The Nature of Halogen ··· Halogen Interactions and the Crystal Structure of 1,3,5,7-Tetraiodoadamantane

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An analysis of halogen···halogen (X···X) intermolecular interactions in crystals, using the Cambridge Structural Database (CSD), is presented. A total of 794 crystal structures yielded 1051 contacts corresponding to symmetrical and unsymmetrical X···X interactions of the type Cl···Cl, Br···Br, I···I, Cl···F, Br···F, I···F, Br···Cl, I···Cl and I···Br. These 1051 contacts are divided mainly into two categories, type I and type II depending upon the values of the two C–X···X angles θ_1 and θ_2 around the X atoms in a fragment of the type C–X···X–C. Type I contacts are defined as those in which $\theta_1 = \theta_2$ while type II are defined as those in which $\theta_1 \cong 90°$ and $\theta_2 \cong 180°$. Our results indicate that as the polarisability of the X atom increases, type II contacts become more significant than type I contacts and the X···X interaction may be more nearly considered to arise from specific attractive forces between the X atoms. A number of these concepts are succinctly illustrated in the crystal structure of 1,3,5,7-tetraiodoadamantane, **1**. This structure has been reported to a very limited accuracy previously and the present work reveals an unusual twinned structure for this compound wherein the geometry of the stabilising I···I interactions is retained across the twin boundary. Compound **1** is tetragonal, space group $I4_1/a$, $a = b = 7.1984(7)$ and $c = 28.582(4)$ Å, and $Z = 4$. The packing of the molecules in the crystal is controlled by I···I interactions. The supramolecular network of I···I connected molecules in crystalline **1** is closely related to that in adamantane-1,3,5,7-tetracarboxylic acid. Indeed, the stabilising nature of the I···I interactions is crucial for the crystallisation of **1** in this particular structure because otherwise, it should also have formed plastic crystals as do the analogous tetrachloro and tetrabromo derivatives.

It has long been known that many intermolecular X···X (X = Cl, Br and I) distances in molecular crystals are significantly less (0.1–0.4 Å) than the sum of the accepted van der Waals radii.[1–3] These short distances are also associated with certain preferred angular geometries and have been investigated by a variety of experimental and theoretical methods.[4–13] These X···X interactions are of special significance in crystal engineering or the deliberate design of organic crystal structures and supermolecules because they may be used to construct layered motifs which are associated with specific solid state reactivity patterns.[14–17] We have analysed these interactions earlier using the Cambridge Structural Database (CSD) and have deduced that short X···X intermolecular distances arise from specific attractive forces between X atoms in crystals.[18] Others have held that these short distances could originate from anisotropic effects between elliptically shaped X atoms.[19–22] To summarise, the nature of X···X interactions has long been a matter of interest and debate and recent evidence hints that a variety of effects may be important leading to distinctions between interactions such as Cl···Cl, Br···Br and I···I and also to distinctions between such symmetrical interactions on the one hand and unsymmetrical interactions such as I···F and I···Cl on the other. We have re-examined this question and this paper presents the results of our CSD searches on symmetrical and unsymmetrical X···X interactions and probes the distinction between the individual halogens through a study of the unusual crystal structure of 1,3,5,7-tetraiodoadamantane, **1**. This structure was reported to a very limited accuracy by Schleyer and coworkers recently[23] and our study originated from a concern for the unacceptably high and unexplained *R*-value of 0.203 in their study.

Experimental

Cambridge Structural Database (*CSD*) *Analysis.*—Data were retrieved from the 1993 update of Version 5.05 of the CSD (109 816 entries)[24] for all ordered, halogen-containing crystal structures ($R \leq 0.10$) with an exact match between chemical and crystallographic connectivity. Polymeric and charged species were excluded. Geometrical calculations were performed on the retrieved data for various X···X interactions using QUEST3D-GSTAT, an automatic graphics non-bonded search program of the CSD. Duplicate hits (identified by the same reference code) were removed from the calculations by eliminating all but the structure with the lowest *R*-value in each case. Unique intermolecular interactions were considered up to the sum of the van der Waals radii for symmetrical halogen interactions (Cl···Cl 3.50, Br···Br 3.70 and I···I 3.96 Å). For unsymmetrical halogen interactions, these limits were relaxed slightly to 0.08 Å beyond the sum of the van der Waals radii (Cl···F 3.30, Br···F 3.40, I···F 3.53, Br···Cl 3.68, I···Cl 3.80 and I···Br 3.91 Å). A typical question for I···I interactions is given in a supplementary publication† and the other questions were formulated analogously.

X-Ray Crystal Structure Determination.—Tetraiodoadamantane, **1**, $C_{10}H_{12}I_4$, $M_r = 640$ was synthesised from adamantane according to literature procedures[25] and recrystallised from $CHCl_3$ to yield colourless isodimensional crystals,

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† For details of the supplementary publications scheme, see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1 [Supp. pub. No. 57029 (6 pp.)].

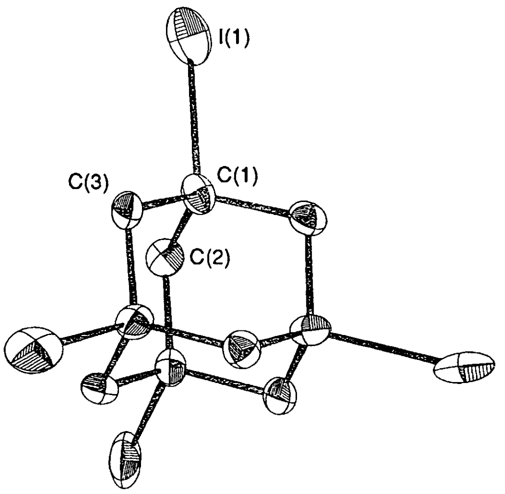

Fig. 1 ORTEP drawing of 1,3,5,7-tetraiodoadamantane, **1**

m.p. 380 °C. A body centred cell of $a = b = 7.1984(7)$, $c = 28.582(4)$ Å, $V = 1481.0$ Å^3, $Z = 4$ was used to collect an octant of *hkl* reflection data, $h \geq 0, k \geq 0, l \geq 0, 2\theta < 50°$ on an Enraf–Nonius CAD4 automatic diffractometer using Mo-Kα radiation. Data were absorption corrected ($\mu = 83.0$ cm^{-1}) using a (12 × 12 × 12) weighted, Gaussian grid. Crystal faces relative to an internal origin were (001) 0.053, (00$\bar{1}$) 0.036, ($\bar{1}$01) 0.069, (011) 0.077, (101) 0.071, (0$\bar{1}$1) 0.084 mm. A 4% error in $I(hkl)$ {2% error in $F(hkl)$ was included along with the counting statistic error in evaluating weights $w = 1/\sigma[F(hkl)]\}^2$ for least-squares refinement. Systematic absences were consistent with space group $I4_1/a$, but not $I4_1/amd$ or $I4_1/acd$. However, merging of absorption corrected data assuming $4/mmm$ diffraction symmetry gave a value of 0.028 for $\Sigma w|\Delta F^2|/\Sigma w|F_{obs}|^2$ implying that twinning of the crystal had occurred. However, only the *h0l* data was merged with *0kl* data avoiding the imposition of an exact 1 : 1 twin by data merging. Only those 600 of the resulting 655 reflections considered to be observed at the 3σ level were used in the subsequent refinements. The crystal structure was initially solved and refined ignoring the twinning but refinement stopped at an unsatisfactory value of $R = \Sigma|\Delta F|/\Sigma|F_{obs}|$ of 0.16, similar to or marginally better than that obtained earlier.[23]

A twinning–disorder model was then refined using the program RAELS89.[26] Each reflection intensity was considered to be described as $I(hkl) = (1 - b)|F(hkl)|^2 + b|F(khl)|^2$ using a refineable twinning parameter b. Attempts to identify the twin mechanism suggested the additional possibility of a disorder that would be imitated by a stacking fault. This disordering would be detectable by a reduction in the apparent scale K_2 of $l = 2n + 1$ data relative to K_1 for $l = 2n$ data. When two such scale constants were refined, the final refinement cycle gave values of 0.0298 for R, 0.979(6) for K_2/K_1 and 0.534(4) : 0.466 for the twin ratio $(1 - b):b$. Assuming a simple translational stacking fault, we obtain the result that $K_2/K_1 = (1 - 2a)$. Therefore the value of a is 0.010(3); a is the occupancy of the minor component of the structure with origin 0, 0, $\frac{1}{2}$ (equivalent to $\frac{1}{2}$, $\frac{1}{2}$, 0) relative to the major component with occupancy $(1 - a)$ and origin 0, 0, 0.

Refinement was also carried out using the operation $\frac{3}{4} - y$, $\frac{1}{4} - x$, $-z$ rather than a translation to create the minor component of a disordered structure. This refinement using a single overall scale constant gave $R = 0.0297$, the same twin ratio and a relative occupancy of 0.0088(24) : 0.9912. This model locates molecules at the same sites as before but with the minor component related to the major component by the twofold rotation operation rather than a translation. Had the inherent $\bar{4}2m$ symmetry aligned perfectly with the lattice then there would be no difference between these two descriptions. The twofold rotation is assumed to be the twinning operation since a translation operation does not reorient the structure. This creates a twinning plane perpendicular to c. The I ··· I contact distances across the twin plane are 4.172(1) Å compared to 4.063(1) Å for the ordered structure and 4.285(1) Å for the translation option.

A feature of the refinement was that atom C(3) has two crystallographically independent bonds to C(1) and its $\bar{4}$ related equivalent. A restraint to make these bond lengths approach equality produced a slightly lower value of R, namely 0.0297 compared to 0.0298 but a higher value for the goodness of fit, 1.847 compared to 1.843, implying that the unconstrained values 1.549(11) and 1.515(11) Å are not significantly different from the restrained values of 1.533(5) and 1.531(5) Å. The lower error estimate in the restrained case is more realistically the error in the mean of the two values, since the restraint used was only on the difference between bond lengths and not on their absolute values. The error in the difference is presumably larger because of pseudosymmetry effects associated with C(1) having approximate fractional coordinates $\frac{1}{8}$, $\frac{3}{8}$, z and C(3) having approximate fractional coordinates 0, $\frac{1}{2}$, $\frac{1}{8}$. Hydrogen atoms were reincorporated with idealised coordinates after each refinement cycle. Fractional coordinates, thermal parameters and intramolecular bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.* Fig. 1 is an ORTEP drawing of **1**.

Results and Discussion

Attractive Nature of X ··· X Interactions.—The difficulty in distinguishing between increased attraction (weak polarisation bonding) and decreased repulsion (anisotropic atomic radii) as the primary cause of the establishment of short X ··· X contacts in molecular crystals has been well recognised.[27] A recent CSD statistical analysis of experimentally observed X ··· X short contacts by Desiraju and Parthasarathy indicates that X ··· X interactions may be represented as specific attractive forces.[18] This analysis was based on the argument that if in a group of compounds, the ratio of X ··· X to X ··· C and X ··· H contacts is greatly out of proportion to the ratio of the halogen to total molecular surface area, the X ··· X contacts are attractive in nature. However, Price and coworkers have noted that a number of Cl ··· Cl short contacts reported by Desiraju and Parthasarathy arise from fully or heavily chlorinated compounds where the likelihood of such short Cl ··· Cl contacts may be higher and that such observations need not impute any particular attractive character to the Cl ··· Cl interaction.[28] Additional calculations were performed by them claiming to show that these short contacts are the result of the packing of elliptically shaped atoms. However, we still believe that the Cl ··· Cl interaction has a specific attractive component because otherwise, it is difficult to understand the stability and indeed the very existence of the Cl_2 dimer in the gas phase.[29,30] Similarly, it is also difficult to rationalise the well known 'chloro-rule' in organic crystal chemistry which states that Cl substituents have an ability to steer the crystal packing towards a layered arrangement.[16,17] Further, the comments of Price and coworkers are based on observations of only Cl-containing compounds while the conclusions of Desiraju and Parthasarathy are based also on Br ··· Br and I ··· I contacts in compounds where full or heavy halogenation is absent. In summary, all these observations indicate a possibly dual

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* For details of the CCDC deposition scheme, see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.

Table 1 Summary of halogen···halogen (X···X) interactions obtained in CSD searches[a]

Interactions	Compounds	Total contacts	Type-I contacts		Type-II contacts	
			b	*c*	*d*	*e*
Cl···Cl	496	694	176	154	364[f]	
Br···Br	172	200	59	35	106[f]	
I···I	42	50	14	0	36[f]	
Cl···F	28	35	0	18	9	8
Br···F	13	16	0	4	8	4
I···F	6	8	0	2	6	0
Br···Cl	34	40	0	4	23	13
I···Cl	6	6	0	0	5	1
I···Br	1	2	0	0	1	1

[a] The angles θ_1 and θ_2 are so defined for unsymmetrical X···X contacts that θ_1 is $C{-}X_{heavy}\cdots X_{light}$ and θ_2 is $C{-}X_{light}\cdots X_{heavy}$ in the fragment C–X···X–C (X = F, Cl, Br and I). [b] $\theta_1 = \theta_2$ (type I). [c] $|\theta_1 - \theta_2| < 20°$ (quasi-type I). [d] $\theta_1 \cong 180°$; $\theta_2 \cong 90°$. [e] $\theta_1 \cong 90°$; $\theta_2 \cong 180°$. [f] Classification as in *d* or *e* is not relevant because the contact is symmetrical.

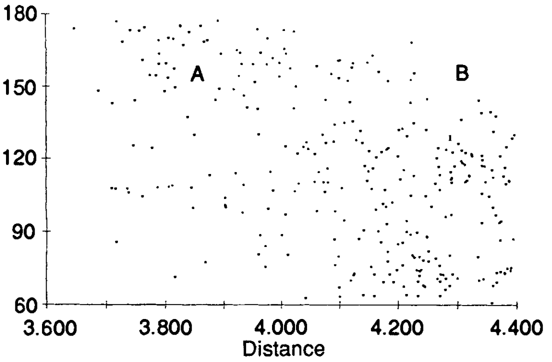
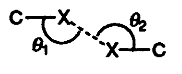


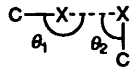
Fig. 2 Scattergram of C–I···I angles θ_1 *vs.* I···I distances. Notice the concentration of points at $\theta \cong 100°$ and $\theta \cong 160°$ in region A.

character for X···X interactions with polarisability being more important for I and Br and perhaps anisotropy for Cl.

Directionality of X···X Interactions.—The early studies of Sakurai, Sundaralingam and Jeffrey distinguished between two possible geometries for Cl···Cl interactions.[1] Parthasarathy and coworkers classified these interactions based on the two C–X···X angles θ_1 and θ_2 with the classes being denoted as type I (θ_1 or θ_2 = 90°), type II (θ_1 or θ_2 = 180°) and type III ($\theta_1 = \theta_2$ and the two X atoms being related by a crystallographic centre of inversion).[31] This nomenclature is ambiguous in that a particular C–X···X–C contact may be both type I and type II. Accordingly, the nomenclature of these X···X interactions was subsequently simplified by Desiraju and Parthasarathy with type I referring to those interactions where $\theta_1 = \theta_2$ and type II to those cases where $\theta_1 \cong 180°$ and $\theta_2 \cong 90°$.[18] We have adopted this latter simplified nomenclature in the present paper. It is generally believed that a type II contact is consistent with a polarisation of adjacent X atoms as δ(+) and δ(−)[31] while a type I contact is a consequence of crystallographic symmetry, the X atoms being located across a centre of inversion.



Type I



Type II

A primary concern in this study was to ascertain if there is any physical basis for this type of classification; in other words are the C–X···X–C geometries truly specific or are they merely artefacts of a limited sampling of crystal structures in the earlier studies? Further, is the grouping of contacts into type I and type II dependent on the choice of the van der Waals radii? These issues have been investigated with the CSD in the present study. Geometrical calculations were performed for both symmetrical (Cl···Cl, Br···Br and I···I) and unsymmetrical (Cl···F, Br···F, I···F, Br···Cl, I···Cl and I···Br) X···X contacts. The results are summarised in Table 1. A scattergram of a representative example, namely I···I distance *vs.* θ_1 is shown in Fig. 2. Two regions A and B can be identified in this scattergram. In region A, (X···X ≤ 4.0 Å) only certain θ values are preferred with some clustering around 160 and 100°. In region B, (X···X ≥ 4.0 Å) all possible θ values are observed. Possibly, the contacts in region B correspond to van der Waals type contacts which arise as a consequence of packing of molecules and contribute only a little to the crystal energy. In contrast, contacts in region A are possibly significant and affect crystal packing. For Cl···Cl and Br···Br contacts, the separation of the regions A and B occurs around 3.35 and 3.65 Å respectively, well before the conventional van der Waals limits of 3.50 and 3.70 Å. These observations suggest that the upper distance limit for significant X···X interactions does not correspond to the van der Waals radii, or alternatively a reassessment of the radii is called for. In fact, possible ambiguities in the values of atomic van der Waals radii were pointed out even by Bondi in his often-cited paper on the subject.[32] Bondi stated that his values of the atomic van der Waals radii 'may not always be suitable for the calculation of contact distances in crystals.' All this notwithstanding, calculations were repeated extending the X···X distance up to the conventional van der Waals radii, because of the practical difficulties in assigning new van der Waals radii and there was no significant difference in the conclusions.

Distinction between Cl···Cl, Br···Br and I···I Interactions.—In the next stage of the analysis, the two angles θ_1 and θ_2 obtained from the fragment types defined above were plotted as scattergrams (Fig. 3) for symmetrical X···X interactions up to the van der Waals limit. This has been performed earlier[31,33] and the object of the present analysis was to investigate if a distinct separation exists between type I and type II contacts. In all these scattergrams, it was observed that there is some clustering but while type I and type II contacts are clearly demarcated for I···I, this demarcation is more blurred for Br···Br and has essentially vanished for Cl···Cl. There are several contacts which bridge the gap between type I and type II and these have $|\theta_1 - \theta_2| < 20°$. These contacts are especially prominent for Cl···Cl and were generally not observed for I···I *even when the distance limits for the contacts were relaxed up to* 4.1 Å. We have termed these contacts quasi-type I and believe that they are the differentiating factor between Cl···Cl and I···I interactions with Br···Br being in an intermediate situation. The presence of these quasi-type I contacts for Cl···Cl and their absence for I···I is not a geometrical artefact but suggests that while polarisation effects are important in I···I, leading to clustering (especially in the type II domain), other effects such as perhaps anisotropy are indeed important for Cl···Cl so that a wide spread is seen in the θ_1 *vs.* θ_2 scattergrams. In effect, quasi-type I contacts bridge type I and type II contacts leading to a continuous angular distribution for Cl···Cl and Br···Br interactions. For I···I contacts [Fig. 3(*c*)] there are no quasi-type I contacts and the distinction between type I and type II is well defined. Interestingly Fig. 3 also indicates that not only do the quasi-type I contacts decrease from Cl···Cl to I···I, but also type I. This observation suggests strongly that polarisation effects are increasingly important in the order Cl···Cl ⟶

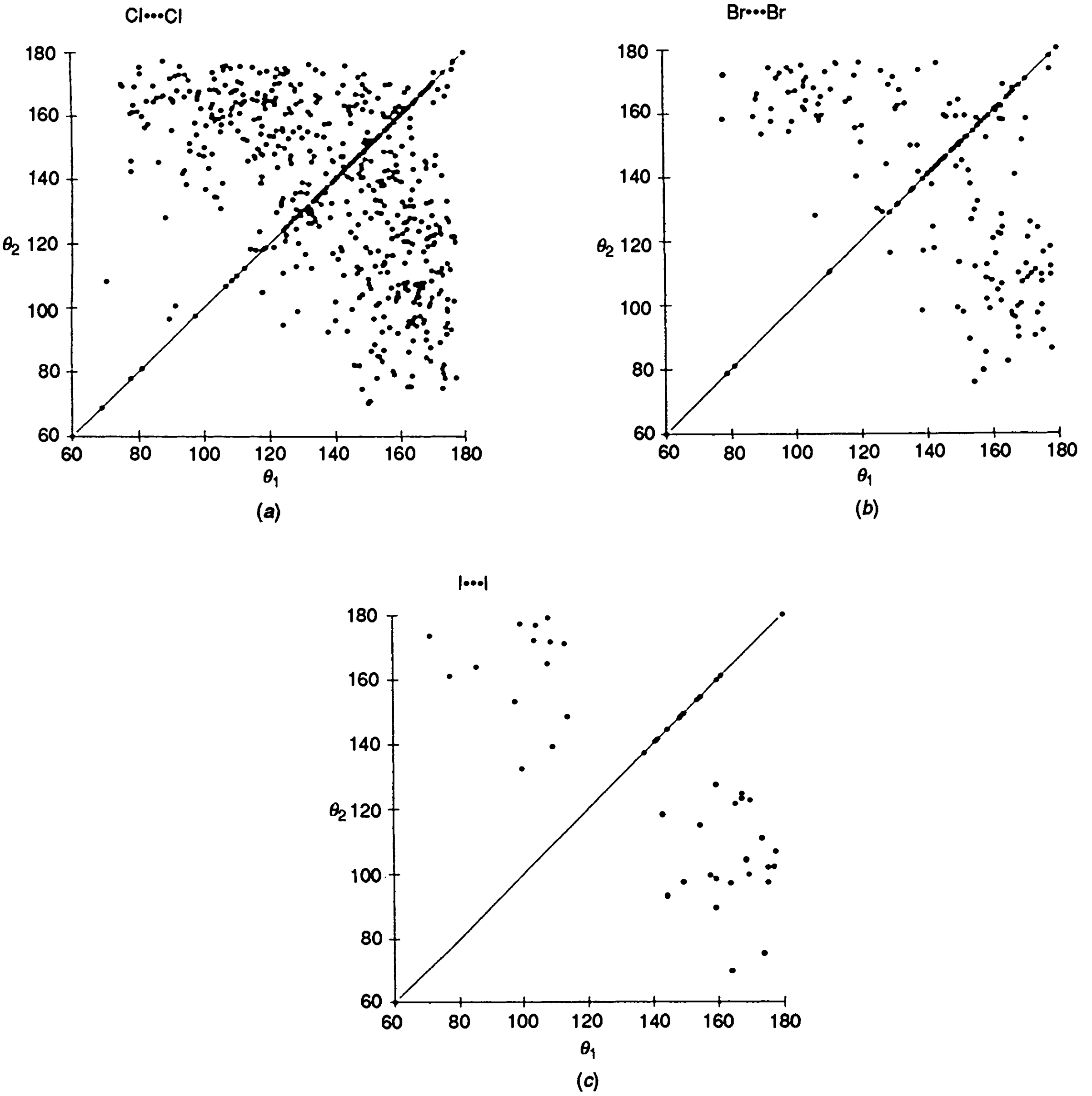


Fig. 3 Type I, quasi-type I and type II contacts for symmetrical halogen ··· halogen interactions. (*a*) Type I has $\theta_1 = \theta_2$ (diagonal contacts); (*b*) quasi-type I has $|\theta_1 - \theta_2| < 20°$; (*c*) type II has $\theta_1 \cong 90°, 180°$ and $\theta_2 \cong 180°, 90°$ (off-diagonal contacts).

Br ··· Br ⟶ I ··· I, so that most I ··· I short contacts are the result of atomic polarisation rather than crystal symmetry, anisotropy or other factors. Table 1 shows that while Cl ··· Cl is represented by an approximately equal number of type I (330 including quasi-type I) and type II (364) contacts, I ··· I is represented by 14 and 36 contacts in the two types, respectively. Br ··· Br interactions are nearly similar to Cl ··· Cl with 94 type I and 106 type II contacts.

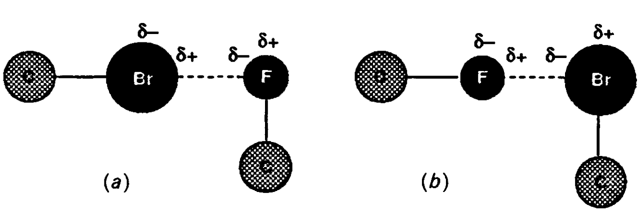


Fig. 4 Schematic diagram to show the polarisation of halogen atoms in unsymmetrical halogen ··· halogen contacts. (*a*) The heavier halogen atom is polarised $\delta(+)$. (*b*) The lighter halogen atom is polarised $\delta(+)$. The situation in (*a*) is generally the more common.

Unsymmetrical X ··· X Contacts.—Our results on Cl ··· Cl, Br ··· Br and I ··· I interactions prompted us to consider unsymmetrical interactions of the type Cl ··· F, Br ··· F, I ··· F, Br ··· Cl, I ··· Cl and I ··· Br. In examples of this kind, one would anticipate a preference for type II contacts with the heavier X atom being polarised $\delta(+)$. Since X atoms are polarised $\delta(-)$ in the equatorial regions and $\delta(+)$ in the polar regions (C–X along the pole),[31] this corresponds to type II contacts with $\theta_1 \cong 180°$ and $\theta_2 \cong 90°$ (rather than $\theta_1 \cong 90°$ and $\theta_2 \cong 180°$) where θ_1 is defined as $\text{C–X}_{\text{heavy}} \cdots \text{X}_{\text{light}}$ and θ_2 is defined as $\text{C–X}_{\text{light}} \cdots \text{X}_{\text{heavy}}$. This is illustrated schematically in Fig. 4. Accordingly, geometry calculations similar to those performed for symmetrical X ··· X interactions were performed for the unsymmetrical contacts. However, X ··· X distances were calculated beyond 0.08 Å of the sum of the van der Waals radii of the non-bonded X atoms. This procedure was carried out because of the general paucity of unsymmetrical X ··· X contacts in organic crystal structures. Scattergrams corresponding to Cl ··· F, Br ··· F and I ··· F are shown as representative examples in Fig. 5 and these may be compared with the symmetrical X ··· X interactions in Fig. 3.

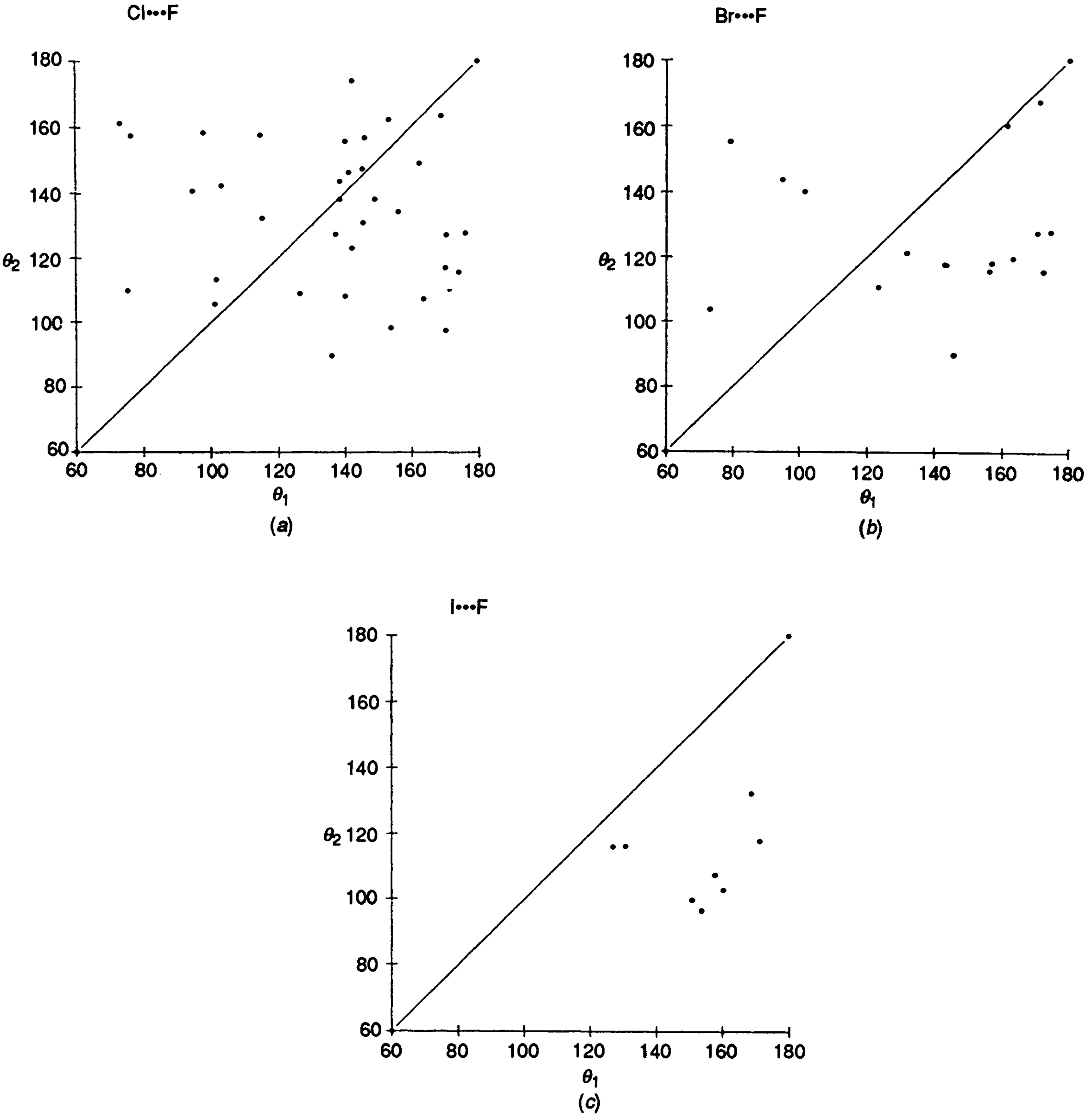


Fig. 5 θ_1 and θ_2 distribution for unsymmetrical halogen ••• halogen contacts. Notice the preferential polarisation of the heavier halogen atom as δ(+).

Fig. 5 shows that the Cl ••• F interaction is similar to the Cl ••• Cl interaction [Fig. 3(*a*)] whereas the I ••• F interaction resembles the I ••• I interaction [Fig. 3(*c*)]. The Br ••• F interaction is again in an intermediate situation acting as a bridge between the Cl ••• F and I ••• F interactions. Fig. 5(*c*) shows that for I ••• F interactions, type II contacts are exclusively linear at I and bent at F (no contacts with $\theta_1 \cong 90°$ and $\theta_2 \cong 180°$). However, for Br ••• F a few contacts (4 out of 12) are bent at the Br atom (see Fig. 4). This may not be surprising because of the decrease in the polarisability of Br relative to I. This trend is continued for Cl ••• F interactions where there are nearly equal populations for contacts with $\theta_1 \cong 180°$, $\theta_2 \cong 90°$ and $\theta_1 \cong 90°$, $\theta_2 \cong 180°$. Inspection of Table 1 also hints at the resemblance of Br ••• Cl and I ••• Cl with I ••• F with 5 and 23 contacts, respectively, bent at F out of 6 and 36 of the total interactions. By definition, it is extremely unlikely that pure type I contacts will be found for unsymmetrical X ••• X interactions barring a fortuitous equality of angles; in practice none were found. Even among the quasi-type I contacts which are observed, the number decreases with an increase in the polarisability of the halogen atom. For instance, 18 Cl ••• F contacts out of a total of 35 are quasi-type I; however, only two out of eight I ••• F contacts are quasi-type I.

Summarising all these features, one may conclude that the polarisability of the halogen atom, X, plays a vital role in establishing symmetrical and unsymmetrical X ••• X interactions associated with the heavier halogen atoms. Regarding interactions associated with the lighter halogen atoms, the features are multivariant and for Cl ••• Cl and Cl ••• F interactions, anisotropy and close packing (crystallographic symmetry) may also be important. The Br ••• Br interaction constitutes a bridge between Cl ••• Cl and I ••• I interactions and is influenced by both polarisation and anisotropy with a tendency towards I ••• I rather than Cl ••• Cl because of the similar polarisabilities of Br and I.

Crystal Structure of Tetraiodoadamantane, **1**.—While it is known that 1,3,5,7-tetrachloroadamantane and 1,3,5,7-tetrabromoadamantane form plastic crystals[34] as do other symmetrical adamantanes,[35] Schleyer and coworkers have reported that the 1,3,5,7-tetraiodo derivative, **1**, crystallises in a tetragonal space group and is disordered.[23] In contrast, 1,3-

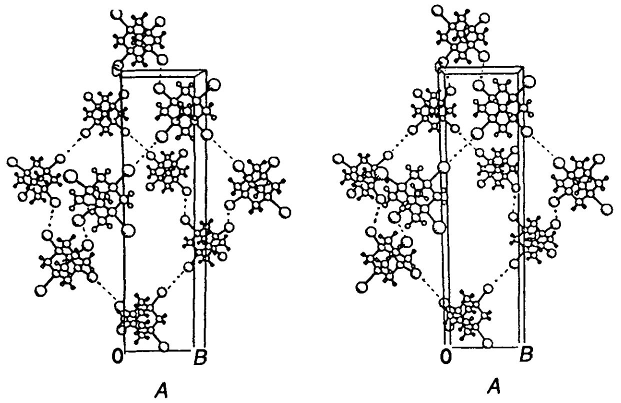


Fig. 6 I $\cdots$ I mediated diamondoid network in the crystal structure of **1**. I $\cdots$ I contacts are shown as dashed lines.

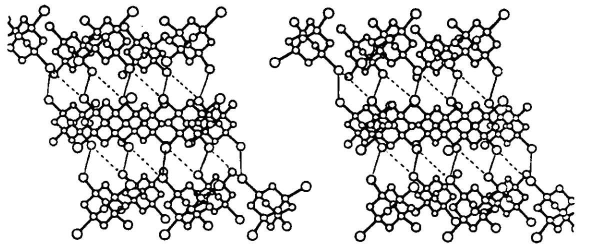


Fig. 7 Crystal structure of **1** to show a layer of molecules perpendicular to (001). Molecules within a particular super adamantoid network as shown in Fig. 6 are connected with undashed lines (——). Molecules in different networks are connected with dashed lines (- - - -). Molecules in all five independent networks are shown in the figure.

difluoro-5,7-diiodoadamantane and 1,3,5-trifluoro-7-iodoadamantane have ordered structures. Such differences in crystallisation behaviour were attributed to the importance of I $\cdots$ I interactions (in compound **1**) and to the importance of the unsymmetrical I $\cdots$ F interactions (in the fluoro iodo derivatives) in other words, to the importance of halogen atom polarisability in X $\cdots$ X interactions. Some of the results of Schleyer and coworkers are, however, ambiguous because the crystal structure of **1**, was determined to an unacceptably high *R*-value of 0.203. Therefore it seemed appropriate to re-examine this crystal structure.

The structure in $I4_1/a$, $Z = 4$, has individual molecules of implicit $\bar{4}2m$ symmetry on sites of $\bar{4}$ symmetry in the crystal (Fig. 6). The origin was chosen to lie on an inversion centre. Fig. 7 shows that the structure can be described in terms of 4_1 screw related layers of molecules, each layer consisting entirely of molecules related by simple translations $na + mb$ where n and m are integers. The symmetry of such a layer is very nearly $P\bar{4}2m$. An intramolecular I $\cdots$ I vector for I atoms at the same height along c for the reference molecule at $0, \frac{1}{4}, \frac{1}{8}$ is 0.609, 0.573, 0 compared with 0.586, 0.586, 0 if the molecule were aligned with the [110] direction for the idealised symmetry. The adjacent layers have molecules b-glide related at $0, \frac{3}{4}, -\frac{1}{8}$ and a-glide related at $\frac{1}{2}, \frac{1}{4}, \frac{3}{8}$. If the pseudo-mirror plane of the pseudo $P\bar{4}2m$ layer is imposed on these molecules, adjacent layers perpendicular to [001] could have molecules at $\frac{1}{2}, \frac{1}{4}, -\frac{1}{8}$ or $0, \frac{3}{4}, \frac{3}{8}$. Alternative I $\cdots$ I contact distances associated with twinning or disorder are then possible and these distances depend on how the alternative layers are created. A stacking fault of $(a + b)/2$ translation creates an I $\cdots$ I contact distance of 4.285(1) Å whereas a twofold rotation $\frac{3}{4} - y, \frac{1}{4} - x, -z$ between adjacent layers creates a contact distance of 4.172(1) Å. These distances may be compared with distances of 4.063(1) Å for the normal interlayer contact and 4.167(1) Å for the closest intermolecular contact between I atoms of molecules at the same z value.

The possible stacking fault mechanism replaces a $P2/b$ bilayer with a $P2/a$ bilayer using a translation of $(a + b)/2$ for one layer relative to the other. This stacking fault option would reduce the scale of $l = 2n + 1$ data relative to that $l = 2n$. Because of the I centring, a translation of $(a + b)/2$ is equivalent to a translation of $c/2$. However, a twinning that superimposes the diffraction patterns of two orientations of the crystal is observed and this is not possible using the stacking fault mechanism. Failure to identify this twinning was the major cause of failure of the previous refinement attempt and not the fact that 'unfortunately the iodine atoms are severely disordered'.[23] It should be appreciated additionally that the subtle disorder actually present mimics the twinning mechanism and is not a distinct structural option in the sense that the frequency of appearance of misaligned layers is greater in the disorder portions of the crystal. However, we would like to emphasise that the refinement is able to treat these two phenomena separately and indeed the identification of both twinning and disorder parameters is essential for meaningful refinement. Such a treatment has been recently reported in the successful refinement of the crystal structure of the Aurivillius phase $Bi_2SrTa_2O_9$.[36]

The differences in contact distances (4.063 and 4.167 Å *vs.* 4.172 and 4.285 Å) are apparently sufficient to minimise disorder in the structure and prevent the reduction of K_2 towards zero, while permitting the observed twinning. If the inherent $\bar{4}2m$ symmetry of the molecule had been aligned perfectly with the lattice, all the distances would have been equal. This alignment would not have altered the space group symmetry but would have altered the apparent symmetry of the density map that corresponds to using only data with l even. It is therefore informative to think of the structure as a modulation of both position and occupancy of a parent structure corresponding to only the $l = 2n$ data. If one regards the occupancy modulation as the primary effect and the displacive modulation as an induced effect then one obtains the observed space group. The occupancy modulation reduces the parent structure symmetry to $I4_1/a$. The rotational displacement maintaining this space group is then induced since the alignment of the molecule symmetry with the lattice is no longer enforced by the space group.

Comparison of the Crystal Structure of **1** *with that of Adamantane*-1,3,5,7-*tetracarboxylic acid*, **2**.—In **1**, the shortest I $\cdots$ I contact distance of 4.063 Å is between centrosymmetrically related molecules of $\bar{4}$ site symmetry at $0, \frac{1}{4}, \frac{1}{8}$ and $1, \frac{3}{4}, -\frac{1}{8}$, a vector of $\boldsymbol{a} + \frac{1}{2}\boldsymbol{b} - \frac{1}{4}\boldsymbol{c}$. The $\bar{4}$ symmetry operation creates a tetrahedrally related vector $-\frac{1}{2}\boldsymbol{a} + \boldsymbol{b} + \frac{1}{4}\boldsymbol{c}$. The sum of these vectors is $\frac{1}{2}\boldsymbol{a}' = \frac{1}{2}\boldsymbol{a} + \frac{3}{2}\boldsymbol{b}$ and the $\bar{4}$ operation acting on this vector creates the vector $\frac{1}{2}\boldsymbol{b}' = -\frac{3}{2}\boldsymbol{a} + \frac{1}{2}\boldsymbol{b}$. The cell $\boldsymbol{a}' = \boldsymbol{a} + 3\boldsymbol{b}$, $\boldsymbol{b}' = -3\boldsymbol{a} + \boldsymbol{b}$, $\boldsymbol{c}' = \boldsymbol{c}$ can then be used to describe a network of molecules connected by the 4.063 Å contact distance and is shown in Fig. 8. The distribution of molecules in this network is exactly the same as in the diamond structure, using eight molecules per F centred cell with a volume ten times that of the $Z = 4$ structure corresponding to $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$. There are thus five interpenetrating networks of close contacting molecules in the structure. This is topologically analogous to the structure of acid **2** described by Ermer.[37] The structure of acid **2** has molecules connected by hydrogen bonds about centres of inversion with no other connections with so strong a bonding. However, Fig. 9 hints that the structure of **1** has an almost equal I $\cdots$ I contact distance of 4.167 Å connecting molecules related by twofold rotation axes. There are four such contacts per molecule and these contacts link molecules at the same Z value (not shown in Fig. 9). The central molecule and the four surrounding molecules each belong to a different one of the five diamond-like substructures. Thus each substructure is connected to each of the other substructures by the symmetry

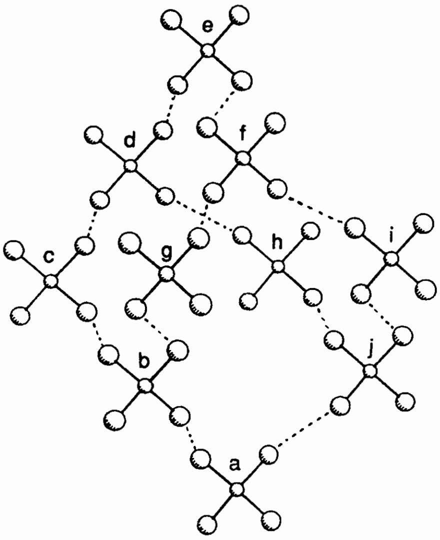


Fig. 8 Schematic drawing of a diamondoid network of molecules of **1**. Compare this with Fig. 6. Only the I atoms and the centroids of the molecules are shown for simplicity. The I ••• I interactions are indicated as dashed lines. The symmetry associated with the molecules a–*j* are as follows: a, x, y, z; b, $\frac{3}{4} - y, -\frac{3}{4} + x, \frac{1}{4} + z$; c, $\frac{3}{2} + x, -\frac{1}{2} + y, \frac{1}{2} + z$; d, $-\frac{5}{4} + y, -\frac{1}{4} - x, \frac{3}{4} + z$; e, $x, y, 1 + z$; f, $\frac{3}{4} + y, \frac{3}{4} - x, \frac{3}{4} + z$; g, $\frac{3}{2} + x, -\frac{1}{2} + y, \frac{1}{2} + z$; h, $-\frac{3}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$; i, $\frac{3}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z$; j, $-\frac{1}{4} - y, \frac{5}{4} + x, \frac{1}{4} + z$.

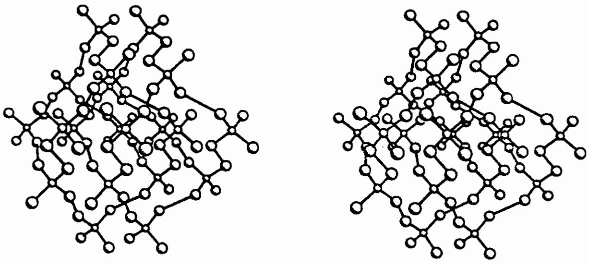


Fig. 9 Two interpenetrating diamondoid networks of **1**. Compare this with Fig. 7. Only two networks are shown for simplicity.

equivalents of this 4.167 Å contact. The contact is facilitated by the rotation of the molecule to align a mirror plane of the inherent $\bar{4}2m$ symmetry of the molecule with the [110] direction rather than the [210] direction as is the case for acid **2**.

Orthonormal crystal coordinates of the I atom from the $\bar{4}$ centre are 2.192, 2.062 and −2.132 Å giving a distance of the I atom from the $\bar{4}$ centre of 3.688 Å. If compound **1** had taken up an idealised structure of five interpenetrating diamond lattices with linear C–I ••• I–C contacts and had the same unit cell volume as the actual structure (presumably the packing coefficient is inherently constant), the axial lengths would then be $a = b = 7.7658$ Å, $c = \sqrt{10}a = 24.558$ Å. For the idealised structure, the vector $\boldsymbol{a} + \frac{1}{2}\boldsymbol{b} - \frac{1}{4}\boldsymbol{c}$ has a magnitude of 10.634 Å, giving a contact distance for I ••• I of 3.258 Å, compared to the actual distance of 4.063 Å. The actual $c{:}a$ ratio in **1** is 3.971 which contrasts with the 2.915 value in acid **2** and $\sqrt{10} = 3.162$ for the idealised structure. The structure has rotated the molecule in the idealised structure and shrunk the a and b axes to facilitate the extra contact while at the same time expanding the c-value in order to lengthen the existing contact. The C–I ••• I angle is 138.4(2)° for the 4.063 Å contact. This compares to 180° for the idealised structure. A similar angle of 144.5(2)° is obtained for C–I ••• I involving the 4.167 Å contact. For the twin plane the C–I ••• I angle involving the 4.172 Å close contact is 134.7(1)°.

Crystal Structure of Compound **1** *and the Nature of X ••• X Interactions.*—The importance of polarisation in the establishment of symmetrical X ••• X interactions is indicated from our CSD studies and also from the crystal structure of the tetraiodo compound, **1**. Statistical analysis has shown that Cl ••• Cl, Br ••• Br and I ••• I interactions are distinct and the contrasting behaviour of the tetrachloro- and tetrabromo-adamantanes (which form plastic crystals) on the one hand and tetraiodo-adamantane (which forms a twinned structure) on the other, confirm this distinction. Curiously, the I ••• I interactions which are strong enough to prevent the formation of a plastic phase of the spherically shaped molecule **1** are not sufficiently strong to produce a fully-ordered structure. The compromise result is an unusual twinned structure with a small disorder component. Yet the geometry of the I ••• I interactions across the twin-boundary is very nearly the optimum geometry seen in the ideal structure and the crystal structure of **1** synthesises beautifully the contrasting dictates of enthalpy and entropy. That polarisation effects are enhanced in unsymmetrical X ••• X interactions is clearly seen from CSD studies and such interactions are surely of greater structural significance than the symmetrical ones because difluorodiiodo- and trifluoroiodo-adamantane are fully ordered in contrast to compound **1**.

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