Structural characterization of crystalline inclusion complexes formed from 1,3,5-triaroylbenzene derivatives—a new family of inclusion hosts

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Received (in Cambridge, UK) 14th July 2000, Accepted 12th October 2000
First published as an Advance Article on the web 14th November 2000

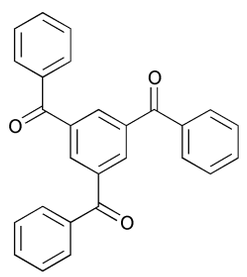
A series of crystalline inclusion complexes formed from substituted 1,3,5-triaroylbenzene hosts and small molecule guests has been structurally characterized by X-ray crystallography. The new inclusion hosts examined do not possess functional groups capable of participating in strong non-covalent interactions, thus C–H · · · O hydrogen bonding appears to significantly influence the crystal packing observed in most of the solid state structures. The thermochemical properties of the inclusion complexes were examined using differential scanning calorimetry.

Introduction

Crystalline inclusion complexes represent an intriguing class of supramolecular assembly that continues to receive considerable attention. The rational design of composite solid state materials has many potential applications in areas such as chemical separation,[1] crystal engineering,[2] and non-linear optics.[3] One tactic commonly employed in the synthesis of potential inclusion hosts is the incorporation of functional groups known to participate in relatively strong hydrogen bonding interactions (such as O–H, N–H, and CO_2H moieties) into rigid and bulky molecular frameworks.[4] The presence of symmetry elements within the host structure also has been identified as a positive attribute.[5] Examples of efficacious inclusion hosts designed in accordance with the strategy described above include certain alicyclic diols,[6] diarylmethanol derivatives,[7] "scissors" shaped hosts,[8] "roof" shaped hosts,[9] and thienothiophene derivatives.[10] These inclusion hosts form supramolecular assemblies with suitable guests either through direct host–guest interaction (*e.g.*, hydrogen bonding) or through the formation of well-defined voids within the crystal lattice that are occupied by included guest molecules.

In recent years the study of crystalline inclusion compounds devoid of functional groups capable of engaging in strong hydrogen bonding interactions has acquired increased significance. In certain instances, such inclusion complexes exhibit host–guest interactions mediated by relatively weak C–H · · · O hydrogen bonding.[11] While the existence of solid state C–H · · · O (and related C–H · · · N) hydrogen bonds has been the subject of some controversy,[12] a considerable amount of empirical[13] and computational[14] evidence has been accumulated that lends credence to the notion of structurally defining non-covalent C–H · · · O interactions. Indeed, it has been postulated that in certain cases numerous C–H · · · O interactions can override stronger O–H · · · O and N–H · · · O bonding motifs. It is, however, generally regarded as much more difficult to design solid state networks assembled solely *via* C–H · · · O hydrogen bonds. Thus, the identification and preparation of new inclusion hosts that utilize C–H · · · O interactions may provide valuable insight relevant to the rational design of new functional solid state supramolecular complexes.

The basic molecular framework of 1,3,5-triaroylbenzene derivatives (as illustrated for the parent compound **1**) exhibits



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many structural features commonly found in inclusion hosts. Specifically, **1**, by virtue of its polyaromatic composition, is relatively rigid and possesses a conformation in which a rotational C_3 symmetry axis is present. Hence, several substituted triaroylbenzenes (**10**–**13**, see Scheme 1) have been prepared and screened for their ability to function as inclusion hosts.[15] Significantly, **10**–**13** do not possess strong hydrogen bonding functional groups. Consequently, a variety of solid state C–H · · · O interactions are observed in most of the structurally characterized inclusion complexes. Preliminary results from this work have been communicated which described the structures of the 1 : 1 inclusion complexes **10**·C_6H_6 as well as **13**·CH_2Cl_2 and **13**·DMSO.[16,17] The structural details of **11**·(no guest) and **13**·(no guest), as well as new inclusion complexes **12**·0.5 C_6H_6, **13**·acetone, and **13**·1.5 CH_3NO_2 are reported herein. In addition, the thermochemical properties of all inclusion complexes thus far obtained have been examined using differential scanning calorimetry (DSC).

Results and discussion

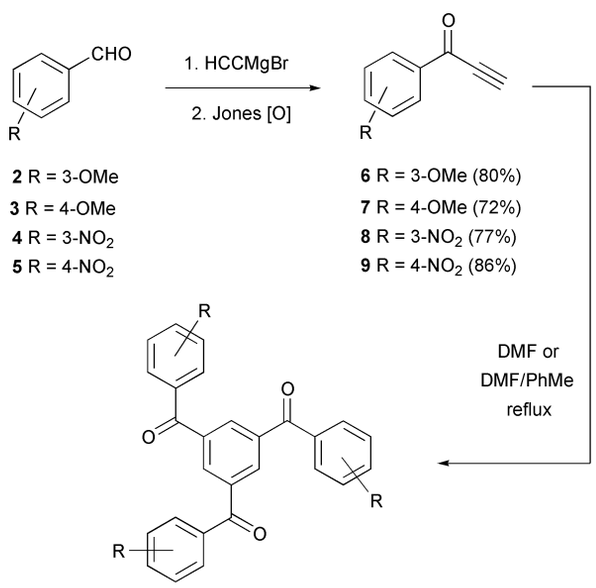
Synthesis

Triaroylbenzenes **10**–**13** were prepared according to the route shown in Scheme 1. Aldehydes **2**–**5** were converted to aryl ethynyl ketones **6**–**9** *via* routine functional group manipulation. Cyclotrimerization of the alkynyl moieties was easily effected in either refluxing DMF or refluxing DMF–toluene in line with procedures first reported by Balasubramanian.[18a] Inclusion complexes were obtained by slow evaporation of solutions of the triaroylbenzene in the appropriate guest solvent.

 DOI: 10.1039/b005702i

Table 1 Crystal data

Compound	**11**·(no guest)	**12**·0.5 C_6H_6	**13**·acetone	**13**·1.5 CH_3NO_2	**13**·(no guest)
Empirical formula	$C_{30}H_{24}O_6$	$C_{30}H_{18}N_3O_9$	$C_{30}H_{21}N_3O_{10}$	$C_{28.5}H_{19.5}N_{4.5}O_{12}$	$C_{27}H_{15}N_3O_9$
M	480.49	564.47	583.50	616.99	525.42
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	13.7018(3)	10.3402(9)	8.8361(2)	9.7537(2)	13.3520(2)
b/Å	14.3753(3)	10.4427(9)	10.4985(2)	10.5838(2)	12.0843(2)
c/Å	14.4362(3)	13.4887(11)	15.1193(3)	14.6243(2)	15.0708(2)
α/°	108.261(2)	87.854(6)	80.305(1)	82.543(1)	90
β/°	107.530(2)	80.536(5)	85.321(1)	81.724(1)	95.994(1)
γ/°	103.187(2)	64.230(5)	80.857(1)	71.179(1)	90
Z	4	2	2	2	4
V/Å^3	2406.02(9)	1292.85(19)	1362.79(5)	1408.47(4)	2418.37(6)
D_{calc}/g cm^{-3}	1.326	1.450	1.422	1.455	1.443
R_1	0.0471	0.0840	0.0622	0.0546	0.0400
wR_2	0.1098	0.2702	0.1838	0.1540	0.1054
Unique reflections	9449	4542	5563	5727	4959
Observed reflections	36777	12255	18957	33013	36596
R_{int}	0.076	0.058	0.061	0.05	0.039
μ/mm^{-1} (Mo-Kα)	0.092	0.109	0.109	0.116	0.111
T/K	173	218	213	223	218



Scheme 1

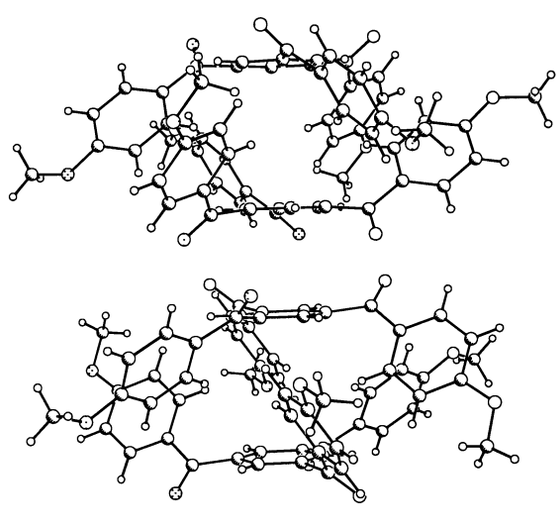


Fig. 1 View of the basic packing motif in **11**·(no guest).

Inclusion complexes—X-ray structural studies

The structural characterization of **10**·C_6H_6 has been reported.[16] In this C_3-symmetrical complex, two molecules of **10** are arranged as stacked dimers in such a way as to allow for the interposition of the *m*-methoxybenzoyl substituents. Dimers of **10** are on opposite sides of channels filled by the carbonyl O atoms. The included benzene molecules are present along the walls of these channels and are held in place by three aromatic C–H···O hydrogen bonds to carbonyl O atoms. To date, attempts to prepare inclusion complexes of **10** with other guests have been unsuccessful. In contrast to **10**, the known[18a] *p*-methoxybenzoyl derivative **11** has shown no propensity to form inclusion complexes with any guest solvents examined thus far (benzene, pyridine, EtOAc, cyclohexane, CH_2Cl_2, and toluene). Nonetheless, crystals of **11** obtained by slow concentration of a benzene solution were found to be suitable for X-ray analysis (see Table 1 for crystallographic data) and the molecular structure was determined. Despite the absence of included benzene, the arrangement of individual molecules of **11** with respect to each other is similar to the intermolecular interactions encountered in the **10**·C_6H_6 complex. Specifically, the central aromatic rings of two molecules of **11** are overlapped (interplanar distance = 4.66 Å) and rotated approximately 60° to allow room for the *p*-methoxyphenyl groups in an arrangement that resembles the so-called "Piedfort" units formed from 2,4,6-triazene derivatives.[19] Pairs of dimers are stacked on either side of a 3.47 Å channel that is filled by carbonyl oxygens. Evidently, switching from an *m*-methoxy to a *p*-methoxy substituent creates enough room for these dimeric units to pack in a manner that leaves no space for included guests and the packing appears to be mediated by ordinary van der Waals attractions (see Fig. 1). Such a packing arrangement results in crystallization in a low symmetry space group ($P\bar{1}$) despite the C_3 symmetry axis present in individual molecules of **11**.

Nitro substituents can be easily incorporated into the triaroylbenzene framework (Scheme 1) and nitroaromatic compounds are known to participate in C–H···O hydrogen bonding interactions.[20] Consequently, crystalline inclusion complexes of both **12** and **13** have been prepared and characterized. In the case of *m*-nitro substituted triaroylbenzene **12**, a 2:1 **12**·C_6H_6 inclusion complex was obtained by slow evaporation of a benzene solution. The packing diagram of

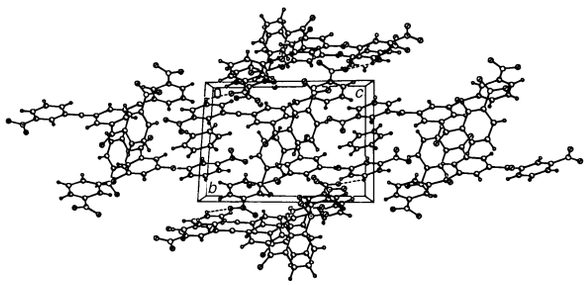


Fig. 2 Packing diagram (down *a*) of **12**·0.5 C_6H_6.

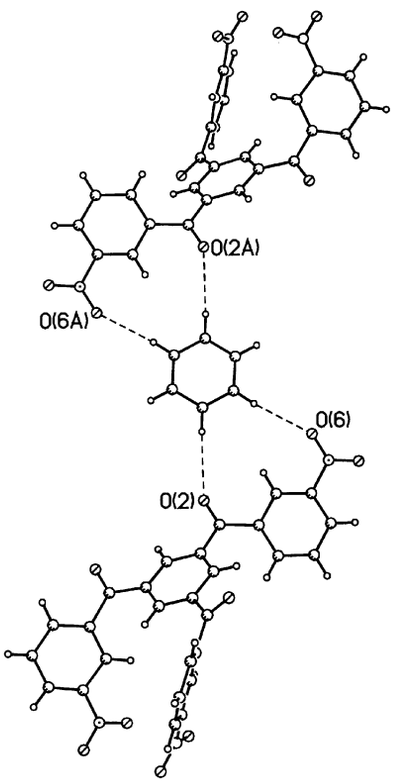


Fig. 3 View of C–H···O bonding in **12**·0.5 C_6H_6. Aryl C–H···O distances (Å): O(2)···H 2.721; O(6)···H 2.606. Angles (°): C–H···O(2) 168.0; C=O(2)···H 146.7; C–H···O(6) 163.4; N–O(6)···H 144.2.

this complex is shown in Fig. 2 with the dashed lines denoting intermolecular aromatic C–H···O interactions between a C–H moiety and a nitro oxygen atom (H···O distance = 2.56 Å, C–H···O angle = 125.9°, N–O···H angle = 171.8°). The benzene guests are sandwiched between two *m*-nitrobenzoyl "arms" emanating from adjacent molecules of **12** and appear to be held in place by two pairs of aromatic C–H···O interactions involving both carbonyl and nitro oxygen atoms as depicted in Fig. 3. While the observed H···O distances of 2.721 and 2.606 Å are somewhat long, the angles about the relevant H and O atoms are consistent with C–H···O hydrogen bonding. Additional evidence of significant attractive interactions between **12** and benzene was obtained from DSC measurements (*vide infra*). Moreover, drying a sample of **12**·0.5 C_6H_6 under vacuum (0.5 Torr) overnight resulted in no loss of benzene as revealed by elemental analysis. Triaroylbenzene **12**, however, appears to be selective for benzene guests as attempts to prepare inclusion complexes with other solvents (*e.g.*, toluene, EtOAc, acetone, nitromethane) have been unsuccessful.

In contrast to the apparent guest selectivity exhibited by **12**, triaroylbenzene **13** has been found to form tractable crystalline inclusion complexes with a number of different solvent guests.

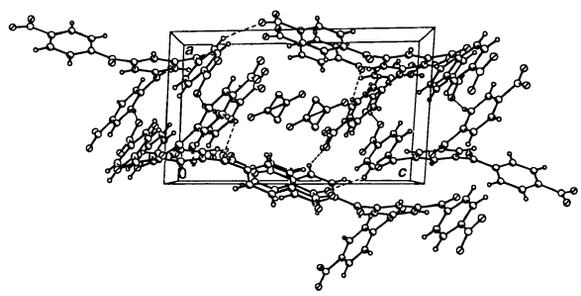


Fig. 4 Packing diagram (down *b*) of **13**·acetone. Acetone molecules are shown at 50% occupancy.

While the nature of the host–guest and host–host interactions varies across this series of compounds, a common feature in all the solid state structures of **13** is a network of inter-host C–H···O hydrogen bonds. The structural details of the 1:1 complexes **13**·CH_2Cl_2 and **13**·DMSO were the subject of a recent communication from this laboratory[17] and will only be discussed here for purposes of comparison with new inclusion complexes. The packing diagram of the complex **13**·acetone (1:1) is shown in Fig. 4. Given certain similarities between acetone and DMSO, one might anticipate similar solid state structures. This is clearly not the case. DMSO in **13**·DMSO serves as a hydrogen bond acceptor toward an aromatic hydrogen *ortho* to a nitro group and individual molecules of **13** are connected *via* an intermolecular C–H···O hydrogen bond involving an aromatic C–H group and a carbonyl oxygen atom. Acetone guest molecules in **13**·acetone, however, are disordered and occupy voids within the crystal lattice without participating in any apparent H-bonding interactions. Given this result, it is noteworthy that C=O and S=O functional groups are reported to possess nearly identical solid state H-bond accepting abilities.[21] Clearly, other factors in addition to H-bonding interactions, such as molecular size, shape, and solvent polarity, also must be important in influencing the solid state structure of inclusion complexes in this system.[22] The host crystalline lattice is formed from a network of H-bonds between aromatic C–H groups and NO_2 substituents. As depicted in Fig. 5, the three nitro substituents present in **13** appear to be participating in intermolecular C–H···O interactions with three adjacent triaroylbenzenes. Two of these interactions involve aromatic C–H groups *meta* to a nitro substituent while the remaining H-bond is formed from an aryl hydrogen donor *ortho* to a nitro group. The carbonyl oxygen atoms, which certainly are better H-bond acceptors than NO_2 groups,[21] appear not to be involved in any non-covalent bonding.

An inclusion complex between **13** and nitromethane (1:1.5) also has been prepared and structurally characterized. Examination of the crystal packing reveals a molecular arrangement similar to that found in the acetone inclusion complex discussed above. Specifically, the three nitro substituents present in **13** act as H-bond acceptors toward aromatic C–H moieties that originate from three adjacent host molecules. The CH_3NO_2 molecules simply occupy voids in the crystalline lattice (Fig. 6). One nitromethane guest is present at 100% occupancy while the 0.5 CH_3NO_2 is disordered and shared equally between two unit cells. As nitromethane is a relatively strong carbon acid, the hydrogen atoms present in the non-disordered guest were located to determine if any H-bonding interactions may be operative. However, the closest intermolecular contact between a methyl hydrogen atom and an H-bond acceptor (NO_2 substituent) was determined to be 2.71 Å with a C–H···O angle of 140.8°. Given the length, deviation from linearity, and theoretical calculations,[23] it was concluded that this contact is most likely not indicative of a bonding interaction and the nitromethane guests are held in place by simple van der Waals attractions. Finally, a further similarity between the nitromethane and acetone inclusion complexes lies in the

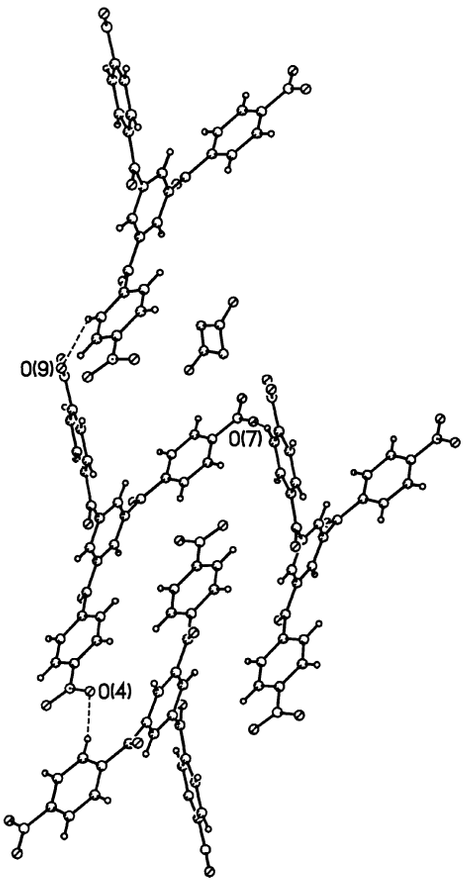


Fig. 5 C–H···O bonding interactions in **13**·acetone. Aryl C–H···O distances (Å): O(4)···H 2.511; O(7)···H 2.463; O(9)···H 2.501. Angles (°): C–H···O(4) 169.3; N–O(4)···H 119.9; C–H···O(7) 147.6; N–O(7)···H 159.1; C–H···O(9) 129.3; N–O(9)···H 124.0.

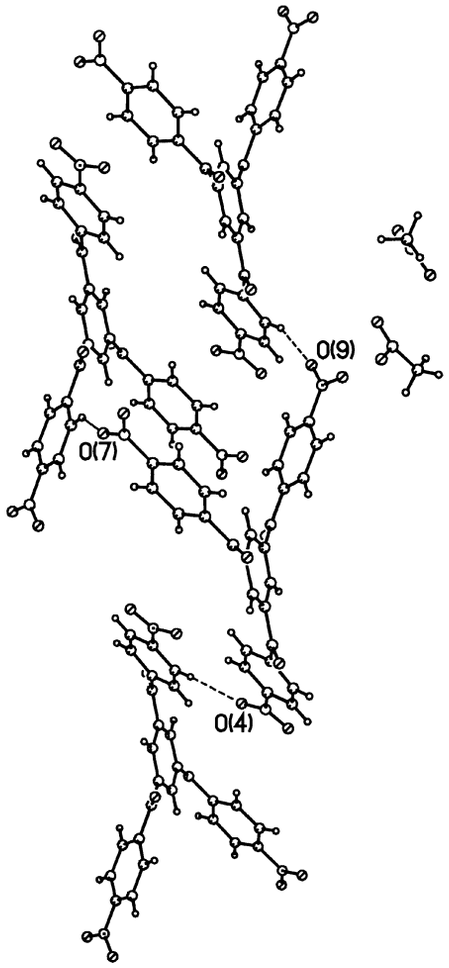


Fig. 6 C–H···O bonding interactions in **13**·1.5 CH_3NO_2. Aryl C–H···O distances (Å): O(4)···H 2.418; O(7)···H 2.546; O(9)···H 2.493. Angles (°): C–H···O(4) 153.4; N–O(4)···H 156.5; C–H···O(7) 147.6; N–O(7)···H 156.7; C–H···O(9) 157.3; N–O(9)···H 171.0.

unsymmetrical conformation adopted by the individual triaroylbenzene molecules. One *p*-nitrobenzoyl substituent is oriented opposite the other two benzoyl "arms" relative to the plane defined by the central 1,3,5-substituted arene ring.

Crystals of **13** suitable for X-ray analysis also were obtained by slow concentration of an acetonitrile solution. Unlike crystalline samples of **13** grown from other solvents, these crystals did not incorporate solvent guest molecules. Since a total of four crystalline inclusion complexes of **13** have been characterized (*vide supra* and ref. 17), it is interesting to compare the packing in **13**·(no guest) with these structures. The packing diagram of **13**·(no guest) is shown in Fig. 7. A notable feature of this solid state network is the presence of spherical void spaces within the crystalline lattice. The volume of these voids was calculated[24] to be ~60 Å^3. To put this value in context, solvent guest molecules present in structurally characterized inclusion complexes of **13** were deleted and the resulting void space calculated using the PLATON program.[24] Of the four complexes considered, **13**·DMSO was found to possess the largest solvent accessible space (~482 Å^3) followed by **13**·1.5 CH_3NO_2, **13**·CH_2Cl_2, and **13**·acetone (void spaces of 275, 262, and 237 Å^3, respectively). Acetonitrile (the solvent from which the crystals were grown) is estimated[25] to have a volume of 273 Å^3, which is comparable with the calculated space available in alternative packing arrangements of **13** (*vide supra*). Acetonitrile, however, is a linear molecule and this shape, coupled with the poor H-bond accepting ability of the nitrile functional group, may not be complementary to the interstitial space present in any of the packing arrangements that have been observed for **13** (Fig. 4 and ref. 17). Indeed, all the inclusion complexes of **13** (irrespective of whether a direct host–guest interaction exists) involve the incorporation of

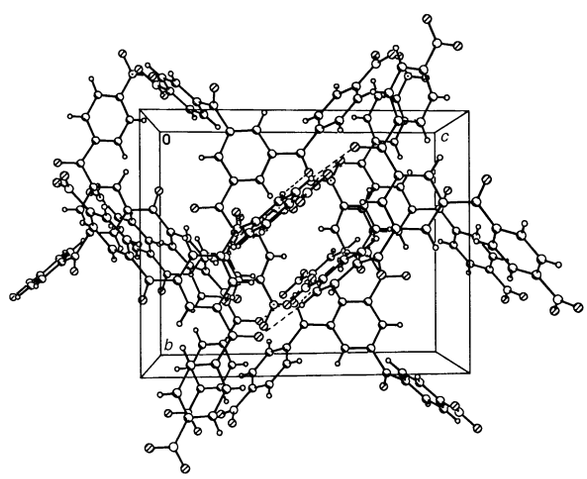


Fig. 7 Packing diagram (down *a*) of **13**·(no guest).

more spherically shaped guests (CH_2Cl_2, DMSO, acetone, nitromethane). While more empirical evidence is necessary before too many conclusions can be drawn, this observation may be indicative of a general trend in the inclusion complexation selectivity of **13**. The intermolecular interactions present in **13**·(no guest) also are intriguing when compared to other structures. As is shown in Fig. 8, the carbonyl moieties in each molecule of **13** are pointing in the same direction relative to the central arene ring. Furthermore, all three of

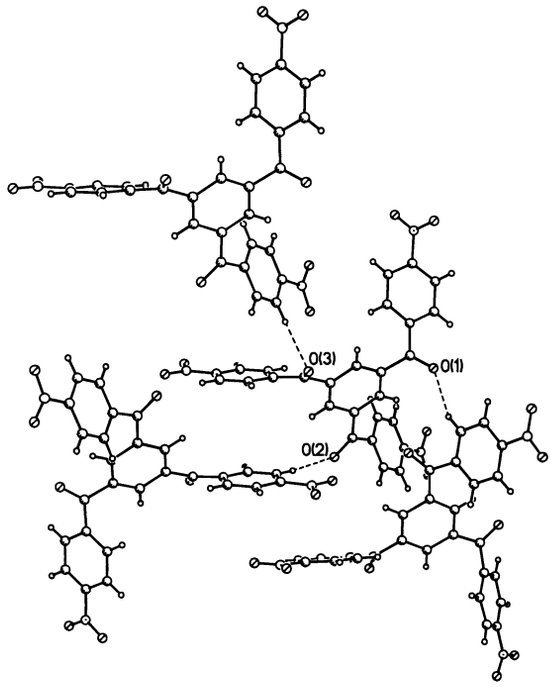


Fig. 8 C–H···O interactions in **13**·(no guest). Aryl C–H···O distances (Å): O(1)···H 2.430; O(2)···H 2.454; O(3)···H 2.406. Angles (°): C–H···O(1) 158.7; C=O(1)···H 126.0; C–H···O(2) 174.6; C=O(2)···H 141.8; C–H···O(3) 172.6; C=O(3)···H 98.1.

these carbonyl groups appear to participate in well-defined C–H···O hydrogen bonding interactions with aromatic C–H donors of adjacent triaroylbenzenes. The H···O distances in these hydrogen bonds are all ~2.4 Å and the angles about the relevant aromatic hydrogen atoms are close to linear. The nitro functional groups appear not to be involved in any bonding interactions. Thus, in the absence of included solvent, **13** packs in such a way as to reduce void space and form relatively strong C–H···O hydrogen bonds. In contrast, inclusion complexes of **13** that require large solvent accessible space within the crystal lattice employ weaker C–H···O interactions that involve a single C=O acceptor (**13**·DMSO), two C=O acceptors (**13**·CH_2Cl_2), or NO_2 acceptors (**13**·acetone and **13**·1.5 CH_3NO_2).

Calorimetric analyses

The thermal behavior of all triaroylbenzene derivatives and their inclusion complexes has been studied using differential scanning calorimetry and the results are summarized in Table 2. In the case of **10**·C_6H_6, a single very broad endothermic transition was observed in the range ~60–70 °C that was accompanied by melting and loss of sample mass (presumably caused by vaporization of some or all of the included benzene). Interestingly, the sample failed to re-solidify after cooling to rt. This observation, coupled with an inability to obtain a solid sample of **10** in the absence of benzene, appears to be indicative of a critical role for this solvent during formation of crystalline material. The DSC trace of *p*-methoxy isomer **11**·(no guest) showed only a single sharp endothermic transition centered at 187 °C corresponding to the mp of the sample. The thermal behavior exhibited by **12**·0.5 C_6H_6 was similar to that of the **10**·C_6H_6 complex in that a single broad endotherm was observed at 110–135 °C accompanied by melting and loss of sample mass (presumably vaporization of benzene). It is notable that this transition occurred at a temperature significantly above the boiling point of benzene.

Calorimetric data also were obtained for complexes of triaroylbenzene **13**. The DSC trace of **13**·(no guest) revealed a single sharp endothermic transition at the melting point of the compound (centered at 232 °C). In general, inclusion complexes of **13** with relatively volatile guests displayed two types of transitions: a lower temperature transition(s), presumably corresponding to vaporization of included solvent, and a higher temperature transition at the melting point of the remaining sample. In the case of **13**·CH_2Cl_2, solvent loss appears to occur readily in air (as determined by elemental analysis) and was not observed in the DSC experiments. In contrast, solvent loss was evident in the DSC traces of **13**·acetone and **13**·1.5 CH_3NO_2. Two broad transitions (in addition to sample melting) were apparent in the trace of **13**·acetone. The first occurred in the range 70–85 °C followed by a second in the range 130–145 °C (the sample melt was revealed by a relatively sharp endotherm at ~232 °C). It is currently not known if both lower temperature transitions are indicative of acetone vaporization. Complex **13**·1.5 CH_3NO_2 exhibited one endotherm centered at 99 °C (close to the boiling point of nitromethane) in addition to the 232 °C transition. Finally, the DSC trace obtained for **13**·DMSO differed significantly from those discussed above. Two broad endothermic transitions were observed, the first centered at 97 °C (which was accompanied by sample melting) and a second near the boiling point of DMSO (~190 °C).

Table 2 Summary of calorimetric data[a]

Compound	T/°C[b]	ΔH/kJ mol^{-1}[c]
10·C_6H_6	58.6	51.8
11·(no guest)	185.1	44.5[d]
12·0.5 C_6H_6	110.6	32.1
13·(no guest)	231.4	50.5[d]
13·CH_2Cl_2	234.3	47.2
13·acetone	70.3	17.3
	132.0	27.5
	229.6	47.1
13·1.5 CH_3NO_2	94.1	13.5
	232.6	45.2
13·DMSO	85.5	16.8
	184.9	29.3

[a] Estimated error ±5%. [b] Onset temperature. [c] Calculated using MW indicated by crystal stoichiometry. [d] ΔH_{fus}.

Conclusions

Substituted triaroylbenzene derivatives have been shown to serve as viable inclusion hosts for several small molecule (solvent) guests. In each of the structurally characterized complexes (except in the case of **11**), C–H···O hydrogen bonding was found to play an important role in defining the triaroylbenzene crystalline lattice. In some instances, direct host–guest interaction *via* C–H···O hydrogen bonding was apparent. The structural rigidity inherent in the triaroylbenzene framework, the significant conformational flexibility offered by the carbonyl linkages, and the ability to establish various host–guest and/or inter-host C–H···O hydrogen bonding networks allow these hosts to attain solid state structures tailored to the demands of suitable guest molecules. While derivatives **10** and **12** appear to be selective in their inclusion complex behavior, the interplay of rigidity/flexibility/H-bonding ability is nicely illustrated in the structures of triaroylbenzene **13**. Current efforts are focused on utilizing the structural information thus far obtained to rationally design more sophisticated triaroylbenzene-derived solid state composites. In addition, the preparation of new molecular receptors and cyclophanes incorporating the triaroylbenzene framework is underway.

Experimental

Synthesis

All commercially available reagents were used as received unless otherwise noted. ^{1}H- and ^{13}C-NMR spectra were measured on a

Varian XL-300 or Varian Unity 300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts (δ) are reported in units of ppm relative to residual $CHCl_3$ (7.26 ppm for ^1H and 77.0 ppm for ^{13}C). Infrared spectra were recorded on a Perkin-Elmer Model 1600 FTIR spectrophotometer. Flash column chromatography was performed using Natland International silica gel 60 (200–400 mesh). Melting points were determined using a Thomas–Hoover melting point apparatus and are uncorrected. Combustion analyses were obtained from Atlantic Microlabs, Norcross, GA. Procedures describing the preparation of **7**, **11**, and **13** have been published.[17,18a] Differential scanning calorimetry was performed using a Perkin-Elmer DSC 7 at a scan rate of 5 °C min^{-1}.

Preparation of aryl ethynyl ketones 6–9

Aryl ethynyl ketone 6. The method used for the preparation of **6** is representative. A solution of *m*-anisaldehyde (1.36 g, 10.0 mmol) in ~5 mL ether was cooled to 0 °C. Ethynylmagnesium bromide (0.5 M in THF, 10.0 mmol, 20.0 mL) was added over 15 min by syringe. The reaction was maintained for 2 h then quenched by addition of saturated NH_4Cl solution. The mixture was diluted with ether and the layers were separated. The organic phase was washed with brine and dried over anhydrous $MgSO_4$. Filtration and removal of the solvent afforded an oily residue that was purified by flash column chromatography (1:1 hexanes–ether) to yield the desired alcohol (1.52 g, 94%) as a yellow oil. δ_H ($CDCl_3$) 2.64 (1H, br s), 2.71 (1H, s), 3.86 (3H, s), 5.46 (1H, br s), 6.93 (1H, m), 7.16 (1H, br s), 7.18 (1H, br s), 7.34 (1H, t, J = 7.5 Hz). Without further characterization the alcohol (1.95 g, 12.0 mmol) was dissolved in ~20 mL acetone. A solution of the Jones reagent was added dropwise until the red color indicative of excess Cr(VI) persisted. The reaction was quenched by addition of propan-2-ol. The insoluble Cr(III) salts were removed by filtration through a pad of Celite® and the filtrate was diluted with ether. The solution was washed sequentially with saturated aq. $NaHCO_3$ solution and brine followed by drying over anhydrous $MgSO_4$. Filtration and removal of the solvent gave a residue that was purified by flash column chromatography (3:1 hexanes–ether) to provide **6** (1.63 g, 85%) as a pale yellow oil. An analytical sample was obtained by distillation (bulb-to-bulb), bp 150 °C/0.5 mmHg. δ_H ($CDCl_3$) 3.50 (1H, s), 3.89 (3H, s), 7.20 (1H, m), 7.43 (1H, t, J = 7.8 Hz), 7.65 (1H, t, J = 2.2 Hz), 7.82 (1H, d, J = 7.8 Hz); δ_C ($CDCl_3$) 55.7, 80.2, 81.4, 113.0, 121.2, 123.1, 129.8, 137.6, 159.8, 177.1; IR (thin film) ν (cm^{-1}) 3255, 2944, 2094, 1649. Anal. Calcd. for $C_{10}H_8O_2$: C 74.98; H 5.04. Found: C 74.72; H 5.06%.

Aryl ethynyl ketone 8. Starting from 3-nitrobenzaldehyde and using the procedures described above, **8** was obtained in 77% overall yield as a yellow solid. Mp (EtOH) 74–75 °C. δ_H ($CDCl_3$) 3.62 (1H, s), 7.73 (1H, t, J = 8.1 Hz), 8.45–8.50 (2H, m), 8.96 (1H, t, J = 1.7 Hz); δ_C ($CDCl_3$) 79.4, 82.7, 124.5, 128.5, 130.0, 134.6, 137.2, 148.3, 174.8; IR (thin film) ν (cm^{-1}) 3248, 3081, 2097, 1654. Anal. Calcd. for $C_9H_5NO_3$: C 61.72; H 2.88; N 8.00. Found: C 61.45; H 2.94; N 7.80%.

Aryl ethynyl ketone 9. Using the method described above starting from 4-nitrobenzaldehyde, **9** was obtained in 86% overall yield. Mp (EtOH) 129–130 °C. δ_H ($CDCl_3$) 3.60 (1H, s), 8.34 (4H, d, J = 2.1 Hz); δ_C ($CDCl_3$) 79.9, 83.0, 124.1, 130.7, 140.2, 175.4; IR (thin film) ν (cm^{-1}) 3278, 2097, 1657. Anal. Calcd. for $C_9H_5NO_3$: C 61.72; H 2.88; N 8.00. Found: C 61.54; H 2.89; N 7.93%.

General procedure for cyclotrimerization of 6–9

Aryl ethynyl ketones **6**–**9** were converted to the corresponding triaroylbenzene derivatives **10**–**13** using the method of Balasubramanian.[18a]

1,3,5-Tris(*m*-methoxybenzoyl)benzene (10). Cyclotrimer **10** was prepared from **6** in refluxing DMF. The crude product was purified by crystallization from MeOH–benzene and was isolated as a 1:1 inclusion complex with benzene (70%). δ_H ($CDCl_3$) 3.90 (9H, s), 7.20 (3H, m), 7.34–7.46 (9H, m), 8.42 (3H, s); δ_C ($CDCl_3$) 55.5, 114.2, 119.6, 122.8, 129.4, 134.0, 137.6, 138.1, 159.7, 194.5; IR (thin film) ν (cm^{-1}) 2938, 1663. Anal. Calcd. for $C_{30}H_{24}O_6 \cdot C_6H_6$: C 77.40; H 5.42. Found: C 77.13; H 5.49%.

1,3,5-Tris(*m*-nitrobenzoyl)benzene (12). Aryl ethynyl ketone **8** was trimerized by heating in a solution of toluene–DMF (1:1). The crude cyclotrimer was purified by crystallization from MeOH–benzene to afford a 2:1 **12**–benzene inclusion complex. δ_H ($CDCl_3$) 7.79 (3H, t, J = 7.8 Hz), 8.21 (3H, dt, J = 7.8 Hz, 1.6 Hz), 8.46 (3H, s), 8.49–8.53 (3H, m), 8.69 (3H, t, J = 1.6 Hz); δ_C ($CDCl_3$) 124.6, 127.7, 130.2, 134.4, 135.2, 137.4, 137.6, 148.2, 191.7; IR (thin film) ν (cm^{-1}) 3084, 1670. Anal. Calcd. for $C_{27}H_{15}N_3O_9 \cdot 0.5\ C_6H_6$: C 63.83; H 3.21; N 7.44. Found: C 63.78; H 3.10; N 7.34%.

Crystallography

Sample preparation. Crystals of **10**·C_6H_6 and **12**·0.5 C_6H_6 suitable for X-ray analysis were obtained as described above. X-Ray quality crystals of known[18a] cyclotrimer **11** were obtained by crystallization from a MeOH–benzene solution. Crystals of **13**·acetone and **13**·1.5 CH_3NO_2 were obtained by slow concentration of the corresponding solutions at room temperature. Crystals of **13**·(no guest) were obtained by concentration of an acetonitrile solution.

X-Ray structure determination. Preliminary examination and data collection were performed using a Bruker SMART Charge Coupled Device (CCD) area detector system single crystal X-ray diffractometer. The double pass method of scanning was used to exclude any noise. SMART and SAINT software packages were used for data collection and data integration.[26] Final cell constants were determined by global refinement of *xyz* centroids of 8192 reflections. Collected data were corrected for systematic errors using SADABS based on the Laue symmetry using equivalent reflections.[27]

Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[28] The structures were solved by direct methods and refined successfully in the space group $P\bar{1}$ for all but **13**·(no guest) which crystallized in the monoclinic space group $P2_1/n$. Full matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were treated using appropriate riding models (AFIX m3). The solvent molecules in the compounds **13**·acetone and **13**·1.5 nitromethane were disordered due to the presence of a crystallographic inversion center (nitromethane) or a pseudo-inversion center (acetone).

Supplementary data. Complete crystallographic details for all structures are available from the author. This material has been deposited with the Cambridge Crystallographic Data Center.†

Acknowledgements

Financial support for this research (University of Missouri—St. Louis Department of Chemistry, Monsanto) is gratefully acknowledged. Support for departmental X-ray facilities was provided by the NSF (CHE-9101834).

† CCDC reference number 188/275. See http://www.rsc.org/suppdata/p2/b0/b005702i/ for crystallographic files in .cif format.

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