Molecular networks in the crystal structures of tetrakis(4-iodophenyl)methane and (4-iodophenyl)triphenylmethane

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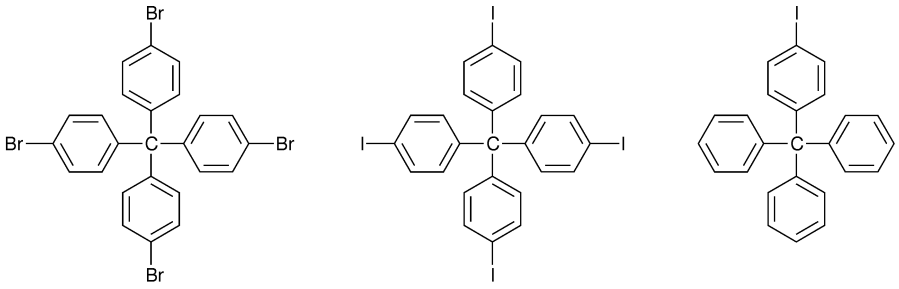
The crystal structure of tetrakis(4-iodophenyl)methane is analysed in terms of molecular networks wherein the tetraphenylmethane moieties and I_4 synthons are considered as molecular and supramolecular nodes. This I_4 cluster plays the same role in generating molecular networks as does the Br_4 cluster in the isomorphous tetrakis(4-bromophenyl)methane derivative. (4-Iodophenyl)triphenylmethane crystallises in a lower symmetry space group but features an unusual I···Ph interaction. In this series of halo-substituted tetraphenylmethanes the molecules exhibit similar columnar packing in the solid state, accounting for their crystallisation in non-centrosymmetric space groups.



I II

A network depiction of an organic crystal structure is intuitive in those cases where strong and directional interactions are responsible for crystal architecture.[1] Thus it comes as no surprise that the crystal structures of hydrogen-bonded solids[2] and those that are held together by coordination bonds[3] may be easily represented in this way. Such a depiction of an organic crystal is not new. In Powell and Palin's classical description of the hydroquinone clathrates, the molecules are shown as points and the network structure is highlighted.[4] The advantage of such an analysis is that it facilitates our understanding of complex packing arrangements. For example, further simplification of the hydroquinone clathrate structure reveals its topological similarity to the easily understood β-polonium structure.[5]

In molecular crystals that are held together by forces weaker and less directional than conventional hydrogen bonds, the relevance of the network depiction is not so obvious.[6] However, in any organic crystal structure, the molecules may be reduced to points and the points joined according to established protocols and criteria to obtain a network. Such an approach is of much utilitarian value in retrosynthetic strategies of crystal engineering based on supramolecular synthons.[7–9] All this has been greatly facilitated by the development and growth of supramolecular chemistry where one looks beyond the molecule and recognises that the entire crystal is a single supramolecular entity.[10]

The structure of tetrakis(4-bromophenyl)methane, **1**, has been recently described as a triply interpenetrated distorted sphalerite network with the molecular centres and the Br_4 synthons, **I**, as the alternating nodes.[11] Here, we report the crystal structures of the isomorphous tetrakis(4-iodophenyl) methane, **2**, and (4-iodophenyl)triphenylmethane, **3**, and analyse them in terms of their network and synthon structures. Additionally, we describe the iodine···phenyl intermolecular interaction which is a special feature in the crystal structure of the monoiodo derivative **3**.

Experimental

Syntheses

The tetraiodo compound **2** was prepared from tetraphenylmethane by iodination in the presence of nitric acid

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Table 1 Crystallographic details for compounds **2** and **3***

Compound	**2**	**3**
Molecular formula	$C_{25}H_{16}I_4$	$C_{25}H_{19}I$
Colour and habit	Colourless needles	Colourless needles
Crystal size/mm	0.15 × 0.20 × 0.20	0.15 × 0.24 × 0.30
Formula weight	824.0	446.3
Crystal system	Tetragonal	Monoclinic
Space group	$I\bar{4}$ (No. 82)	$P2_1$ (No. 4)
Unit cell parameters/Å, °	$a = 13.113(2)$	$a = 7.329(8)$
	$b = 7.237(2)$	$b = 10.774(3)$
		$c = 12.23(4)$
		$\beta = 97.25(1)$
Volume/Å^3	893.8(5)	958.2(9)
Density (calculated)/mg m^{-3}	3.062	1.547
$F(000)$	756	444
Diffractometer used	Rigaku AFC7R	Siemens P4
Absorption coefficient/mm^{-1}	6.986	1.676
Collection range $2\theta_{max}$/°	50	55
Unique data measured	1051	3033
Observed data	691[$F > 4.0\sigma(F)$]	2053[$F > 4.0\sigma(F)$]
Weighting scheme w	$w^{-1} = \sigma^2(F) + 0.0005F^2$	$w^{-1} = \sigma^2(F) + 0.0005F^2$
Goodness-of-fit	1.55	1.57
Final R indices (obs. data)	0.0508	0.0539
R Indices (all data)	0.0639	0.0745

* Details in common: Solution by direct methods, using full-matrix least-squares refinement, Mo-Kα (λ = 0.710 73 Å), largest and mean Δ/σ, 0.000 e Å^{-3}.

Table 2 Atomic coordinates (× 10^4) for tetrakis(4-iodophenyl)-methane **2**

Atom	x	y	z
I(1)	1322(1)	877(1)	8180(2)
C(1)	5000	0	2500
C(2)	4065(9)	230(8)	3777(17)
C(3)	3468(10)	1072(9)	3602(18)
C(4)	2688(11)	1261(11)	4871(20)
C(5)	2473(9)	575(10)	6233(19)
C(6)	3081(10)	−316(10)	6445(18)
C(7)	3860(10)	−464(10)	5192(16)

Table 3 Atomic coordinates (× 10^4) for (4-Iodophenyl)triphenyl-methane **3**

Atom	x	y	z
C(1)	2029(11)	1759(8)	2680(6)
C(2)	790(12)	2885(8)	2781(7)
C(3)	−526(12)	2820(9)	3560(7)
C(4)	−1648(14)	3820(12)	3733(9)
C(5)	−1573(15)	4871(11)	3123(10)
C(6)	−384(16)	4949(11)	2351(10)
C(7)	813(15)	3956(11)	2218(10)
C(8)	744(13)	593(10)	2539(8)
C(9)	−743(12)	588(11)	1693(8)
C(10)	−1884(15)	−421(12)	1547(11)
C(11)	−1666(14)	−1449(10)	2225(9)
C(12)	−225(13)	−1450(11)	3055(8)
C(13)	963(13)	−447(9)	3216(8)
C(14)	3467(11)	1610(9)	3709(7)
C(15)	3476(12)	2272(10)	4661(6)
C(16)	4844(15)	2128(12)	5563(8)
C(17)	6218(14)	1260(11)	5519(9)
C(18)	6274(14)	563(11)	4566(9)
C(19)	4905(13)	737(9)	3662(8)
C(20)	3151(11)	1930(8)	1694(6)
C(21)	4542(12)	2799(10)	1791(7)
C(22)	5688(12)	2994(10)	975(7)
C(23)	5403(12)	2267(8)	35(7)
C(24)	4000(14)	1391(10)	−114(8)
C(25)	2898(12)	1229(10)	726(8)
I(1)	71 173(9)	25 000	−11 870(5)

and iodine.[12] The monoiodo compound **3** was prepared by diazotisation of the amino derivative[13] and subsequent treatment with aqueous KI solution.

Tetraiodo 2. A mixture of tetraphenylmethane (640 mg, 2 mmol), iodine (2.5 g, 10 mmol), fuming HNO_3 (2 mL), conc. H_2SO_4 (4 mL) and $C_2H_5CO_2H$ (10 mL) was refluxed for 10 h, cooled to room temperature and the precipitated crude product was crystallised from THF–EtOH (1 : 1), followed by recrystallisation from benzene to provide **2** in low yield (120 mg, 8%); m.p. >350 °C. ^{1}H NMR ($CDCl_3$) δ 7.58 (d, $J = 9$ Hz, 8H), 6.88 (d, $J = 9$ Hz, 8H).

Monoiodo 3. A mixture of triphenylmethanol (520 mg, 2 mmol), aniline (0.3 mL, 3 mmol), conc. HCl (1 mL) and glacial AcOH (10 mL) was refluxed for 48 h, the precipitated solid was filtered and washed with 2–3 mL of AcOH. The intermediate amino derivative was dissolved in EtOH (15 mL) and conc. H_2SO_4 (1 mL) diazotised at 0 °C with isopentyl nitrite (0.6 mL) and after 45 min treated with a solution of KI (660 mg, 4 mmol) in water (1 mL). After filtration, the crude product was purified by column chromatography (hexanes) to yield **3** (220 mg, 25%); m.p. 242–244 °C. ^{1}H NMR ($CDCl_3$): δ 7.58 (d, $J = 9$ Hz, 2H); 7.32–7.12 (m, 15H); 6.96 (d, $J = 9$ Hz, 2H).

Crystallography

Colourless crystals of **2** were obtained from slow evaporation of a benzene solution. Attempts to crystallise **3** in a variety of solvents (CH_2Cl_2, $CHCl_3$, benzene) were unsuccessful, but cocrystallisation of **3** with 1,4-dinitrobenzene in $CHCl_3$ afforded X-ray quality crystals of pure **3**. The details of X-ray data collection and structure refinement are listed in Table 1. Atomic coordinates for **2** and **3** are presented in Tables 2 and 3, respectively.

Version 5.11 (April 1996) of the Cambridge Structural Database (CSD)[14] was used to search for I···Ph interactions. Screens 17 and −28 were used. Iodonium compounds were excluded.

CCDC reference number 440/005.

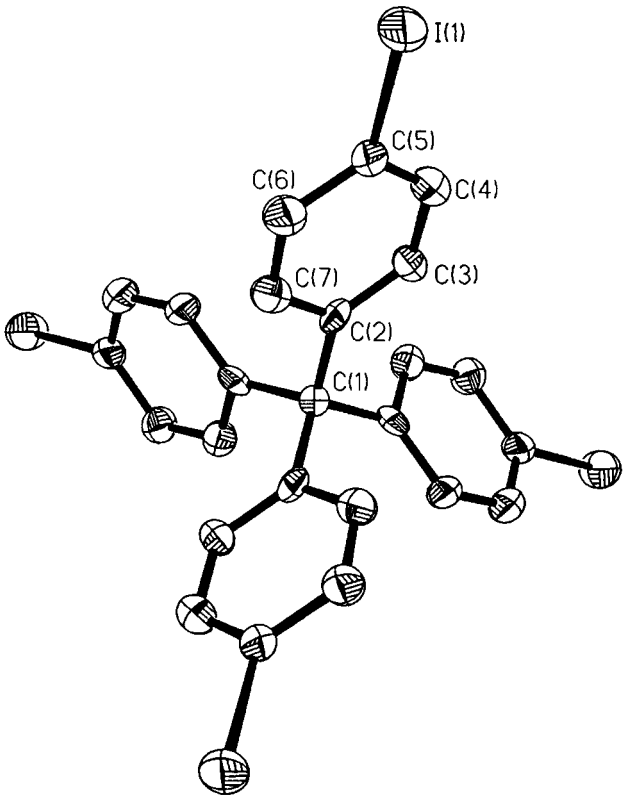


Fig. 1 Molecular structure of **2** (thermal ellipsoids drawn at 35% probability level) showing the atom labelling scheme. Bond lengths (Å) and angles (°) are I(1)—C(5) 2.102(13), C(1)—C(2) 1.564(12), C(2)—C(3) 1.360(16), C(2)—C(7) 1.396(17), C(3)—C(4) 1.397(19), C(4)—C(5) 1.363(19), C(5)—C(6) 1.423(18), C(6)—C(7) 1.379(18), C(1)—C(2)—C(3) 123.5(10), C(1)—C(2)—C(7) 117.3(9), C(3)—C(2)—C(7) 119.1(11), C(2)—C(3)—C(4) 120.3(12), C(3)—C(4)—C(5) 120.7(13), I(1)—C(5)—C(4) 120.6(10), I(1)—C(5)—C(6) 119.0(9), C(4)—C(5)—C(6) 120.2(12), C(5)—C(6)—C(7) 117.4(12), C(2)—C(7)—C(6) 122.2(12)

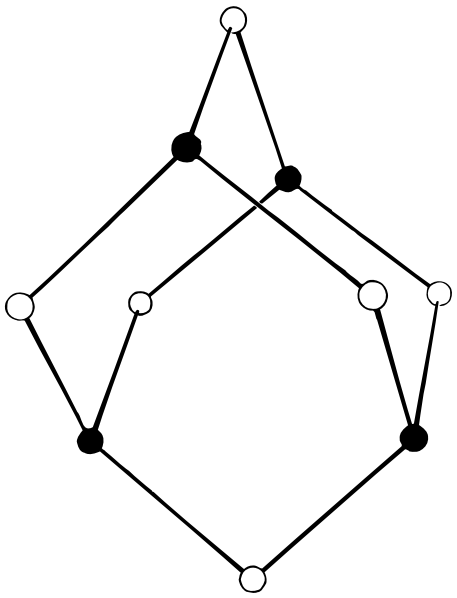


Fig. 3 Schematic representation of the network structure in compound **2**. Shaded and unshaded circles represent I_4 synthons and tetraphenylmethane moieties, respectively

Results and Discussion

The tetraiodo compound **2** crystallises in space group $I\bar{4}$ like its bromo analogue **1**, except that the *a*- and *c*-axes are slightly elongated ($a = 12.713$ Å and $c = 7.114$ Å in **1**) in the tetragonal unit cell. Fig. 1 shows a single molecule of **2** while Fig. 2 shows the disposition of four neighbouring molecules to generate the I_4 synthon **II**. The iodine atoms of the I_4 synthon **II** are separated from each other by 3.949 Å and 4.161 Å compared to the corresponding Br_4 synthon **I**, in which the

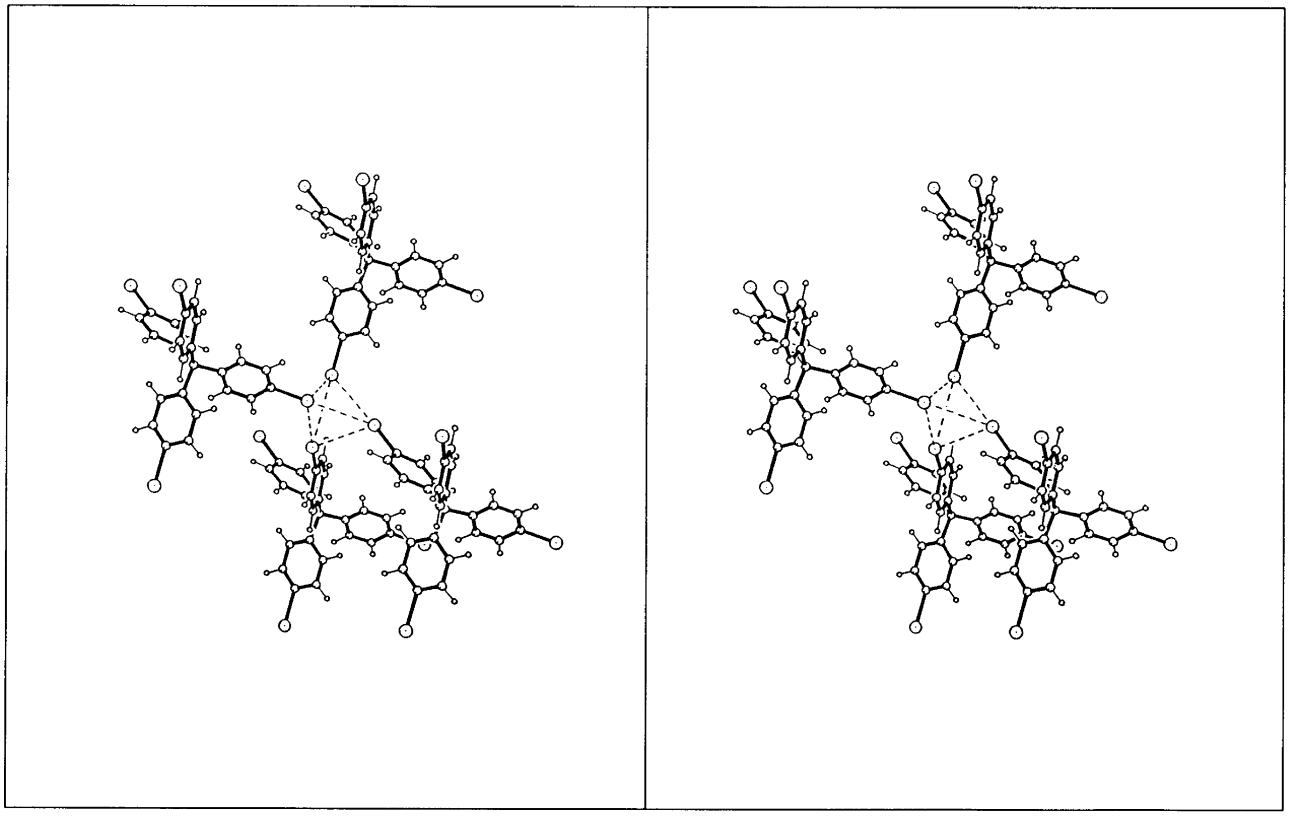


Fig. 2 Formation of the I_4 synthon, **II**, in the crystal structure of **2**

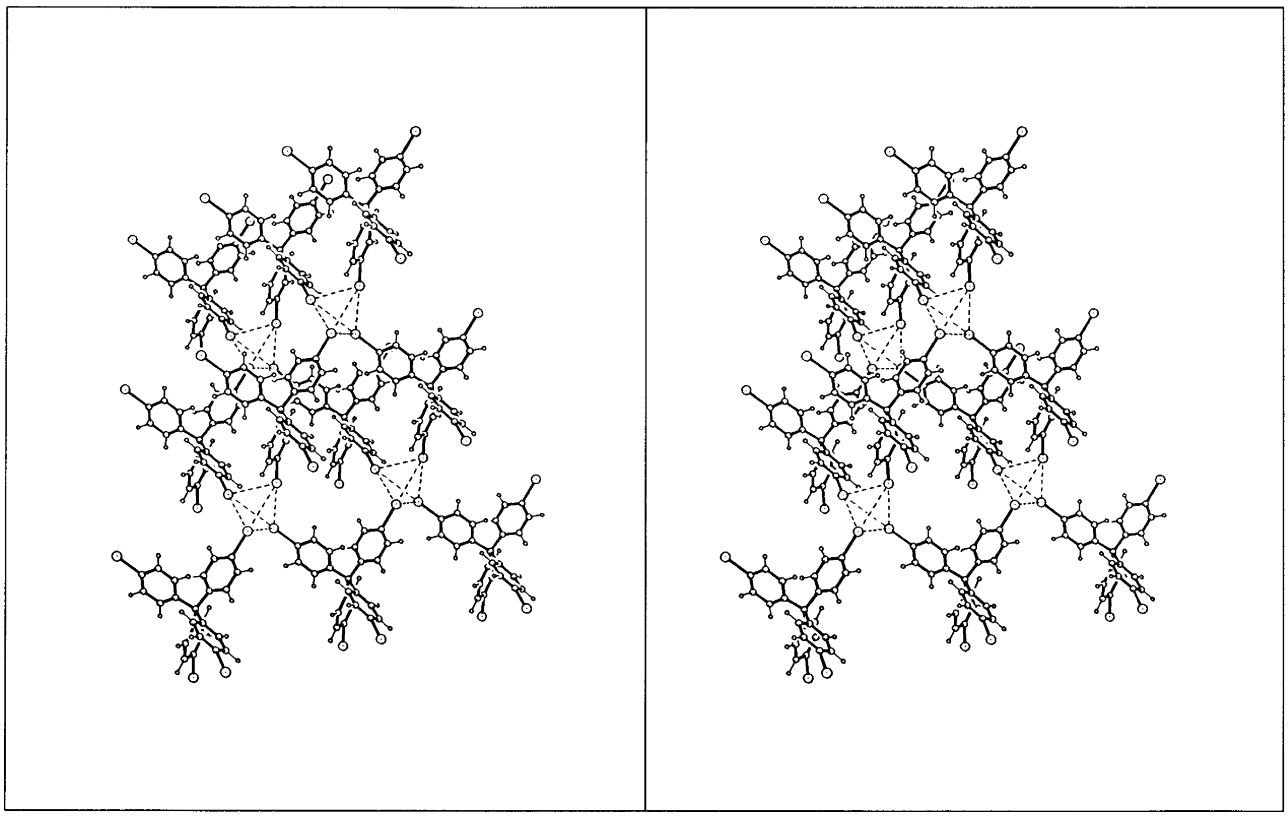


Fig. 4 Stereoview of a single molecular network comprising I_4 synthons and tetraphenylmethane moieties in the crystal structure of **2**, which contains three interpenetrating networks

Br···Br distance is 3.910 Å. Fig. 3 is a schematic view of the distorted sphalerite network structure with the molecular centres and the **II** synthons as the alternating nodes. The actual structure of a single molecular network of **2** is depicted in Fig. 4.

The molecular structure of the monoiodo compound **3** is illustrated in Fig. 5. The *a* axis is similar in length to the tetragonal axis of **2** and to that found in several tetraphenylmethanes.[15] The dovetailed packing of adjacent phenyl rings along *a* is shown in Fig. 6. The ubiquity of this packing arrangement was pointed out many years ago by Kitaigorodskii.[15] Columns of molecules stacked along *a* are held together by the unusual I···Ph interactions (I···centroid distance 3.747 Å). There is evidence that the relatively electropositive halogen atoms are able to polarise aromatic rings and the directional

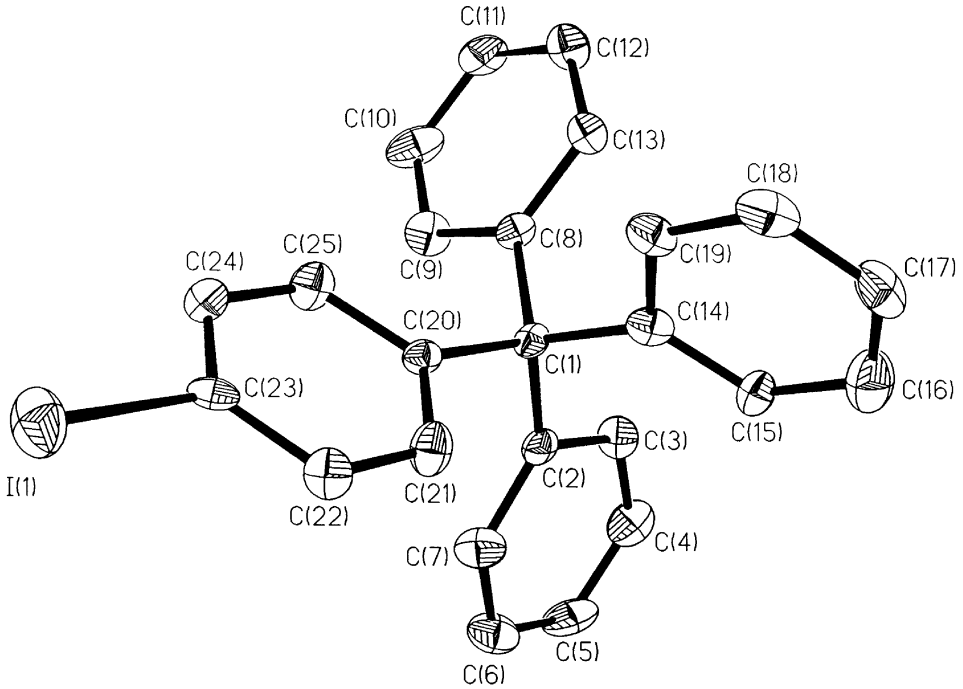


Fig. 5 Molecular structure of **3** (35% thermal ellipsoids) showing the atom labelling scheme. Selected lengths (Å) and angles(°): C(1)—C(2) 1.530(12), C(1)—C(8) 1.567(14), C(1)—C(14) 1.544(11), C(1)—C(20) 1.554(12), C(2)—C(3) 1.440(13), C(3)—C(4) 1.388(15), C(4)—C(5) 1.361(17), C(5)—C(6) 1.366(18), C(6)—C(7) 1.406(17), C(2)—C(7) 1.345(15); C(1)—C(2)—C(3) 117.9(7), C(2)—C(3)—C(4) 121.5(9), C(3)—C(4)—C(5) 119.7(10), C(4)—C(5)—C(6) 120.3(11), C(5)—C(6)—C(7) 119.6(11), C(2)—C(7)—C(6) 123.1(11), C(1)—C(2)—C(7) 126.4(9), C(2)—C(1)—C(8) 106.9(7), C(14)—C(1)—C(20) 105.8(6), C(2)—C(1)—C(14) 111.6(7), C(2)—C(1)—C(20) 110.2(7)

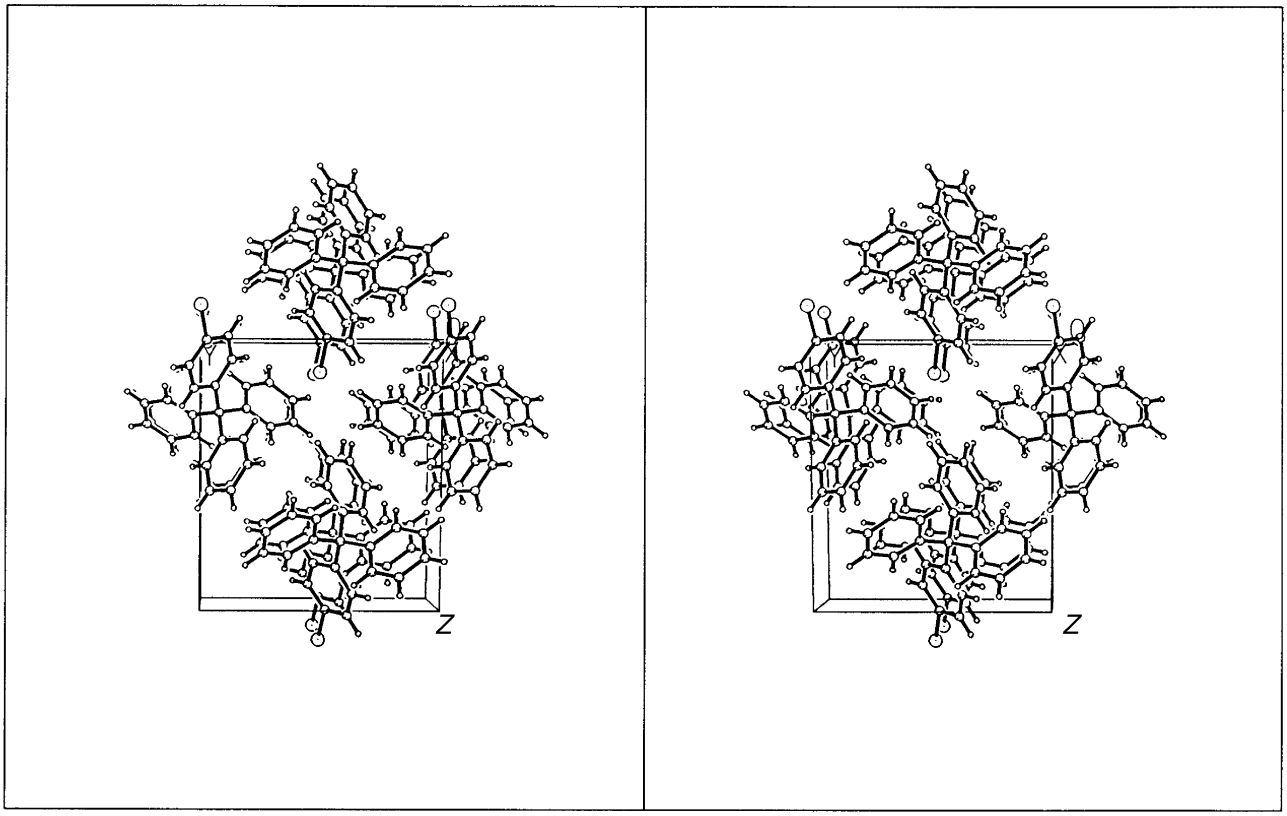


Fig. 6 Formation of columns of molecules along the *a* axis in the crystal structure of **3**

characteristics of these weak interactions have been described recently.[16] Fig. 7 shows that the I···Ph interactions define a zigzag network along the *a* axis. A search of the CSD for the fragment C—I···Ph (centroid = X) (I···X = 2.00–4.30 Å, C—I···X = 100.0–180.0°) gave 60 entries with 75 hits which are displayed in the scatterplot (Fig. 8). There are more hits with a somewhat linear iodo to phenyl contact (C—I···X > 140°) and very few entries with contacts that are both short an non-linear. The chemical structures of compounds in the three populated regions as well as in the empty quarter were individually examined to correlate the geometry of the I···Ph contact with chemical effects. Such analysis revealed that C—I groups tend to approach electron-rich phenyl rings in a linear manner and electron-deficient rings in a bent manner. For example, in ITYAEA10 the I atom

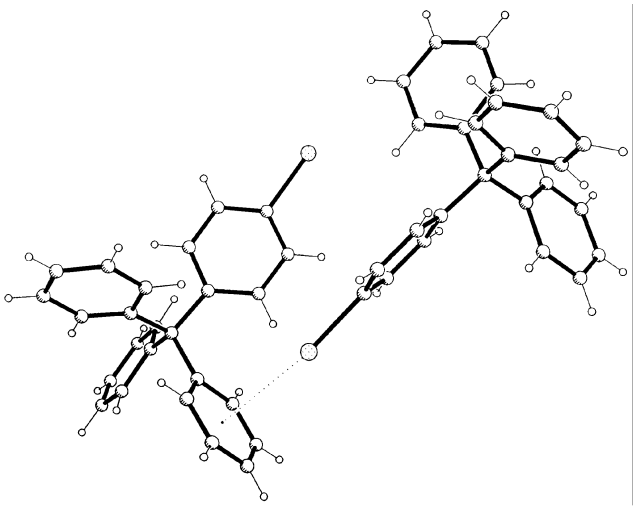
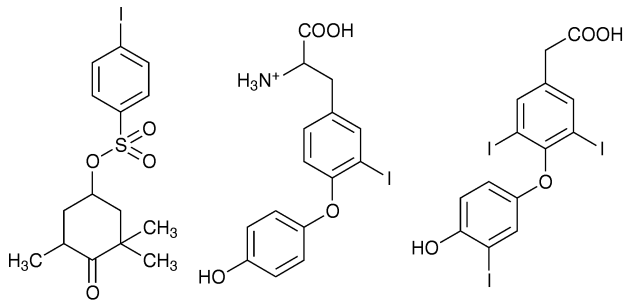


Fig. 7 Diagram showing a zigzag chain of molecules linked by an I···Ph interaction in the crystal structure of **3**



approaches the phenyl ring with iodo and hydroxy substituents at a C—I···X angle of 139° and the ring with the acetic acid residue and diiodo substituents at an angle of 103°. In the related COWTEN structure, two different iodine atoms approach the same phenolic ring nearly linearly at angles of 163 and 170°. On the other hand, in BANMUY the C—I···X approach (114°) to the electron-deficient phenylsulfonyl ring is non-linear. These observations add support to the suggestion that the I atom is polarised δ(+) in the polar region and δ(−) in the equatorial region of the C—I bond.[17]

Conclusions

Compounds **1** and **2** form isomorphous crystal structures. The reproducibility of essentially the same molecular network by either Br_4- or I_4-synthons clearly demonstrates the importance of weak intermolecular interactions in ordering crystal packing arrangements. Therefore it may be useful to treat crystal structures with weak interactions in terms of molecular networks, which can be generated by molecular or supramolecular nodes. The other interesting feature that has emerged in the present study is the formation of molecular columns and it is noteworthy that a similar molecular packing is satisfyingly repeated in the tetraphenylmethane family of crystal structures, leading to the generation of non-centrosymmetry in these crystalline materials. We have tried

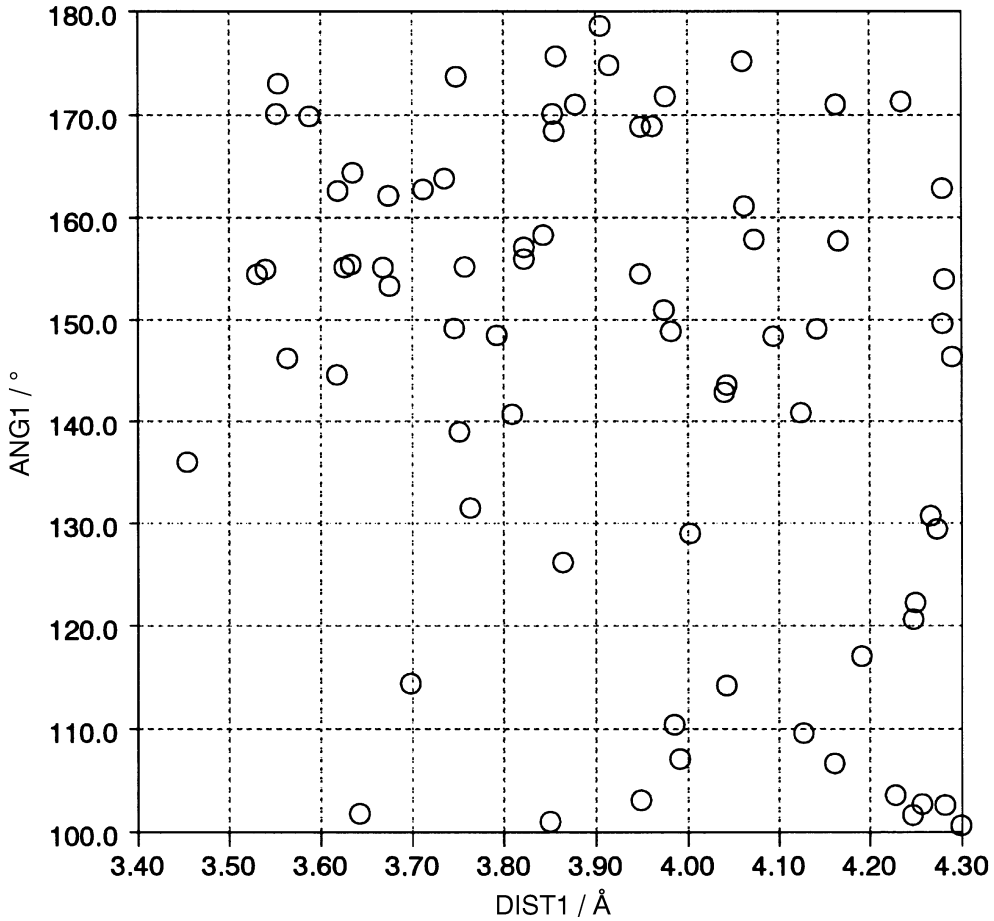


Fig. 8 Scatterplot of I···X distance (DIST1, Å) and C—I···X angle (ANG1, °) for the 75 hits retrieved from the CSD. Note the scarcity of points in the lower left hand region of the scattergram

to replace I_4 synthons with CI_4 molecules by co-crystallising carbon tetraiodide with tetraphenylmethane, but in most of the solvents used, CI_4 decomposed to release iodine.

Acknowledgements

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