Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Halogen trimer synthons in crystal engineering: low-temperature X-ray and neutron diffraction study of the 1:1 complex of 2,4,6-tris(4-chlorophenoxy)-1,3,5-triazine with tribromobenzene

Charlotte K. Broder,[a] Judith A. K. Howard,[a] David A. Keen,[b] Chick C. Wilson,[b] Frank H. Allen,[c]* Ram K. R. Jetti,[d] Ashwini Nangia[d] and Gautam R. Desiraju[d]

[a]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England, [b]ISIS, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England, [c]Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, England, and [d]School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

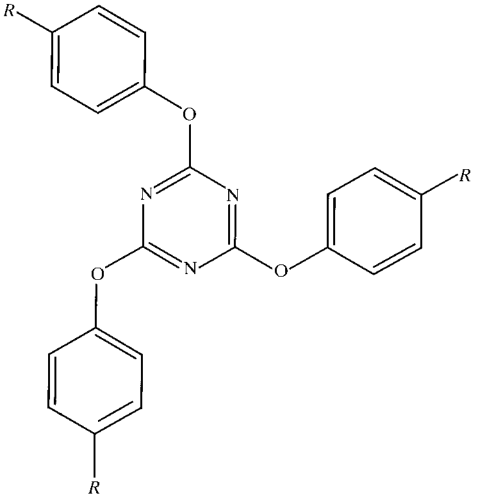
Correspondence e-mail: allen@ccdc.cam.ac.uk

Received 31 May 2000
Accepted 22 August 2000

The title complex has been studied using low-temperature X-ray (150 K) and neutron (100 K) diffraction. Molecules of the triazine host form a two-dimensional hexagonal network mediated by trigonally symmetric Cl_3 synthons having $Cl\cdots Cl$ interactions of 3.441 (3) Å, a $C—Cl\cdots Cl$ angle of 165° and a $Cl\cdots Cl—C$ angle of 105°, close to the ideal values of 180 and 90°, respectively. The guest molecules are of an appropriate size to fit the hexagonal networks and interact with the host *via* $C—H\cdots\pi$ (phenyl) and $C—Br\cdots\pi$ (phenyl) interactions which stabilize the overall structure. Both C-donor bond vectors are directed more closely towards the mid-point (X) of an individual aromatic bond, rather than the ring centroid, with $H\cdots X$ 2.817 (9) Å and $C—H\cdots X$ 174.0 (9)°, and $Br\cdots X$ 3.353 (4) Å and $C—Br\cdots X$ 158.1 (2)°.

1. Introduction

Crystal structures of a number of *sym*-triaryloxytriazines (1) have recently been determined (Anthony *et al.*, 1998; Thalladi *et al.*, 1998, 1999; Jetti *et al.*, 1999) as part of developing strategies for engineering structures containing high-symmetry supramolecular networks. It was found (Anthony *et al.*, 1998; Thalladi *et al.*, 1998) that the tris(4-chlorophenoxy) compound (1*a*) and its bromo analogue (1*b*) are isostructural in space group $P6_3/m$ and form the hexagonal network illustrated in



(1*a*) R = Cl
(1*b*) R = Br
(1*c*) R = Me

Fig. 1, which assembles *via* the mediacy of trigonally symmetric Cl_3 or Br_3 supramolecular synthons (Desiraju, 1995). These trimeric synthons are structurally equivalent to the well recognized and more robust *triangulo*-trihydroxy

© 2000 International Union of Crystallography
Printed in Great Britain – all rights reserved

synthon $(OH)_3$ (Ermer & Robke, 1994). The structures of the halogeno-derivatives (1*a*) and (1*b*) contrast with that of the tris(4-methylphenoxy) compound (1*c*) (Thalladi *et al.*, 1999), which adopts a non-centrosymmetric packing in space group *R*3*c*.

Crystals of (1*a*) and (1*b*) are difficult to handle and could not be cooled without destroying them. Thus, their structures were determined at room temperature and even then with limited accuracy [(1*a*), $R1 = 0.12$; (1*b*), $R1 = 0.10$]. However, the hexagonal networks in (1*a*) and (1*b*) (Fig. 1) contain large tubular cavities, 90–100 Å^2 in cross-section, filled with highly disordered benzene solvent. These cavities offer the strong possibility for the inclusion of ordered guest molecules of a more appropriate size and chemical constitution, and stable crystals of (1*b*) with hexachlorobenzene, 2,4,6-collidine, 1-methylnaphthalene and mesitylene have been obtained and studied using X-ray methods (Jetti *et al.*, 1999).

For (1*a*), crystals of the host–guest complex with tribromobenzene (1*a*):tbb were sufficiently robust to withstand cooling, and of sufficient quality and size to be suitable for neutron diffraction. We have studied this complex using both X-ray and neutron methods at low temperature, in order to provide more accurate geometrical data on the trimeric Cl_3 synthon, and on the hydrogen-mediated intermolecular interactions that stabilize complexation of the guest. The importance of neutron diffraction results to the accurate study of hydrogen bonding is unquestionable, especially in the case of bonds to diffuse π-acceptor density.

2. Experimental

Compound (1*a*) was synthesized using the general methods described by Jetti *et al.* (1999). Colourless crystals of the complex were grown by recrystallization of 2,4,6-tris-(4-chlorophenoxy)-1,3,5-triazine (1*a*) and tribromobenzene (tbb) in 1:1 stoichiometry from benzene and ethyl acetate at room temperature.

The X-ray data were collected at 150 K on a Bruker SMART CCD diffractometer equipped with an Oxford Cryosystems Cryostream open-flow cryostat. The crystal used ($0.35 \times 0.27 \times 0.27$ mm^3) was cut from the end of a large needle. Structure determination and refinement were carried out using *SHELX*97 (Sheldrick, 1997). Crystal data and refinement details are summarized in Table 1. Complete structural results for the X-ray study have been deposited.[1]

For the neutron diffraction experiment, a large crystal ($6.0 \times 1.5 \times 1.0$ mm^3) was mounted on a Displex closed-cycle refrigerator inside a (χ,φ) orienter, and the temperature held at 100 ± 5 K throughout the experiment. Data were collected on the SXD instrument at the ISIS spallation neutron source, using the time-of-flight Laue diffraction method (Wilson, 1990, 1997). This method uses a wavelength-sorted white neutron beam, along with large area position-sensitive detectors, to allow a large volume of reciprocal space to be measured in a single-crystal setting (a 'frame'). The full data collection comprises a series of such frames, each collected with a stationary crystal-detector arrangement. A total of 42 frames, each containing information from two detectors, was collected, with a typical exposure time of 3 h for each frame. The intensities were extracted and reduced to structure factors using standard SXD procedures (Wilson, 1997). A total of 30 681 reflections were collected, which on merging gave 3102 unique reflections. The neutron structure factor set of 3102 unique, merged reflections was prepared for structural refinement using *SHELX*97 (Sheldrick, 1997). Crystal data and refinement details are given in Table 1 and atomic coordinates are in Table 2. All geometry reported in this paper has been derived using the neutron results.

3. Results and discussion

3.1. Structure description

Fig. 2 shows a view of the structure of (1*a*):tbb along the hexagonal *c* axis. As expected, molecules of (1*a*) form two-dimensional hexagonal networks mediated by trigonally symmetric halogen trimer synthons, which are nearly identical to the networks seen for (1*a*) and (1*b*) with (disordered) benzene, see Fig. 1. The networks stack along the *c* axis to form tubular cavities of approximately circular cross-section which accommodate the tribromobenzene guest molecules, with the plane of each guest being approximately 1 Å below that of the associated *sym*-triazine molecule. This brings the plane of the guest molecule approximately level with the edge of the phenyl ring of the host.

Inclusion of tribromobenzene in the complex generates significant changes in the mutual orientations of the phenyl

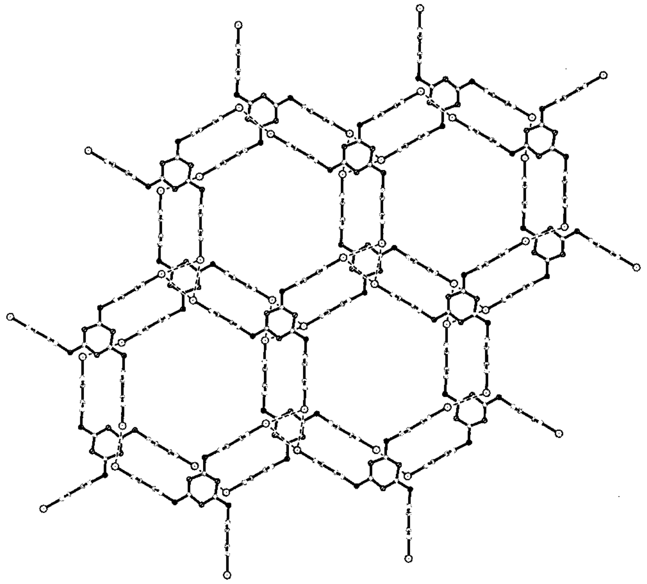


Figure 1
The structure of 2,4,6-tris-(4-chlorophenoxy)-1,3,5-triazine (Anthony *et al.*, 1998). Note that the phenyl rings are grouped in pairs that are parallel to each other and that heavily disordered benzene guest molecules (not shown for clarity) are present in the host lattice.

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0035). Services for accessing these data are described at the back of the journal.

rings by comparison with the (disordered) benzene complex. In molecules of (1*a*) in that structure (Anthony *et al.*, 1998; Thalladi *et al.*, 1998) the adjacent phenyl rings are parallel (Fig. 1), but in the (1*a*):tbb complex they are twisted to give an angle of 51.3 (1)° to each other. This twisting of the phenyl rings on complexation results in the loss of mirror symmetry in the structure and the space group of (1*a*):tbb is $P6_3$, rather than the $P6_3/m$ of the benzene complex. Despite these structural adjustments, there are minimal changes in the cell dimensions. Taking account of temperature differences, the 293 K values of $a = b = 15.364\ (3)$, $c = 6.855\ (2)$ Å for (1*a*):benzene are directly comparable to the X-ray (150 K) data and the neutron (100 K) data presented in Table 1.

In common with the other structures of 2,4,6-triaryl-1,3,5-triazine derivatives studied so far (Thalladi *et al.*, 1998, 1999; Jetti *et al.*, 1999), the structure of (1*a*):tbb is stabilized by a variety of weak intermolecular interactions, particularly Cl···Cl, C—Br···π (host) and C—H···π (host). The observed geometry of these interactions, discussed below, optimizes small electrostatic attractive forces to generate a host:guest complex whose structure is considerably more stable than that of (1*a*):benzene, where the gross disorder of the guest reflects its inability to bind closely into the host cavities.

3.2. Chlorine···chlorine interactions

The nature of halogen···halogen interactions, particularly Cl···Cl interactions, has been the subject of considerable debate over the past decade. Studies by Desiraju & Parthasarathy (1989) and Pedireddi *et al.* (1994) using the Cambridge Structural Database (CSD: Allen & Kennard, 1993) indicated the occurrence of two types of interactions. If we denote the larger of the two C—Cl···Cl angles as θ_1, and the smaller as θ_2, then type I interactions have $\theta_1 = \theta_2$ and type II have $\theta_1 = 180°$ and $\theta_2 = 90°$. Although the vast majority of type I examples arise from interactions across a crystallographic centre of symmetry, situations having a linear C—Cl···Cl—C system, $\theta_1 = \theta_2 = 180°$, are seldom observed. Type II interactions were deemed to arise due to the polarizability of the halogen, which increases from Cl through Br to I. Calculations of interaction energies using intermolecular perturbation theory (Hayes &

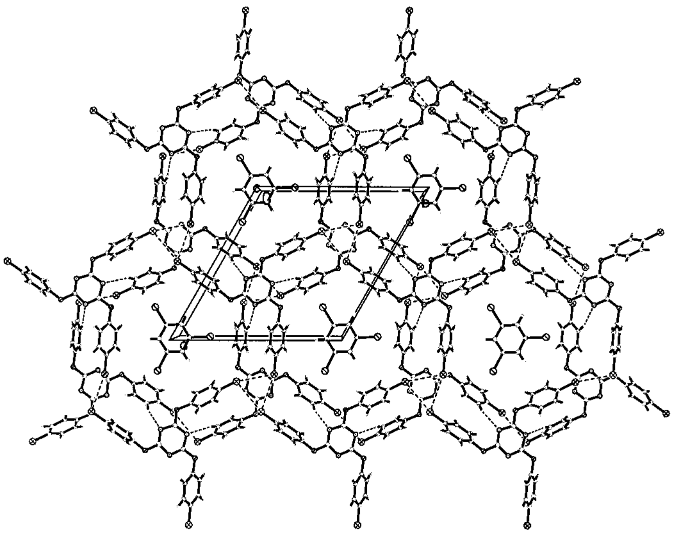


Figure 2
2,4,6-Tris-(4-chlorophenoxy)-1,3,5-triazine co-crystallized with tribromobenzene, viewed down the *c* axis.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{12}Cl_3N_3O_3{\cdot}C_6H_3Br_3$
Chemical formula weight	771
Cell setting	Hexagonal
Space group	$P6_3$
a (Å)	15.166 (6)
b (Å)	15.166 (6)
c (Å)	6.743 (2)
V (Å^3)	1343 (1)
Z	2
D_x (Mg m^{-3})	1.906
Radiation type	Neutron
No. of reflections for cell parameters	25
Temperature (K)	100 (5)
Crystal form	Irregular prism
Crystal size (mm)	6.0 × 1.5 × 1.0
Crystal colour	Colourless
Data collection	
Diffractometer	SXD
Data collection method	Time-of-flight LAUE diffraction
Absorption correction	Empirical
$T_{\min}$	0.30
$T_{\max}$	0.91
No. of measured reflections	30 681
No. of independent reflections	3102
No. of observed reflections	3102
Criterion for observed reflections	$I > 2\sigma(I)$
$R_{\rm int}$	0.071
$\theta_{\max}$ (°)	16.92
Range of h, k, l	$0 \rightarrow h \rightarrow 30$ $0 \rightarrow k \rightarrow 30$ $0 \rightarrow l \rightarrow 15$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0834
$wR(F^2)$	0.2121
S	1.230
No. of reflections used in refinement	3102
No. of parameters used	163
H-atom treatment	All H-atom parameters refined
Weighting scheme	$w=1/[\sigma^2(F_o^2) + (0.0383P)^2 + 59.8510P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.000
$\Delta\rho_{\max}$ (e Å^{-3})	3.229
$\Delta\rho_{\min}$ (e Å^{-3})	−3.980
Extinction method	Becker–Coppens Lorentzian model
Extinction coefficient	0.56
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs	
Structure solution	*SHELXS*97 (Sheldrick, 1997)
Structure refinement	*SHELXL*97 (Sheldrick, 1997)
Preparation of material for publication	*SHELXL*97 (Sheldrick, 1997)

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

$$U_{\text{eq}} = (1/3)\Sigma_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl1	0.28248 (4)	0.51759 (4)	0.65111 (9)	0.02579 (10)
C1	0.33892 (13)	0.44198 (13)	0.6510 (4)	0.0202 (3)
C2	0.39612 (15)	0.44579 (15)	0.8120 (3)	0.0224 (4)
C3	0.44300 (15)	0.38693 (15)	0.8123 (3)	0.0215 (4)
C4	0.42989 (12)	0.32615 (12)	0.6503 (4)	0.0177 (3)
C5	0.37199 (14)	0.32150 (13)	0.4900 (4)	0.0217 (4)
C6	0.32559 (14)	0.38076 (14)	0.4893 (4)	0.0231 (4)
O1	0.47036 (9)	0.26041 (9)	0.6491 (2)	0.0193 (3)
C7	0.57159 (12)	0.30103 (13)	0.6516 (3)	0.0169 (3)
N1	0.59961 (11)	0.23038 (11)	0.6523 (3)	0.0179 (3)
Br1	0.78087 (2)	0.98944 (2)	1.00678 (6)	0.04690 (9)
C8	0.90847 (16)	0.99571 (17)	1.0167 (5)	0.0292 (4)
C9	0.99560 (17)	1.09001 (16)	1.0164 (5)	0.0294 (4)

Table 3
Comparative geometries of trigonally symmetric trihalogeno synthons located in the CSD.

CSD refcode	Reference	Space group	Hal···Hal (Å)	θ_1 (°)	θ_2 (°)
Cl···Cl					
(1*a*):$C_6H_3Br_3$	(*a*)	$P6_3$	3.441 (3)	164.9 (1)	104.9 (1)
VALQUE01 (1*a*)	(*b*)	$P6_3/m$	3.467	171.0	111.0
ROFHUP	(*c*)	$P6_3/m$	3.382	173.7	113.7
VITRUL	(*d*)	$P\bar{6}2c$	3.518	172.9	112.9
Br···Br					
HEXWIQ (1*b*)	(*b*)	$P6_3/m$	3.501	169.6	109.6
BROFRM03	(*e*)	$P\bar{3}$	3.678	155.3	100.8
NABVIV	(*f*)	$P\bar{6}2c$	3.609	172.8	112.8

(*a*) This work; (*b*) Anthony *et al.* (1998) and Thalladi *et al.* (1998); (*c*) Rakitin *et al.* (1996); (*d*) Starova *et al.* (1990); (*e*) Myers *et al.* (1983); (*f*) Valkonen *et al.* (1985).

Stone, 1984) have been carried out for Cl···Cl by Price *et al.* (1994) and for C—Cl···O interactions by Lommerse *et al.* (1996). In broad terms, all of these authors agree that carbon-bound halogens in a sufficiently electron-withdrawing environment will present an anisotropic charge distribution, δ^+ forward of the halogen along the C–halogen bond vector (θ_1 = 180°), and δ^- perpendicular to the bond vector (θ_2 = 90°). In these cases, stabilizing interaction energies of up to about 10 kJ mol^{-1} can be attained for linear C—Cl···O interactions, about one-half to one-third of the interaction energy for a strong hydrogen bond (Lommerse *et al.*, 1996). These authors also found evidence that the interactions become stronger for the more readily polarisable halogens, Br and I.

Figs. 2 and 3 show the key intermolecular interactions in the structure of (1*a*):tbb. The Cl···Cl distance in the trigonal Cl_3 synthon, at 3.441 (3) Å, is some 0.06 Å shorter than the van der Waals separation based on a radius of 1.75 Å (Bondi, 1964), and the two independent C—Cl···Cl angles (θ_1, θ_2) are 165.0 (1) and 105.0 (1)°, necessarily differing from each other by 60° owing to the imposed crystallographic symmetry. These data are compared in Table 3 with corresponding results for (1*a*):benzene (Cl···Cl, CSD refcode VALQUE01) and (1*b*):benzene (Br···Br, CSD refcode HEXWIQ).

Searches of the CSD (Version 5.18, October 1999) were also carried out to locate other halogen trimer synthons. Intermolecular non-bonded searches used limiting distance constraints of 3.60, 3.80 and 4.05 Å for halogen···halogen contacts in Cl_3, Br_3 and I_3 synthons, respectively. Only error-free organic structures with $R < 0.10$ were considered. Four other examples of trigonally symmetric synthons were located, two examples of Cl_3 systems and two of Br_3 systems, and these are included in Table 3. In all cases except BROFRM03, the space-group symmetry requires coplanarity of the C_3Cl_3 or C_3Br_3 units and permits a geometry that fits well with that expected for the type II interactions discussed above. This advantageous situation should be compared with those (single) interactions that form across symmetry centres and which dictate exact type I geometry. The trigonally symmetric synthons of Table 3 can therefore adopt an almost ideal type II interaction geometry that is likely to be reinforced by some degree of cooperativity in the system.

A further 14 examples of asymmetric trihalogeno synthons were also located within the geometrical constraints employed: ten examples of Cl_3, three examples of Br_3 and a single example of I_3. In all of these cases two, and sometimes all three of the halogen···halogen interactions can readily be classified as type II in the terminology above. We note that the specific geometrical constraints employed in the trihalogen synthon search have a significant effect on the results obtained. Thus, Jetti *et al.* (1999) report five (rather than two) additional symmetrical Br_3 synthons, and six (rather than three) unsymmetrical examples, by increasing the Br···Br

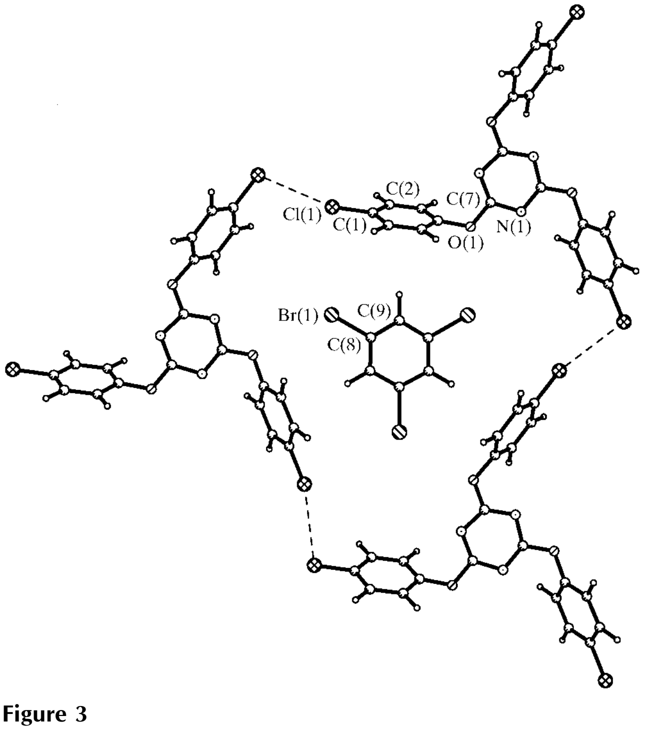


Figure 3
A tribromobenzene molecule surrounded by three 2,4,6-tris-(4-chlorophenoxy)-1,3,5-triazine.

Table 4
Geometry of C—Br$\cdots\pi$ (host) and C—H$\cdots\pi$ (host) interactions.

X is the midpoint of the closest aromatic CC bond, *R* is the centroid of the aromatic ring; distances are in Å, angles are in °.

Br$\cdots X$	3.353 (4)	C—Br$\cdots X$	158.1 (2)
Br$\cdots R$	3.508 (4)	C—Br$\cdots R$	138.5 (2)
H$\cdots X$	2.817 (9)	C—H$\cdots X$	174.0 (9)
H$\cdots R$	3.460 (9)	C—H$\cdots R$	164.2 (9)

limit to 4.0 Å. A more complete geometrical analysis of trihalogen synthons is currently being undertaken and will be reported later.

3.3. Complexation of the tribromobenzene guest

The position of the guest tribromobenzene molecules within the *sym*-triazene (1*a*) network is illustrated in Fig. 3; the trigonally symmetric tribromobenzene fitting almost exactly into the trigonal holes within one network layer of the *sym*-triazene. There is a rotation of phenyl groups with respect to their parallel arrangement in (1*a*):benzene (Fig. 1) and this rotation allows the optimization of the host–guest interactions through three C—Br(δ^+)$\cdots\pi$(host) contacts and three C—H(δ^+)$\cdots\pi$(host) contacts. This is in contrast to the six (symmetrical) C—Cl$\cdots$O interactions observed in the (1*b*):hexachlorobenzene complex (Jetti *et al.*, 1999), where the guest interacts equally with the *sym*-triazene planes above and below it. By contrast, the tribromobenzene interacts with only one *sym*-triazene plane. It should be remembered that the plane of the guest tribromobenzene is ~1 Å below the *sym*-triazene host plane, *i.e.* the plane of the guest is approximately level with the edge of the phenyl rings, not the ring centroids.

The geometries of the C—Br interactions with the π-acceptor sites in (1*a*):tbb, taken as (*a*) the midpoint of the closest aromatic C—C bond (*X*) and (*b*) the phenyl ring centroid (R), are given in Table 4. Obviously, these interactions are more closely associated with the bond centroid *X*, although the interactions are weak, as discussed more fully elsewhere (Desiraju & Steiner, 1999). What is clear, though, is that directionality is important in guest binding and the precise values obtained from the current neutron experiment are well within the range expected from examination of relevant plots in the IsoStar library of intermolecular interactions (Bruno *et al.*, 1997), which forms part of the distributed CSD system.

4. Conclusions

The interlocking ring motif propagated by the trimeric X_3 supramolecular synthon seems to be the preferred structure of the title triazine, regardless of the 'solvent' used. The inclusion of tribromobenzene is accompanied only by a twisting of the phenyl rings, not a change in the overall structure to give a different supramolecular assembly.

The EPSRC (UK) are thanked for financial support to CKB and JAKH (Senior Research Fellowship) and the DST (India) for financial support to RKRJ. This work has been conducted under the Indo-UK bilateral cooperation project No. INT/UK/P-15/99 of the Department of Science and Technology, Government of India and the British Council.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Anthony, A., Desiraju, G. R., Jetti, R. K. R., Kuduva, S. S., Madhavi, N. N. L., Nangia, A., Thaimattam, R. & Thalladi. V. R. (1998). *Cryst. Engng, 1, Mater. Res. Bull.* Suppl. S, 1–18.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Bruno, I. J., Cole, J. C., Lommerse, J. P. M., Rowland, R. S., Taylor, R. & Verdonk, M. L. (1997). *J. Comput.-Aided Mol. Des.* **11**, 525–537.

Desiraju, G. R. (1995) *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.

Desiraju, G. R. & Parthasarathy, R. (1989). *J. Am. Chem. Soc.* **111**, 8725–8726.

Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology.* Oxford University Press.

Ermer, O. & Robke, C. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1755–1757.

Hayes, I. C. & Stone, A. J. (1984). *Mol. Phys.* **53**, 83–105.

Jetti, R. K. R., Feng, X., Mak, T. C. W. & Nangia, A. (1999). *Cryst. Engng*, **2**, 215–224.

Lommerse, J. P. M., Stone, A. J., Taylor, R. & Allen, F. H. (1996). *J. Am. Chem. Soc.* **118**, 3108–3116.

Myers, R., Torrie, B. H. & Powell, B. M. (1983). *J. Chem. Phys.* **79**, 1495–1504.

Pedireddi, V. R., Reddy, D. S., Goud, B. S., Craig, D. C., Rae, A. D. & Desiraju, G. R. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 2353–2360.

Price, S. L. & Stone, A. J. (1994). *J. Am. Chem. Soc.* **116**, 4910–4918.

Rakitin, O. A., Rees, C. W., Williams, D. J. & Torroba, T. (1996). *J. Org. Chem.* **61**, 9178–9185.

Sheldrick, G. M. (1997). *SHELX*97. University of Göttingen, Germany.

Starova, G. L., Frank-Kamenetskaya, O. V. & Makarskii, V. V. (1990). *Kristallografiya*, **35**, 769–771.

Thalladi, V. R., Boese, R., Brasselet, S., Ledoux, I., Zyss, J., Jetti, R. K. R. & Desiraju, G. R. (1999). *Chem. Commun.* pp. 1639–1640.

Thalladi, V. R., Brasselet, S., Weiss, H. C., Blaser, D., Katz, A. K., Carrell, H. L., Boese, R., Zyss, J., Nangia, A. & Desiraju, G. R. (1998). *J. Am. Chem. Soc.* **120**, 2563–2577.

Valkonen, J., Pitkanen, I. & Pajunen, A. (1985). *Acta Chem. Scand. Ser. A*, **39**, 711–716.

Wilson, C. C. (1990). *Neutron Scattering Data Analysis 1990*, edited by M. W. Johnson, IoP Conference Series 107, pp. 145–163. Bristol: Adam Hilger.

Wilson, C. C. (1997). *J. Mol. Struct.* **405**, 207–217.