_2Cl_2 acts as an H-bond donor. The packing diagram of $\mathbf{2} \cdot DMSO$ (down *b*) is shown in Fig. 4. The DMSO guests are slightly disordered and the molecules shown are at 90% occupancy. Once again, the intrinsic C_3 symmetry present in **2** is not evident in the supramolecular host-guest structure. In fact, host molecules **2** can best be described as forming chains connected *via* aromatic C–H···O hydrogen bonds (Fig. 5, H···O distance = 2.436 Å, C–H···O angle = 175.2°, C=O···H angle = 97.9°) that result in creation of a local pseduo-C_2 symmetry element. The DMSO guest molecules are located along the periphery of these molecular chains and accept a hydrogen bond from an aromatic C–H group *ortho* to nitro (H···O distance = 2.413 Å, C–H···O angle = 138.9°, S–O···H angle = 124.0°).

In conclusion, the triaroylbenzene derivative **2** forms crystalline inclusion complexes with both CH_2Cl_2 and DMSO. These inclusion complexes are stabilized by various types of C–H···O hydrogen bonding involving sp^3 and sp^2 C–H hydrogen bond donors and carbonyl, nitro and sulfoxide hydrogen bond acceptors. An intriguing feature of these materials is the overall lack of crystal symmetry encountered in the host–guest complexes, in spite of the close structural similarity to C_3 symmetrical inclusion host **1**.[11] Indeed, the ability of **2** to deviate from strict C_3 symmetric conformations almost certainly contributes to the successful inclusion of hydrogen bond donating (CH_2Cl_2) as well as hydrogen bond accepting (DMSO) guests. It is, therefore, interesting to speculate as to the importance of host rigidity and symmetry in inclusion complexes governed exclusively by relatively weak C–H···O interactions. It may be that a certain degree of structural flexibility and/or asymmetry (structural features generally deemed to be anathema for efficient inclusion host behavior)[3] are desirable so that positive C–H···O inter-host and host-guest contacts can be maximized.[15] Currently, the synthetic accessibility and the proven inclusion host behavior of triaroylbenzene derivatives are being utilized in studies

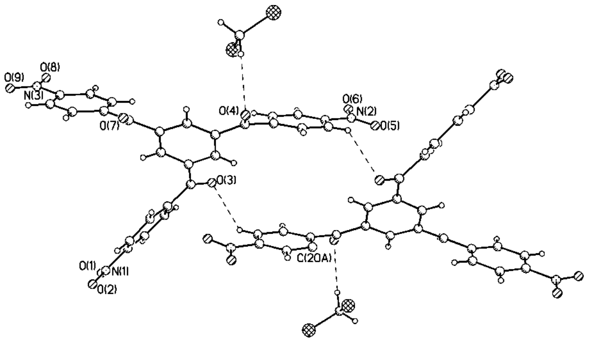

Fig. 2 View of $2 \cdot CH_2Cl_2$ "dimers." H-bond distances (Å): O(4)···H(1SC) = 2.577; O(3)···H(17A) = 2.654. The aryl hydrogen attached to C(20A) has been omitted for clarity.

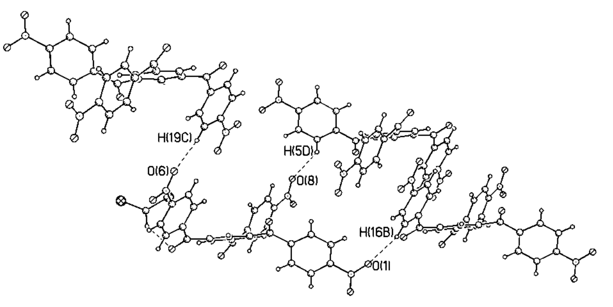

Fig. 3 View of C–H···O_2N H-bonding interactions in $2 \cdot CH_2Cl_2$. H-bond distances (Å): O(6)···H(19C) = 2.465; O(8)···H(5D) = 2.555; O(1)···H(16B) = 2.449.

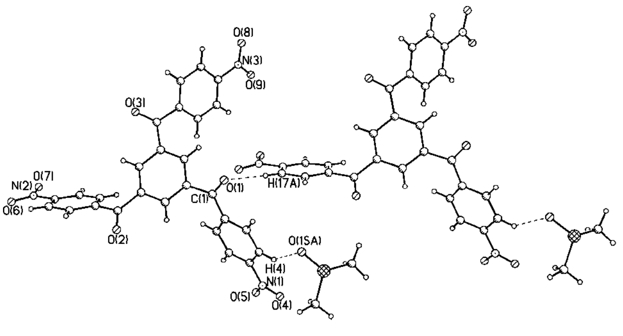

Fig. 5 Inter-host and host–guest interactions in $2 \cdot DMSO$. H-bond distances (Å): O(1)···H(17A) = 2.436; O(1SA)···H(4) = 2.413.

aimed at systematically addressing this issue. The utility of the triaroylbenzene framework as a building block for the preparation of alternative supramolecular complexes (such as solution phase receptors and new cyclophanes) also is being explored.

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Notes and references

† Synthesis: Aryl ethynyl ketone **3** (prepared from *p*-nitrobenzaldehyde) was dissolved in a 1 : 1 mixture of DMF : toluene and heated to reflux for 48 h. The solvent was evaporated and the residue was purified by flash column chromatography using CH_2Cl_2 as the eluent to afford **2** in 72% yield. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 8.09 (d, $J = 8.4$ Hz, 6H), 8.34 (s, 3H), 8.41 (d, $J = 8.7$ Hz, 6H). ^{13}C-NMR (75 MHz, DMSO-d$_6$) δ 123.69, 131.03, 134.30, 136.70, 141.04, 149.71, 192.73. Crystals of **2**$\cdot CH_2Cl_2$ were grown by slow evaporation of a CH_2Cl_2 solution. The inclusion complex was stable in air for short periods of time, however CH_2Cl_2 was slowly lost over several days (~10% loss after 10 days according to combustion analysis). The CH_2Cl_2 could be completely removed by heating to 100 °C under vacuum for 10 h. Such treatment gave analytically pure host **2**. Anal. calcd. for $C_{27}H_{15}N_3O_9$: C 61.72; H 2.88; N 8.00. Found: C 61.45; H 2.95; N 7.84. Crystals of **2**$\cdot$DMSO were grown by slow evaporation of a DMSO-d$_6$ solution and were found to be stable in air for prolonged periods of time. Anal. calcd. for $C_{27}H_{15}N_3O_9\cdot CD_6SO$: C 57.13; H 3.48; N 6.89; S 5.26. Found: C 57.09; H 3.46; N 6.77; S 5.37.

‡ Crystal data: **2**$\cdot CH_2Cl_2$: $C_{28}H_{17}Cl_2N_3O_9$, $M_r = 610.35$, triclinic, space group $P\bar{1}$, $a = 9.7093(1)$, $b = 10.3943(2)$, $c = 14.4467(2)$ Å, $\alpha = 83.177(1)$, $\beta = 84.037(1)$, $\gamma = 73.265(1)°$, $U = 1382.62(4)$ Å^3, $Z = 2$, $T = 213(2)$ K, $F(000) = 624$, $\mu = 0.295$ mm^{-1}, 18 778 reflections measured of which 5130 were independent, full matrix least squares refinement on F^2 for 379 parameters, $R_1(F) = 6.65\%$, $wR_2(F^2) = 22.76\%$. H atoms were treated using appropriate riding models. Data collection: SMART; data reduction: SAINT; solution refinement: SHELX-TL (Bruker-axs, Madison, WI, 1999). **2**$\cdot$DMSO: $C_{29}H_{21}N_3O_{10}S$, $M_r = 603.55$, monoclinic, space group $P2_1/n$, $a = 12.8116(2)$, $b = 12.1494(2)$, $c = 18.2432(2)$ Å, $\beta = 107.197(1)°$, $U = 2712.67(7)$ Å^3, $Z = 4$, $T = 213(2)$ K, $F(000) = 1248$, $\mu = 0.186$ mm^{-1}, 49 620 reflections measured of which 5548 were independent, full matrix least squares refinement on F^2 for 398 parameters, $R_1(F) = 3.80\%$, $wR_2(F^2) = 9.29\%$. H atoms were treated using appropriate riding models. Data collection: SMART; data reduction: SAINT; solution refinement: SHELX-TL (Bruker-axs, Madison, WI, 1999). CCDC reference number 440/166. See http://www.rsc.org/suppdata/nj/a9/a910190j/ for crystallographic files in .cif format.

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