

Isostructurality, Polymorphism and Mechanical Properties of Some Hexahalogenated Benzenes: The Nature of Halogen...Halogen Interactions

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Abstract: The nature of intermolecular interactions between halogen atoms, $X\cdots X$ ($X = \text{Cl}, \text{Br}, \text{I}$), continues to be of topical interest because these interactions may be used as design elements in crystal engineering. Hexahalogenated benzenes (C_6Cl_6 , C_6Br_6 , C_6I_6) crystallise in two main packing modes, which take the monoclinic space group $P2_1/n$ and the triclinic space group $P\bar{1}$. The former, which is isostructural to C_6Cl_6 , is more common. For molecules that lack inversion symmetry, adoption of this monoclinic structure would necessarily lead to crystallographic disorder. In C_6Cl_6 , the planar molecules form $\text{Cl}\cdots\text{Cl}$ contacts and also $\pi\cdots\pi$ stacking interactions. When crystals of C_6Cl_6 are compressed mechanically along their needle length, that is, [010], a bending deformation takes place, because of the stronger interactions in the stacking direction. Further compression propagates con-

secutively in a snakelike motion through the crystal, similar to what has been suggested for the motion of dislocations. The bending of C_6Cl_6 crystals is related to the weakness of the $\text{Cl}\cdots\text{Cl}$ interactions compared with the stronger $\pi\cdots\pi$ stacking interactions. The triclinic packing is less common and is restricted to molecules that have a symmetrical (1,3,5- and 2,4,6-) halogen substitution pattern. This packing type is characterised by specific, polarisation-induced $X\cdots X$ interactions that result in threefold-symmetrical X_3 synthons, especially when $X = \text{I}$; this leads to a layered pseudohexagonal structure in which successive planar layers are inversion related and stacked so that

bumps in one layer fit into the hollows of the next in a space-filling manner. The triclinic crystals shear on application of a mechanical stress only along the plane of deformation. This shearing arises from the sliding of layers against one another. Nonspecificity of the weak interlayer interactions here is demonstrated by the structure of twinned crystals of these compounds. One of the compounds studied (1,3,5-tribromo-2,4,6-triiodobenzene) is dimorphic, adopting both the monoclinic and triclinic structures, and the reasons for polymorphism are suggested. To summarise, both chemical and geometrical models need to be considered for $X\cdots X$ interactions in hexahalogenated benzenes. The $X\cdots X$ interactions in the monoclinic group are nonspecific, whereas in the triclinic group some $X\cdots X$ interactions are anisotropic, chemically specific and crystal-structure directing.

Keywords: crystal engineering • crystal plasticity • halogens • intermolecular interactions • supramolecular synthons

Introduction

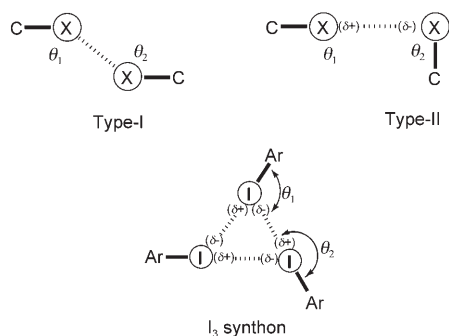
It has long been noted that recognition between molecules during crystallisation is governed by geometrical or chemical factors, that is, because of shape complementarity and size compatibility (short-range repulsion),^[1,2] or specific anisotropic interactions of electrostatic or polarisation origin (long-range attraction).^[3,4] In the process of minimisation of the total free energy, a balance between these geometrical and chemical factors is reached.^[5] But, where exactly does this balance lie? Do atoms approach one another more because of a need for a good geometrical fit or because of particular chemical effects?^[6] This question is especially difficult to answer for $\text{C}-\text{X}\cdots\text{X}-\text{C}$ interactions ($X = \text{Cl}, \text{Br}, \text{I}$)^[7] in crystals because they seem to be of two types based on the values of the two $\text{C}-\text{X}\cdots\text{X}$ angles, θ_1 and θ_2 .^[7b,e] The

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type-I interactions ($\theta_1 \approx \theta_2$) represent close packing of X atoms in a geometrical model because identical portions of the halogen atoms make the nearest approach. The type-II interactions ($\theta_1 \approx 180^\circ$, $\theta_2 \approx 90^\circ$) are understood on the basis of X-atom polarisation, $X^{(\delta+)} \cdots X^{(\delta-)}$, and represent a chemical model with each halogen atom polarised positively in the polar region and negatively in the equatorial region (Scheme 1). Type-II interactions are included in a larger category of $X^{(\delta+)} \cdots Y^{(\delta-)}$ “halogen bonds”, so termed because an electrophilic halogen is involved.^[8]



Scheme 1.

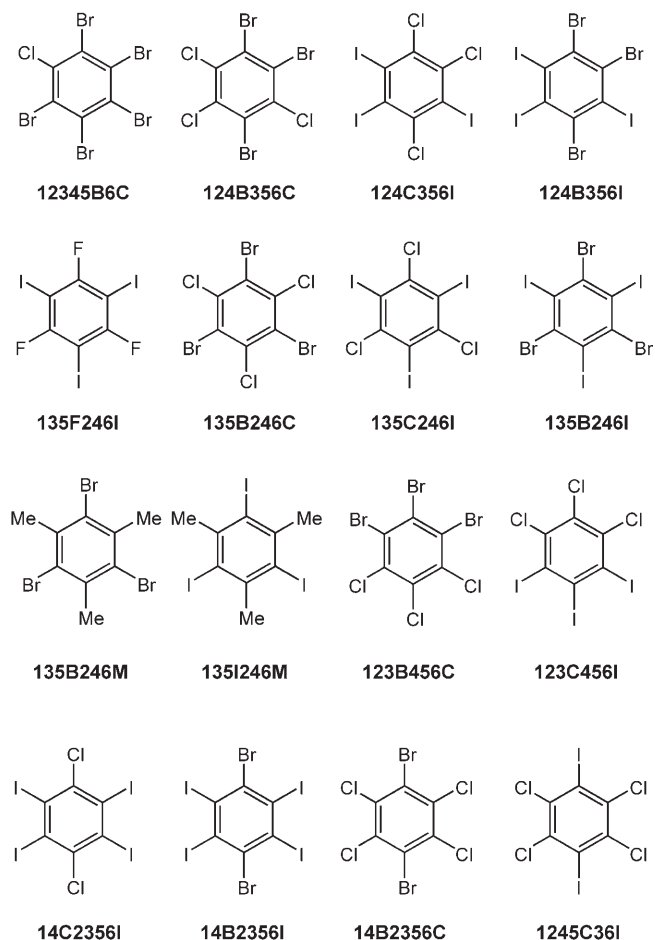
Difficulties in understanding the nature of $X \cdots X$ interactions also arise from the fact that the halogens are of low to high electronegativity (I to F) and polarisability (F to I). They act, depending on the circumstances, as either electro-positive or electronegative entities in an intermolecular interaction, or in some cases with no particular electrostatic character.^[9] Iodine is somewhat easier to understand in the context of halogen bonding when compared to the other halogens because it is more readily polarised as $I^{(\delta+)}$. Accordingly, contacts such as $I \cdots Cl$ and $I \cdots Br$ may be represented as $I^{(\delta+)} \cdots Cl^{(\delta-)}$ and $I^{(\delta+)} \cdots Br^{(\delta-)}$ and they generally have the type-II geometry. Fluorine is very hard and nonpolarisable, and it is still not really possible to deduce the nature of its interactions with other halogens;^[10] we have stated elsewhere that the $F \cdots F$ interaction is not really viable.^[11] Perhaps the $I \cdots F$ interaction is polarisation induced. Chlorine and bromine belong to an intermediate region and various researchers, subscribing to one of the two models given above, have attributed the observed geometries of $X \cdots X$ contacts to either a van der Waals (nonspherical atoms) or polarisation ($\delta^+ \cdots \delta^-$) character of the interaction.^[7] What is possible is that the type-I contacts formed by Cl and Br are of the van der Waals variety whereas the type-II contacts are polarisation induced. If all contacts in a crystal were of the van der Waals type, one would expect a greater degree of isotropy in the packing—a Kitaigorodskii solid.^[1] As the intermolecular contacts acquire some distinctiveness, anisotropy enters the crystal with a change in properties.^[4] In a one-dimensional structure involving halogen atoms, molecules are held relatively strongly in this one direction.^[12] In a layered or two-dimensional crystal structure, the interactions within a layer (intralayer) are stronger and more directional than the interactions between layers (interlayer).^[13]

Whether these layered structures arise on account of type-II halogen interactions or the ubiquitous $\pi \cdots \pi$ stacking interactions^[14] is hard to say. However, there is a fundamental distinction between stacked (two-dimensional) and cross-linked (three-dimensional, Kitaigorodskii type) structures with respect to the nature of the intermolecular interactions. We maintain that the default packing for all organic molecular solids is the three-dimensional Kitaigorodskii packing. Therefore when a stacked structure is obtained, there must be specific reasons for its formation.^[4]

In this paper, we report the structural chemistry and some mechanical properties^[15] in a series of hexahalogenated benzenes. Our measurements on these crystals enable us to identify geometrical and chemical features of $X \cdots X$ interactions. We show that for a realistic description of these crystals, both chemical and geometrical factors need to be considered.

Results and Discussion

The monoclinic structure type—Hexachlorobenzene: We examined 16 hexahalogenated benzenes C_6X_6 ($X = Cl, Br, I$) in this study (Scheme 2) and also some of their mixed crystals.^[16] These compounds adopt two broad packing modes, triclinic and monoclinic (Table 1). The monoclinic forms are



Scheme 2.

Table 1. Crystallographic data and structure refinement parameters.

	C ₆ Br ₆	C ₆ Cl ₆	124B356I	124C356I	124B356C	123B456C
formula	C ₆ Br ₆	C ₆ Cl ₆	C ₆ Br ₃ I ₃	C ₆ Cl ₃ I ₃	C ₆ Br ₃ Cl ₃	C ₆ Br ₃ Cl ₃
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	8.3262(16)	7.967(3)	8.5007(6)	8.7025(7)	8.1454(8)	8.2578(17)
<i>b</i> [Å]	3.9491(8)	3.7609(14)	4.0812(3)	4.1087(3)	3.8704(4)	3.9429(8)
<i>c</i> [Å]	15.271(3)	14.670(5)	15.6911(10)	15.0989(12)	15.0160(15)	15.137(3)
α [°]	90	90	90	90	90	90
β [°]	92.929(3)	92.459(6)	92.6560(10)	93.5890(10)	92.385(2)	92.34(3)
γ [°]	90	90	90	90	90	90
<i>V</i> [Å ³]	501.46(17)	439.2(3)	543.79(7)	538.82(7)	472.98(8)	492.46(17)
<i>Z</i>	2	2	2	2	2	2
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	3.653	2.153	4.229	3.446	2.936	2.82
<i>F</i> [000]	492	276	600	492	384	384
μ [mm ⁻¹]	23.957	1.884	19.588	9.388	13.575	13.038
θ [°]	2.73–26.07	2.78–26.03	2.67–26.07	2.63–26.03	2.72–26.03	2.69–28.13
index ranges	–10 ≤ <i>h</i> ≤ 10 –4 ≤ <i>k</i> ≤ 4 –16 ≤ <i>l</i> ≤ 18	–9 ≤ <i>h</i> ≤ 9 –4 ≤ <i>k</i> ≤ 4 –18 ≤ <i>l</i> ≤ 18	–10 ≤ <i>h</i> ≤ 10 –4 ≤ <i>k</i> ≤ 5 –19 ≤ <i>l</i> ≤ 19	–10 ≤ <i>h</i> ≤ 10 –5 ≤ <i>k</i> ≤ 4 –18 ≤ <i>l</i> ≤ 18	–10 ≤ <i>h</i> ≤ 10 –4 ≤ <i>k</i> ≤ 4 –16 ≤ <i>l</i> ≤ 18	–10 ≤ <i>h</i> ≤ 10 –4 ≤ <i>k</i> ≤ 4 –19 ≤ <i>l</i> ≤ 9
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)	100(2)	293(2)
<i>R</i> ₁	0.0218	0.0449	0.0199	0.0195	0.0162	0.0765
<i>wR</i> ₂	0.0519	0.1097	0.0492	0.0469	0.0397	0.1994
<i>R</i> _{merge}	0.0317	0.0317	0.0253	0.0159	0.0301	0.0759
parameters	56	55	68	68	67	73
GOF	1.098	1.15	1.093	1.105	1.09	1.013
reflns total	4469	3112	5470	4377	6318	2542
unique reflns	986	861	1059	1051	923	1075
obsd reflns	913	812	1015	1033	880	822
CCDC ^[a]	257165	257166	281004	280886	280885	280883
	123C456I	14C2356I	14B2356I	14B2356C	1245C36I-M1	1245C36I-M2
formula	C ₆ Cl ₃ I ₃	C ₆ Cl ₂ I ₄	C ₆ Br ₂ I ₄	C ₆ Br ₂ Cl ₄	C ₆ Cl ₄ I ₂	C ₆ Cl ₄ I ₂
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	8.720(4)	8.7829(19)	9.3109(19)	8.0578(6)	8.6484(6)	6.5276(6)
<i>b</i> [Å]	4.1170(19)	4.2989(9)	4.2609(9)	3.8484(3)	4.1259(3)	5.9682(5)
<i>c</i> [Å]	15.582(7)	15.320(3)	14.776(3)	14.9122(11)	15.7424(11)	13.3913(11)
α [°]	90	90	90	90	90	90
β [°]	92.667(7)	94.908(4)	93.33(3)	92.1900(10)	92.1300(10)	98.7720(10)
γ [°]	90	90	90	90	90	90
<i>V</i> [Å ³]	558.8(4)	576.3(2)	585.2(2)	462.08(6)	561.34(7)	515.60(8)
<i>Z</i>	2	2	2	2	2	2
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	3.323	3.749	4.197	2.686	2.767	3.012
<i>F</i> [000]	492	564	636	348	420	420
μ [mm ⁻¹]	9.053	11.225	17.426	9.86	6.499	7.076
θ [°]	2.73–25.97	2.58–27	2.52–29.06	2.73–26.20	2.59–26.01	3.08–26.03
index ranges	–7 ≤ <i>h</i> ≤ 10 –5 ≤ <i>k</i> ≤ 5 –19 ≤ <i>l</i> ≤ 19	–6 ≤ <i>h</i> ≤ 11 –5 ≤ <i>k</i> ≤ 5 –19 ≤ <i>l</i> ≤ 19	–12 ≤ <i>h</i> ≤ 12 0 ≤ <i>k</i> ≤ 5 –19 ≤ <i>l</i> ≤ 19	–9 ≤ <i>h</i> ≤ 9 –4 ≤ <i>k</i> ≤ 4 –17 ≤ <i>l</i> ≤ 18	–10 ≤ <i>h</i> ≤ 10 –5 ≤ <i>k</i> ≤ 5 –19 ≤ <i>l</i> ≤ 16	–8 ≤ <i>h</i> ≤ 8 –7 ≤ <i>k</i> ≤ 7 –16 ≤ <i>l</i> ≤ 16
<i>T</i> [K]	293(2)	293(2)	293(2)	100(2)	100(2)	100(2)
<i>R</i> ₁	0.0536	0.0397	0.0401	0.0147	0.034	0.0136
<i>wR</i> ₂	0.1512	0.1055	0.1031	0.037	0.0866	0.0324
<i>R</i> _{merge}	0.0721	0.0662	0.0462	0.0183	0.0204	0.0220
parameters	74	56	41	68	59	56
GOF	1.108	1.099	1.084	1.092	1.09	1.105
reflns total	2733	2977	2676	5435	5638	9332
unique reflns	1079	1243	1340	919	1089	1007
obsd reflns	946	1168	1142	896	1012	1000
CCDC ^[a]	280884	280882	280881	280880	280892	280893
	12345B6C	135B246C	135C246I	135B246I-T	135B246I-M1	135B246I-M2
formula	C ₆ Br ₃ Cl	C ₆ Br ₃ Cl ₃	C ₆ Cl ₃ I ₃	C ₆ Br ₃ I ₃	C ₆ Br ₃ I ₃	C ₆ Br ₃ I ₃
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	8.2742(14)	8.1859(9)	7.7131(11)	7.9452(3)	8.5045(16)	9.3129(50)

Table 1. (Continued)

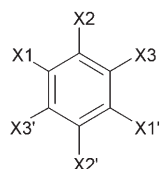
	12345B6C	135B246C	135C246I	135B246I-T	135B246I-M1	135B246I-M2
<i>b</i> [Å]	3.9205(7)	3.8619(4)	9.4269(13)	9.4962(4)	4.0444(8)	4.1977(20)
<i>c</i> [Å]	15.196(3)	15.0355(16)	9.4299(18)	9.5119(6)	15.608(3)	14.7054(80)
α [°]	90	90	60.213(2)	60.1370(10)	90	90
β [°]	92.729(2)	92.766(2)	66.116(3)	66.202(2)	92.842(3)	93.296(6)
γ [°]	90	90	85.575(2)	85.5120(10)	90	90
<i>V</i> [Å ³]	492.39(15)	474.77(9)	537.43(15)	562.61(5)	536.17(18)	573.9(5)
<i>Z</i>	2	2	2	2	2	2
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	3.42	2.925	3.455	4.088	4.289	4.007
<i>F</i> [000]	465	384	492	600	600	600
μ [mm ⁻¹]	20.613	13.524	9.413	18.933	19.866	18.56
θ [°]	2.68–26.04	2.78–26.01	2.52–26.01	2.50–26.00	2.61–26.03	2.52–26.02
index ranges	–10 ≤ <i>h</i> ≤ 10 –4 ≤ <i>k</i> ≤ 4 –18 ≤ <i>l</i> ≤ 16	–10 ≤ <i>h</i> ≤ 10 –4 ≤ <i>k</i> ≤ 4 –18 ≤ <i>l</i> ≤ 18	–9 ≤ <i>h</i> ≤ 9 –11 ≤ <i>k</i> ≤ 11 –11 ≤ <i>l</i> ≤ 11	–9 ≤ <i>h</i> ≤ 9 –11 ≤ <i>k</i> ≤ 11 –11 ≤ <i>l</i> ≤ 11	–10 ≤ <i>h</i> ≤ 9 –4 ≤ <i>k</i> ≤ 4 –19 ≤ <i>l</i> ≤ 19	–4 ≤ <i>h</i> ≤ 11 –5 ≤ <i>k</i> ≤ 5 –14 ≤ <i>l</i> ≤ 15
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
<i>R</i> ₁	0.0209	0.0172	0.0284	0.0213	0.0242	0.1455
<i>wR</i> ₂	0.0504	0.0409	0.0754	0.0528	0.0687	0.3945
<i>R</i> _{merge}	0.0319	0.0273	0.0315	0.0297	0.0256	0.1369
parameters	67	56	110	110	55	25
GOF	1.051	1.091	1.224	1.102	1.107	1.697
reflns total	4060	4781	7213	8971	5041	1470
unique reflns	965	932	2116	2195	1049	1000
obsd reflns	904	891	2091	2104	993	912
CCDC ^[a]	280894	257163	257164	257162	257161	280887

	135F246I	135C246I:135B246I	135B246I:135I246M	135C246I:135B246M	135C246I:135I246M
formula	C ₆ F ₃ I ₃	0.863(C ₆ Cl ₃ I ₃) 1.137(C ₆ Br ₃ I ₃)	0.922(C ₆ Br ₃ I ₃) 1.078(C ₉ H ₉ I ₃)	0.154(C ₆ Cl ₃ I ₃) 1.846(C ₉ H ₉ Br ₃)	0.154(C ₆ Cl ₃ I ₃) 1.846(C ₉ H ₉ I ₃)
crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	13.937(4)	7.8534(8)	7.9146(5)	7.6549(9)	7.8342(8)
<i>b</i> [Å]	4.7919(15)	9.4683(9)	9.5156(6)	9.0787(10)	9.4966(10)
<i>c</i> [Å]	15.488(5)	9.4810(9)	9.5282(6)	9.1025(10)	9.5031(10)
α [°]	90	60.1420(10)	60.1830(10)	60.0510(10)	60.2820(10)
β [°]	107.486(3)	66.2530(10)	66.6090(10)	67.6180(10)	66.7010(10)
γ [°]	90	85.656(2)	85.9680(10)	85.0940(10)	86.2450(10)
<i>V</i> [Å ³]	986.6(5)	552.69(9)	564.10(6)	502.49(10)	556.34(10)
<i>Z</i>	4	1	1	1	1
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	3.432	3.814	3.458	2.461	3.12
<i>F</i> [000]	888	553	516	348	463
μ [mm ⁻¹]	9.493	14.887	13.147	11.837	8.666
θ [°]	1.73–26.03	2.51–26.04	2.50–26.03	2.61–26.04	2.50–26.12
index ranges	–17 ≤ <i>h</i> ≤ 15 –5 ≤ <i>k</i> ≤ 5 –19 ≤ <i>l</i> ≤ 18	–9 ≤ <i>h</i> ≤ 9 –11 ≤ <i>k</i> ≤ 11 –11 ≤ <i>l</i> ≤ 10	–9 ≤ <i>h</i> ≤ 9 –11 ≤ <i>k</i> ≤ 10 –11 ≤ <i>l</i> ≤ 11	–9 ≤ <i>h</i> ≤ 9 –11 ≤ <i>k</i> ≤ 11 –11 ≤ <i>l</i> ≤ 11	–9 ≤ <i>h</i> ≤ 9 –11 ≤ <i>k</i> ≤ 11 –11 ≤ <i>l</i> ≤ 11
<i>T</i> [K]	298(2)	100(2)	100(2)	100(2)	100(2)
<i>R</i> ₁	0.0317	0.0244	0.0173	0.0208	0.0177
<i>wR</i> ₂	0.0799	0.0641	0.041	0.0518	0.0433
<i>R</i> _{merge}	0.0241	0.0283	0.0152	0.0242	0.0167
parameters	109	120	123	131	123
GOF	1.049	1.175	1.134	1.028	1.175
reflns total	5283	7021	6198	7763	7617
unique reflns	1923	2178	2216	1991	2211
obsd reflns	1642	2127	2150	1821	2178
CCDC ^[a]	261303	280889	280888	280890	280891

[a] Deposition number.

dominant among the compounds we studied and one of these, as exemplified by the classical hexachlorobenzene structure, was found to be especially common.^[17,18] The unit cell of C₆Cl₆ at 100 K has the dimensions *a* = 7.967(3), *b* = 3.7609(14), *c* = 14.670(5) Å and β = 92.459(6)°. The space group is *P*2₁/*n*, with two molecules in the unit cell. The mol-

ecule lies on an inversion centre in the crystal. For molecules that lack inversion symmetry (**12345B6C**, **124B356C**, **124C356I**, **124B356I**, **135B246C**, **123B456C**, **123C456I**), adoption of this structure would lead to crystallographic disorder. Accordingly, there are three distinct sites for the halogen atoms, which we refer to as X1, X2 and X3



Scheme 3.

(Scheme 3). The planar molecules form $\pi\cdots\pi$ stacks; within these stacks the molecules are 3.44 Å apart (perpendicular distance) and tilted 63.3° to the stack direction so that $\pi\cdots\pi$ interactions are optimised (Figure 1a). The rest of the structure is close-packed in the usual way. There are two categories of Cl $\cdots$ Cl interaction in the overall distance range of 3.44–3.67 Å. The type-I contacts at

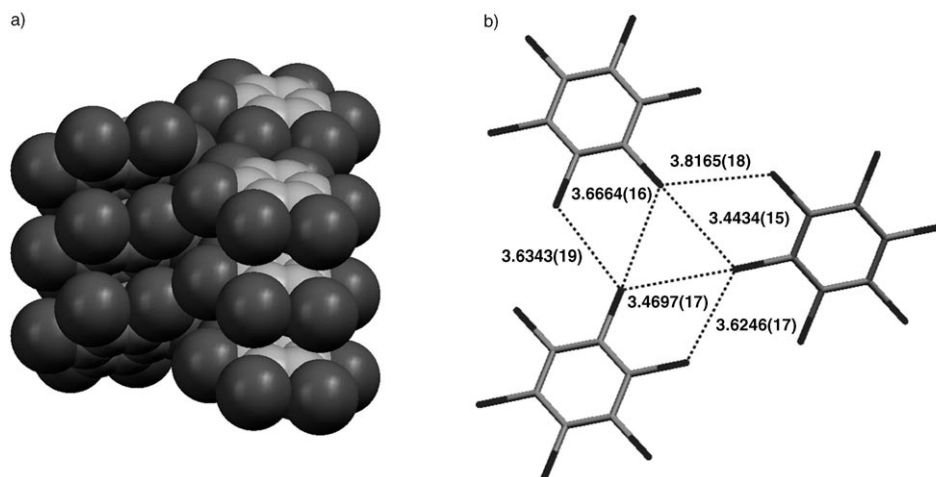


Figure 1. Monoclinic form for hexahalogenated benzenes: a) corrugated layer in C_6Cl_6 ; b) Cl $\cdots$ Cl distances [Å] between stacks in C_6Cl_6 . Cl atoms are shown in dark grey and C atoms in light grey.

sites X1, X2 and X3 (only the last lies on an inversion centre) have Cl $\cdots$ Cl distances of 3.8165(18) (107.48(13)°), 3.6246(17) (119.52(13)°) and 3.6343(19) Å (124.51(13)°) and are unremarkable. The second category does not appear to be type-I and the distances are nominally shorter (3.4434(15) Å, 175.05(15)°, 116.79(13)°; 3.4697(17) Å, 174.56(13)°, 124.47(13)°; 3.6664(16) Å, 171.25(13)°, 123.18(13)°) but the smaller angle (θ_2) is not so close to 90°, which would be more characteristic of type-II (Figure 1b). No Cl $\cdots$ Cl interaction appears to be particularly important and $\pi\cdots\pi$ stacking dominates this packing as it also does in the isostructural C_6Br_6 and C_6I_6 .^[19,20] Not surprisingly, the unit-cell volume increases uniformly in these three structures with the size of the halogen substituent (C_6Cl_6 : 439.2(3) Å³ at 100 K; C_6Br_6 : 501.46(17) Å³ at 100 K; C_6I_6 : 618.642 Å³ at 298 K).

We found that when crystals of C_6Cl_6 (m.p. 500 K) are compressed along the needle length, that is, [010], a bending deformation occurs (Figure 2), which on further compression propagates continuously in a consecutive motion through the crystal (Figure 3). Although the typical organic crystal is not mechanically robust and is susceptible to bending or breakage on application of stress, and crystallographers have surely noted crystals with unusually deformed morphologies over the years, we are unaware of any system-

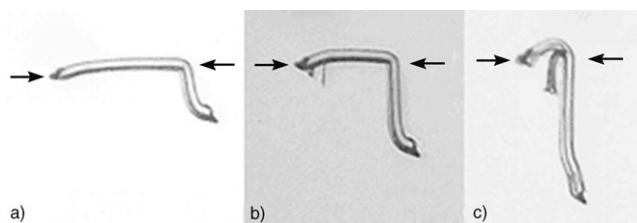


Figure 2. Hexachlorobenzene: a), b) and c) show the propagation of the bend through the crystal on continuous stress application. Arrows show the point and direction of the stress applied.

atic study that has attempted to correlate these mechanical properties with crystal structure and more particularly with the nature of the intermolecular interactions contained therein.^[21] Along these lines, we have recently reported a structural model for the bending of organic crystals.^[22] In this paper, we wish to use this model to correlate the bending of C_6Cl_6 crystals with the nature of their Cl $\cdots$ Cl interactions (Figure 4).

When a crystal with flat external faces bends, two parallel opposite faces become curved. We define these as the bending

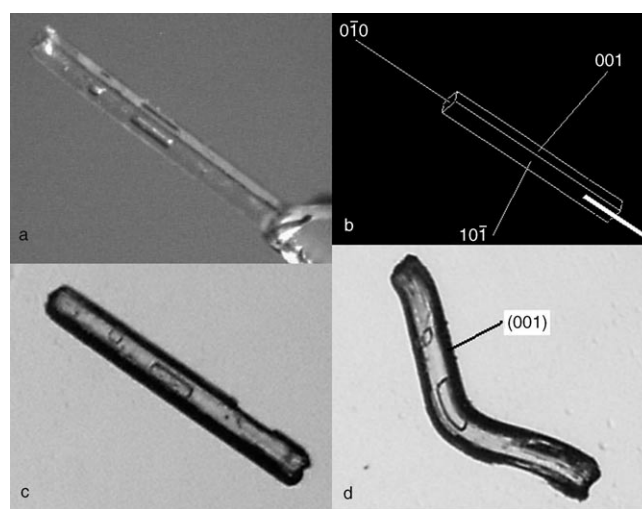


Figure 3. Hexachlorobenzene: a) crystal as mounted for face indexing; b) SMART face indexing graphic; c) same crystal before bending; d) crystal bent on (001) face. The occlusion on the crystal surface has no specific role in its mechanical properties.

faces and the crystal bends when it is subject to a mechanical stress perpendicular to this pair of opposite faces. Plastic bending (no volume change) occurs under compression

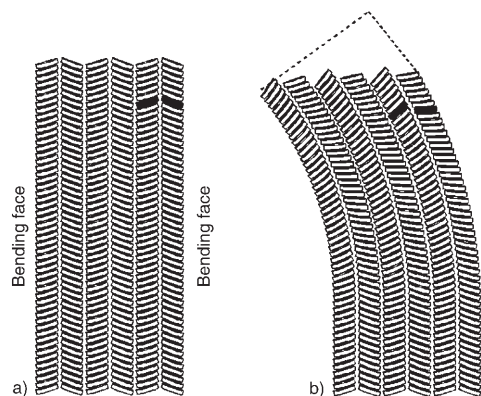


Figure 4. A model for bending (half-sectional view): a) undeformed crystal (the spaces between stacks represent the weakest interactions); b) bent crystal (note the pronounced deformation in some of the interfacial angles).

when the structure is constituted of layers parallel to the bending faces.^[23] In other words, for bending to take place there must be a strong type of interaction in one direction and only weak interactions in a perpendicular direction normal to the bending faces.^[22] So, bending occurs in the direction of the weak interaction as shown in Figure 4. This figure also shows that there can be significant changes in the interfacial angles upon bending. Whether this involves breaking and making of intermolecular interactions, or rotation coupled with sliding between molecules, or whether some other processes are at work is being currently explored. As strong interactions are often associated with faster crystal growth, interaction anisotropy is also accompanied by morphology anisotropy. Therefore many crystals that bend are also needle shaped and C_6Cl_6 is no exception.

The direction of bending shows that the strong interaction in C_6Cl_6 is the $\pi\cdots\pi$ stacking. The fact that the crystal bends on (001) suggests that the $Cl\cdots Cl$ contacts that emerge from this face are weaker. Are these contacts type-I or type-II? Ideal type-I and type-II geometries are distinctive but these $Cl\cdots Cl$ geometries in C_6Cl_6 (3.4434(15) Å, 175.05(15)°, 116.79(13)°; 3.4697(17) Å, 174.56(13)°, 124.47(13)°) are intermediate and difficult to classify. The results on crystal bending indicate, however, that these $Cl\cdots Cl$ interactions are weak and nonspecific. They are easily deformed as the stacks of molecules slide against each other during bending. Distance and angle criteria are particularly poor indicators of the nature of $Cl\cdots Cl$ interactions especially when the geometry is ambiguous and does not correspond strictly to type-I or type-II. For a type-I interaction that lies on an inversion centre, a decrease in the distance to below the van der Waals separation would be repulsive. For a type-II geometry, however, such a decrease might be moderately attractive. By merely inspecting the crystal structure of C_6Cl_6 and noting the $Cl\cdots Cl$ distances and $C-Cl\cdots Cl$ angles, it would be very difficult to ascribe any particular chemical character to these quasi type-II interactions. In contrast, the bending results show that these interactions are weak and of low importance in the packing. To summarise, terminologies

like type-I and type-II might permit some sort of classification but they cannot be used to draw definitive chemical inferences about the nature of the respective intermolecular interactions.

The feeble nature of the $Cl\cdots Cl$ interactions in C_6Cl_6 is further indicated by the variation in the shape of the bent specimens as a function of the mode of the applied force. Figure 5a results from a compressive force applied at both

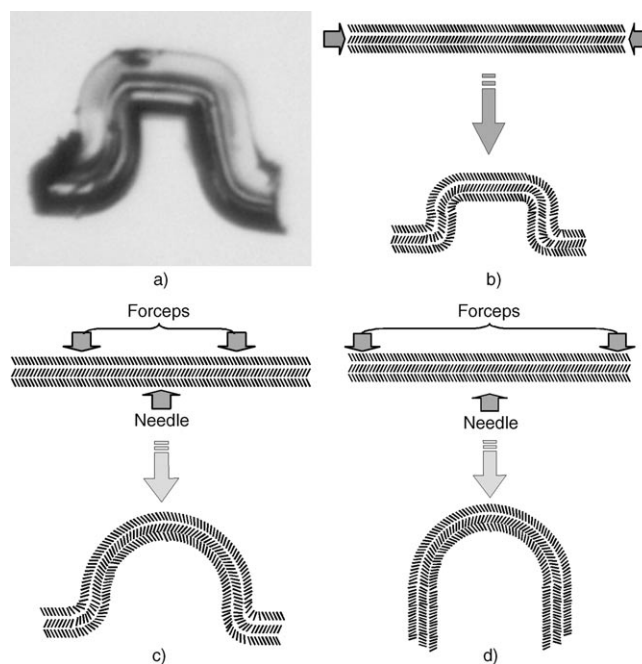


Figure 5. Bending of normal crystal into different shapes. a) A crystal of C_6Cl_6 bent in four regions by a compressive force applied at both ends, parallel to the longitudinal axis. b) Schematic depiction of the process described in (a). c) Bending into an Ω shape. The two bends in the flat portion of the crystal occurred without additional anchoring—the forceps' tips were enough. d) Bending into an n shape by changing the points of anchoring. Arrows indicate the point and direction of force applied.

ends, parallel to the longitudinal axis. Figure 5b shows the situation when the crystal volume remains unchanged as in plastic bending, if care is taken to prevent buckling.^[24a] We also subjected the crystal to three-point bending to obtain a bent shape, the schematic of which is shown in Figure 5c.^[24] The cartoon depictions in Figure 5 show that the sliding of molecules past each other is very easy, and that the internal stresses between molecules in the stacks are dissipated with these kinds of deformation. Again, the conclusion is clear enough: interactions between halogen atoms between stacks are weaker and/or less specific than the $\pi\cdots\pi$ interactions within a stack.

The bending experiments on C_6Cl_6 crystals were also carried out by using a nanoindenter. The crystal was placed on a small iron washer, which had a hole in the middle, and with the bending face (001) upwards, as shown in Figure 6a. The middle part of the crystal was unsupported. The indenter tip was used to press the crystal in the middle portion by

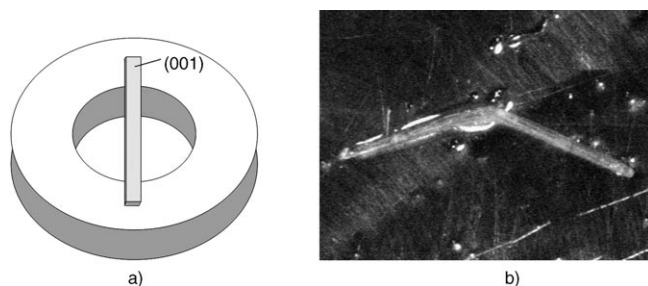


Figure 6. Bending of C_6Cl_6 crystal by using a nanoindenter tip. a) Schematic depiction of crystal as mounted on sample holder. b) Crystal after bending.

applying a load of 10 g (a force of 98 mN). The direction of the indenter movement was [001] with a constant rate of indenter tip displacement. The crystal underwent deformation as shown in Figure 6b. Two crystals that were used in this experiment had almost the same thickness (0.3 mm) and the displacement (measured by using a graduated optical microscope) was approximately 1 mm for both. Notably, when a crystal of C_6Cl_6 was placed on the washer with the (100) face pointing upwards, indentation led to immediate breakage. This reveals the strongly anisotropic nature of the plastic bending present/inherent in these molecular crystals.

The isostructural C_6Br_6 did not bend and this appeared, initially, to be counterintuitive. However, by using the well-known idea that the correct way of comparing the mechanical response of materials is in terms of similar/identical homologous temperature^[24] (equal to T/T_m in which T is the temperature of deformation and T_m is the melting temperature), we repeated the bending experiment at 403 K. Bending took place, as it did for C_6Cl_6 at room temperature (300 K). The higher melting point of C_6Br_6 relative to C_6Cl_6 is surely of enthalpic origin because the entropic change upon melting is expected to be very similar for both compounds. Accordingly, we may conclude that the $Br\cdots Br$ interactions are stronger than the $Cl\cdots Cl$ interactions in these compounds, and this is not incompatible with their dispersive nature.

The 1,2,4-trisubstituted compounds **124B356C**, **124B356I** and **124C356I** also have the same monoclinic structure. These molecules lie on the inversion centre and as mentioned above, they must be disordered. However, the disorder is not statistical over the three positions; the site occupancy factors for Br at X1/X2/X3 are 0.76/0.34/0.40 in **124B356C**, for I in **124B356I** they are 0.76/0.35/0.39 and for I in **124C356I** they are 0.82/0.64/0.04. All three structures prefer to have the biggest atom in the X1-position where it can avoid a type-I contact with itself. There is a big increase in cell volume going from **124B356C** (473 Å³) to **124C356I** (539 Å³) whereas the exchange of Cl by Br in **124B356I** (544 Å³) has only a small effect on the volume. This is unlike the uniform volume increases in C_6Cl_6 , C_6Br_6 and C_6I_6 and shows that in the 1,2,4-trisubstituted compounds the biggest substituent determines the cell volume. A fully statistical disorder would perhaps lead to more uniform cell

volume increments on going from **124B356C** to **124C356I** to **124B356I**. Perhaps these structures have ordered domains of I atom clusters that cannot be resolved in the X-ray experiment. The 1,2,3-trisubstituted compounds also give the same monoclinic structure but the two disordered orientations in **123B456C** and **123C456I** are equally occupied as shown in Figure 7. This type of disorder could be linked to the molecular shape.^[25]

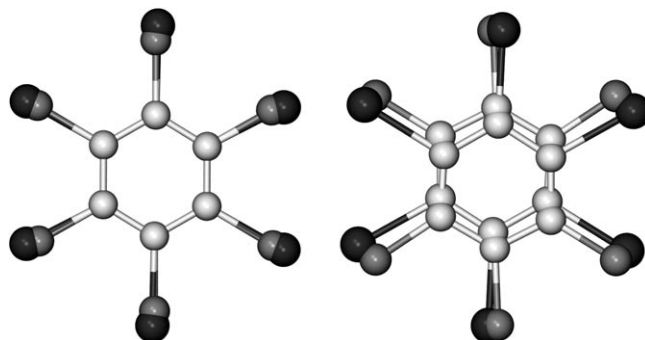


Figure 7. Disorder in the monoclinic structures **124C356I** (left) and **123C456I** (right). Notice the differences in the relative positions of halogen atoms and ring C atoms in the two cases. The heavier atoms are shown darker in colour than the lighter atoms.

The 1,4-disubstituted compounds **14B2356C**, **14C2356I**, **14B2356I** and **1245C36I** show a slightly different behaviour. The first is isostructural to C_6Cl_6 and (although the molecule has C_i symmetry) is disordered like the 1,2,4-trisubstituted compounds.^[26] The second and the third take a variant of the C_6Cl_6 structure but they are ordered (Figure 8). The

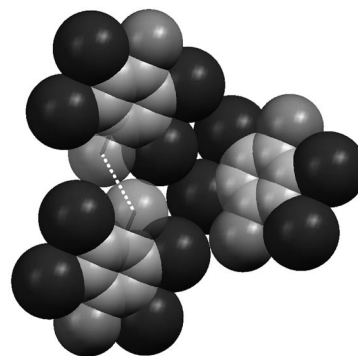


Figure 8. Ordered structure of 1,4-dichloro-2,3,5,6-tetraiodobenzene (**14C2356I**). Notice the type-I $Cl\cdots Cl$ interaction.

reader will note that the Cl (or Br) and I positions might well have been disordered in this packing, but they are not. The reason for the ordering is suggested by the fact that the $Cl\cdots Cl$ (or $Br\cdots Br$) interaction is exclusively type-I whereas the $I\cdots I$ interactions are both type-I and quasi type-II. So, even among these marginal $X\cdots X$ contacts, there seems then to be some preference for the $Cl\cdots Cl$ (or $Br\cdots Br$) interactions to be more dispersive than the other interactions.

There is just a hint therefore that Cl (or Br) and I are chemically distinguishable in these two structures.^[27] **1245C36I**, however, has two polymorphs. For the first, which occurs as needles, only a cell could be found that matches C_6Cl_6 (8.6484(6), 4.1259(3), 15.7424(11) Å; 90, 92.1300(10), 90°) but the structure could not be solved adequately. The second crystallised from CCl_4 as monoclinic rhombs with cell dimensions of $a=6.5276(6)$, $b=5.9682(5)$, $c=13.3913(11)$ Å and $\beta=98.7720(10)^\circ$. The packing is not dominated by $\pi\cdots\pi$ stacks; rather there is a herringbone arrangement of molecules to form a zig-zag chain of type-II $I\cdots I$ interactions (3.8957(3) Å, 170.52(6)°, 79.48(6)°; Figure 9). In this respect, **1245C36I-M2** is more reminiscent

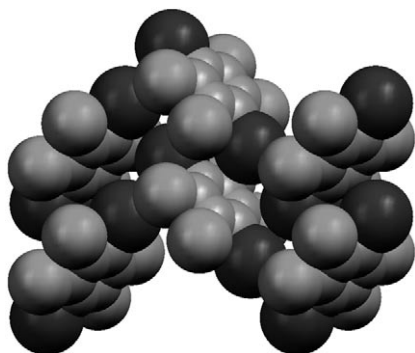


Figure 9. 1,2,4,5-Tetrachloro-3,6-diiodobenzene (**1245C36I**). Notice the herringbone arrangement of molecules to form a zig-zag chain of type-II $I\cdots I$ interactions.

of 1,4-diiodobenzene rather than any of the other hexahalo-substituted benzenes. Unfortunately, crystals of these four 1,4-disubstituted compounds were very small and detailed bending experiments could not be performed on them.^[28] Still, there is an indication here that the introduction of iodine causes some structural perturbation.

The question now arises as to why C_6Cl_6 , C_6Br_6 , C_6I_6 and the above-mentioned mixed hexahalogenated benzenes adopt the same monoclinic structure. When molecules that are of the same shape and size adopt the same crystal structure, geometrical factors are presumed to operate.^[29] When molecules of different sizes and shapes adopt the same crystal packing, chemical factors are supposedly more dominant. However, these generalisations are not very helpful here. Although Cl (18.1 Å³), Br (24.4 Å³) and I (33.0 Å³) are clearly of different sizes, all the experimental observations on bending and crystallographic disorder in the monoclinic group seem to indicate that geometrical factors are more important. There is, however, a hint of the importance of chemical factors from the different site-occupation

factors and varying volume increments and perhaps there are ordered domains, especially when iodine is introduced. The adoption of an ordered structure of the C_6Cl_6 type by **14C2356I** and **14B2356I** is surely suggestive of chemical differences between Cl (or Br) and I.^[30] In the end, however, it is the bending experiments that provide the clinching evidence; they show that most of the $X\cdots X$ interactions in these structures are weak and nonspecific.

The triclinic structure type—Supramolecular synthons: We now discuss the triclinic structures. **135B246I** crystallises from THF concomitantly in the C_6Cl_6 monoclinic form **135B246I-M** (thin needles) and a triclinic form **135B246I-T**, which was obtained as thick blocks, some of which are boomerang shaped.^[31] The molecules in the triclinic form are arranged in planar layers parallel to (100) and in a nearly hexagonal arrangement with clusters of three I atoms from three neighbouring molecules and correspondingly, clusters of three Br atoms (Figure 10). The I_3 clusters are distinctive with particularly short $I\cdots I$ distances of 3.7548(4) Å (174.24(12), 119.68(13)°), 3.7762(4) Å (176.56(12), 119.68(12)°) and 3.7979(5) Å (170.06(12), 119.06(12)°).^[32] The θ_2 values are all close to 120° and, despite the short $I\cdots I$ distances, it would once again not be possible to say whether these contacts are type-II, which ideally has $\theta_1 \approx 180^\circ$ and $\theta_2 \approx 90^\circ$. The I_3 cluster or synthon is supposedly stabilised co-operatively as $I^{(\delta+)}\cdots I^{(\delta-)}$.^[33] The Br_3 clusters have $Br\cdots Br$ distances of 4.0660(7), 4.0937(7) and 4.0946(7) Å and are somewhat loosely packed because of the bigger size of the I

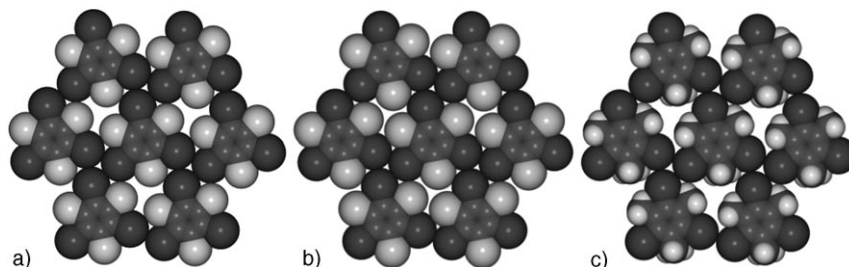


Figure 10. Planar layer in a) **135C246I**, b) **135B246I-T** and c) **135I246M**. The three I atoms in the I_3 synthon are in close contact in each case, but the Cl, Br and Me groups are not. This indicates the structural importance of the I_3 synthons.

atoms. Successive planar layers are inversion related and stacked so that bumps in one layer fit into the hollows of the next. The interlayer interactions are nonspecific in that they are based on close packing of spheres in hollows.

An important aspect of chemically directed recognition is the repeated appearance of specific supramolecular synthons, which are substructural units containing directional interactions.^[34] The planar layer structure in **135B246I-T** is reproduced in other related hexasubstituted benzenes. In the corresponding chloro derivative **135C246I**, the intralayer $I\cdots I$ distances are 3.7985(6), 3.8250(6) and 3.8646(8) Å (nearly the same as in **135B246I-T**). Because of this, the

Cl...Cl distances are pushed apart as far as 4.3360(17), 4.3667(17) and 4.3697(18) Å (longer than the Br...Br distances in **135B246I-T**) and the Cl atoms are not even in contact. In **135I246M**,^[35,36] the I...I distances in the I_3 synthon are 3.851, 3.897 and 3.933 Å and the Me groups are well separated, a case of Cl/Me exchange.^[8a] The I atom is crucial in all these cases, and its size determines the overall layer structure. We suggest that the Br clusters in **135B246I-T**, the Cl clusters in **135C246I** and the Me clusters in **135I246M** are mere spectators in a layer structure that is determined by the robustness of the I_3 synthons. In **135F246I** a simple geometrical calculation showed that the F...F distances would need to be at an unrealistic distance of 5.01 Å if the layered structure of **135B246I-T** were adopted with the I_3 synthons conserved. Instead, the experimental structure is three-dimensionally corrugated and not layered, with I and F atoms at van der Waals separation (I...F; 3.53, 3.59 Å).

Many crystals of **135B246I-T** and **135C246I** were found to have a definitely curved appearance. Curvature was also observed when an undeformed crystal was held at one end and disturbed with a needle at the other—a shearing movement occurs easily. This phenomenon although not unprecedented is certainly unusual;^[37] as mentioned earlier, organic crystals usually break when subject to mechanical deformation (by the application of a bending moment or a shear force) and do not shear in this way. Inspection of Figure 11 shows a

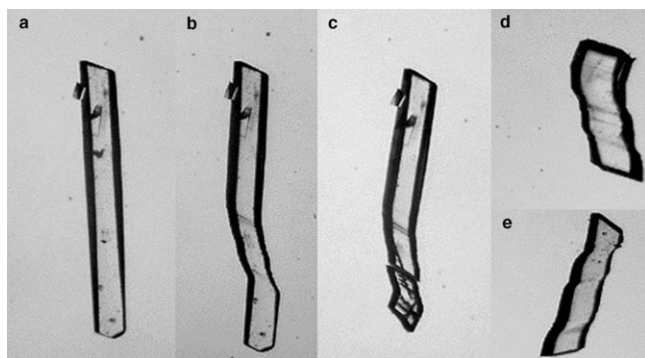


Figure 11. Shearing of crystals of **135C246I**: a) unsheared specimen elongated along [100]; b) after shearing (notice the striations of slip along (100)); c) broken specimen after an attempt to cut it in a direction perpendicular to the shear plane; d) and e) multiple shearing.

number of striations that correspond to the shearing movement within a crystal of **135C246I**. Notably, the shearing direction corresponds to sliding of the bc planes past one another. In contrast, when we attempted to shear or cut the crystal in other directions, the crystal fractured. These directions would correspond to disrupting the layer structure—the difficulty in doing so attests to the fact that the intralayer interactions are strong and directionally specific (synthon forming).^[38] When these crystals were subjected to a three-point bend test they simply broke along the bc plane.

A necessary (but not sufficient) condition for shearing of the kind seen in this family of aromatic compounds is the

presence of three halogen atoms in a 1,3,5-arrangement. For example, **135I246M** and **135B246M** also contain this pattern and shear just as easily. Compounds that lack this substitution pattern take the monoclinic disordered structure (which is not layered) and do not show shearing on application of mechanical stresses.^[39] They either break or bend. There is a clear relationship between the appearance of a layered structure and susceptibility to mechanical shearing of layers, which is well known in plasticity of inorganic crystals. This relationship is mediated by dislocation movements within each layer, analogous to basal slip in hexagonal inorganic crystals like Zn, Cd and Mg; this aspect is under investigation. This deformation process has other parallels in the inorganic solid state and resembles the shearing of graphite^[40] (which has a layered structure) and the polytypism in the layered CdI_2 .^[41] In the context of X...X interactions, the significant fact obtained from these experiments is that in **135B246I-T** the intralayer I...I interactions are much more important than the interlayer I...I and I...Br interactions. These intralayer interactions may be considered to be synthon forming and are chemically significant, arising as they do from polarisation of the I atoms.

The nonspecificity of the weak interlayer interactions is further demonstrated by the structure of the boomerang-shaped (and other shaped) crystals of **135C246I** and **135B246I-T** (Figure 12). Crystals with these distinctive

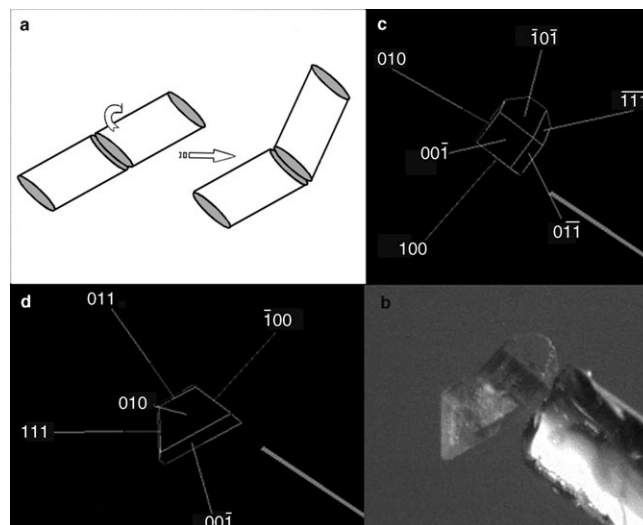


Figure 12. Twinning in **135B246I-T**: a) rotation of 60° to achieve boomerang shape; b) twinned crystal used for X-ray measurements; c) and d) indexing of twin faces showing common plane (100) (note that this is the plane that contains the structure-determining I_3 supramolecular synthons).

shapes were obtained for every compound for which shearing was possible. X-ray data were collected for a boomerang-shaped crystal of **135B246I-T**. Twinning occurs at the hinge plane and the common plane between the twins is (100), which is the shearing layer mentioned above. A plausible twinning model is one in which two consecutive invert-

ed layers in the normal structure are twisted by 60° and layers across the twin boundary are packed in a bumps-in-hollows fashion. In general, the stacking of layers across the twin boundary is not as satisfactory as for the inverted layers in the untwinned crystal. In the 2:98 solid solution of **135B246M**:**135C246I** grown from THF, multiple twinning was observed within the same crystal (Figure 13). In addi-



Figure 13. Crystals of **135C246I**:**135B246M**: triple hinged (w-type) crystal (left) and multiple-hinged ("alkyl-chain" type) crystal (right).

tion to the usual single-hinged (V-shape) crystals, we observed double-hinged (N-shape), triple-hinged (W-shape) and multiple-hinged ("alkyl-chain-type zigzag") crystals. All these crystals were grown as such from solution and obtained without mechanical deformation. The fact that twinning is easy^[42] suggests that normal and twinned stacking are energetically comparable. In other words, the interlayer I...I, Br...Br and I...Br interactions are nonspecific and comparable to the easily deformable Cl...Cl interactions in the bent crystals of C_6Cl_6 . To further confirm the anisotropy of the 1,3,5-substituted compound, we determined the cell parameters of **135B246I-T** and **135C246I** at six different temperatures between 100 and 300 K (Figure 14). The *a*-axis

length increases markedly with temperature compared with the other parameters. Clearly, the interlayer interactions are weaker than the intralayer ones. An analogous situation in inorganic crystals is the anisotropic thermal expansion seen in metals like Zn and U.

A series of solid solutions was prepared, using equimolar concentrations in the crystallisation solvent, 1,4-dioxane. All take the triclinic packing of **135B246I-T**, with the heavier atom forming the X_3 synthon. The solid solutions **135B246I**:**135C246I**, **135B246I**:**135I245M** and **135C246I**:**135I245M** are rather close to equimolarity in the solid state (57:43, 46:56 and 41:59, respectively) and have nearly the same cell volumes (553, 564 and 556 Å³, respectively). By using the same method, a solid solution of **135C246I**:**135B246M** with a molar ratio of 8:92 was obtained.

The crystallographically determined ratio was also confirmed by HPLC. Perhaps the lack of I atoms in one of the constituents prevents a more equimolar crystallisation product, once again hinting at the importance of I in forming these layered structures. The importance of I in this regard is also shown by the fact that **135B246C** adopts the disordered monoclinic structure of C_6Cl_6 . This crystal also shows bending at 413 K, which matches the bending temperature of C_6Br_6 .

Polymorphism: A comment on the occurrence or non-occurrence of polymorphs in some of these compounds is in order. Although **135B246I** is trimorphic (triclinic layered,

monoclinic C_6Cl_6 , monoclinic as in **14B2356I**), **135C246I** gives only the triclinic layered structure and **135B246C** only the C_6Cl_6 form. Despite repeated and exhaustive attempts, we were never able to obtain the absent polymorphs **135B246C-T** and **135C246I-M**. We believe that the monoclinic C_6Cl_6 structure (and the attendant disorder) is favoured when the two halogen atoms are similar in size as Cl and Br are. The triclinic structure is tolerated even with large differences in halogen size as in Cl and I. In the combination Br/I both situations occur, but the cell volume of the triclinic form (563 Å³) is higher than that of the mono-

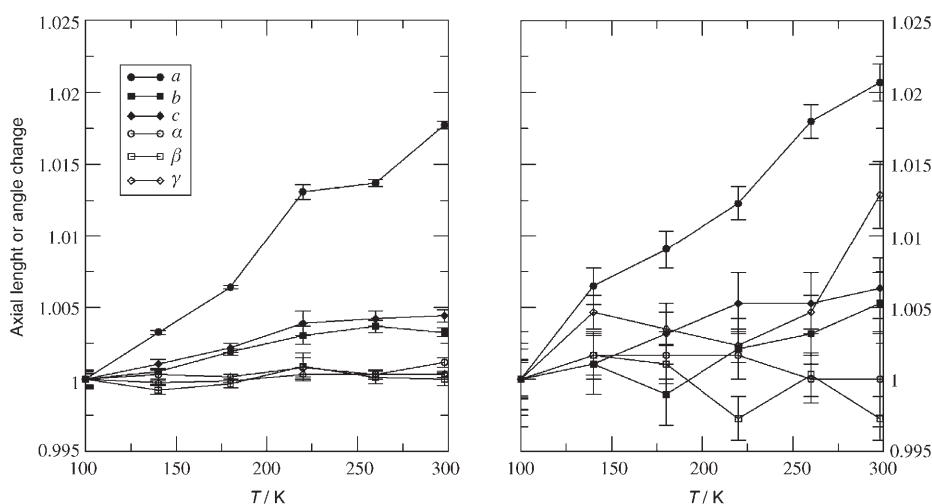


Figure 14. Variation of cell parameters with respect to temperature for compounds **135C246I-T** (left) and **135B246I-T** (right). Notice the *a*-axis length increases markedly with temperature compared with the other parameters.

clinic form ($536 \text{ \AA}^3$) because of the empty spaces in the Br_3 clusters in the former.

Conclusion

Halogen...halogen interactions ($\text{X}\cdots\text{X}$) have been investigated in a series of hexahalogenated benzenes. These compounds occur in two broad structural groups. The more common one is a monoclinic packing that is isostructural with C_6Cl_6 . The less common one is a layered triclinic packing that is exclusive, although not mandated, to compounds in which different halogen atoms occupy the 1,3,5- and 2,4,6-positions. Compounds $\text{C}_6\text{Cl}_{(6-n)}\text{Br}_n$ adopt the disordered monoclinic structure irrespective of their substitution pattern. The 1,3,5/2,4,6-arrangement of distinct halogen atoms is compatible with a threefold-symmetrical X_3 -synthon-based pseudo-hexagonal layer structure. $\text{X}\cdots\text{X}$ interactions have been traditionally classified by using geometrical criteria as type-I and type-II. Although there might be a general consensus that the symmetrical type-I interactions are of the van der Waals type and the unsymmetrical type-II contacts are polarisation induced, some of the interactions in these structures do not lend themselves easily to this classification. Crystals of these hexahalogenated benzenes undergo two types of deformation when subject to a mechanical stress. The monoclinic C_6Cl_6 type crystals undergo bending but only along certain planes: this can happen only when interactions in a direction orthogonal to these planes are particularly weak. Because it is the $\text{X}\cdots\text{X}$ interactions that emerge at the bending faces, we conclude that these interactions are weak and nonspecific despite their geometry, which is more like type-II than type-I. The triclinic crystals undergo shear along layers within which the $\text{X}\cdots\text{X}$ interactions, mostly $\text{I}\cdots\text{I}$, are much stronger than $\text{X}\cdots\text{X}$ interactions between layers. The strong and specific intralayer $\text{I}\cdots\text{I}$ interactions assemble to form I_3 supramolecular synthons, which are the most important structural element in the triclinic group. Accordingly, we conclude that $\text{X}\cdots\text{X}$ interactions ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) are of several types and that it is sometimes difficult to characterise them by using geometrical criteria only. The use of an independent technique, like observation of the mechanical behaviour of the crystal, offers a much clearer insight into their nature. The mechanical response of these molecular crystals resembles in some respects that of certain types of inorganic crystals. As the latter class of crystals has been investigated extensively, we conclude that there is scope for understanding the mechanical behaviour of these two different classes of crystals on a common basis.

Experimental Section

Materials: All reagents and solvents employed were commercially available (Lancaster) and were used as supplied without further purification. All these compounds were characterised by means of NMR and IR spectroscopy. The ^1H NMR spectra were recorded on a Bruker Avance in-

strument at 400 MHz. IR spectra were recorded on a Jasco 5300 spectrometer. All melting points were measured by using a Fisher-Jones melting point instrument.

Synthesis: All the mixed halogenated compounds were synthesised by either bromination or iodination of the corresponding halogenated starting materials. The general bromination and iodination procedures used to prepare these compounds are given for **135B246C** and **135C246I**.^[43]

Bromination: A mixture of 1,3,5-trichlorobenzene (3 mmol, 556 mg) and electrolytic Fe powder (19 mmol, 1 g) was placed in a round-bottomed flask and Br_2 (0.23 mol, 6 mL) was added dropwise at 273 K. After this, the mixture was heated at 408–413 K for 1 h. The resulting mixture was poured into a saturated NaHSO_3 solution (500 mL), the precipitate filtered off and then crystallised from THF to give **135B246C** (900 mg). IR (KBr): $\tilde{\nu}=1317, 1271, 623 \text{ cm}^{-1}$; MS (70 eV): m/z (%): 414 [M^+], 416 [M^++2], 418 [M^++4], 420 [M^++6], 422 [M^++8], 424 [M^++10], 335, 258, 107, 77.

Iodination: H_5IO_6 (1.66 mmol, 380 mg) was dissolved in concentrated H_2SO_4 (6 mL) and crushed I_2 (5 mmol, 1.27 g) was added followed by stirring for 0.5 h. Then 1,3,5-trichlorobenzene (1 mmol, 186 mg) was added to the reaction mixture and followed by stirring for 24 h at room temperature and then for 36 h at 333 K. The reaction mixture was cooled and poured onto crushed ice. The solid was filtered and recrystallised from THF to yield **135C246I** (390 mg). IR (KBr): $\tilde{\nu}=1647, 1292, 559, 416 \text{ cm}^{-1}$; MS (70 eV): m/z (%): 558 [M^+], 560 [M^++2], 562 [M^++4], 431, 304, 234, 179, 142, 127, 107, 72.

Characterisation: ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C, TMS): No peaks were found in any of the spectra of the hexahalogenated compounds. IR (KBr): **135F246I**: $\tilde{\nu}=1560, 1404, 1323, 1049, 702, 652 \text{ cm}^{-1}$; **1245C36I**: $\tilde{\nu}=1309, 1282, 1246, 679, 582 \text{ cm}^{-1}$; **14B2356C**: $\tilde{\nu}=1325, 1286, 686, 623 \text{ cm}^{-1}$; **135B246I**: $\tilde{\nu}=1263, 1224, 1028 \text{ cm}^{-1}$; **124C356I**: $\tilde{\nu}=1539, 1516, 1288, 1269, 632, 555 \text{ cm}^{-1}$; **135C246I**: $\tilde{\nu}=1292, 1255, 1222, 1026 \text{ cm}^{-1}$; **135C246I**: $\tilde{\nu}=2948, 1120, 1020, 949, 644, 559, 470 \text{ cm}^{-1}$.

Crystallisation: All the compounds were crystallised from either CCl_4 , THF or 1,4-dioxane by slow evaporation at ambient temperature.

X-ray crystallography: Intensity data were collected on a Bruker Nonius Smart Apex CCD with graphite monochromated MoK_α radiation. Gaussian face-indexed absorption corrections by Xprep were applied before empirical data correction by Sadabs 2.10. The structures were solved by direct methods and refined anisotropically by full-matrix least-squares methods using the Shelxtl 6.14 software package. Crystal data are given in Table 1. The supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Nanoindentation experiments: Nanoindentation experiments were performed by using a nanoindenter model XP, supplied by MTS Systems Corporation, USA. The diamond indenter had a Berkovich (three-sided) pyramidal geometry. The bending experiments were carried out at 293 K using the load control mode. The maximum allowed drift was set to 0.1 nm s^{-1} and the indenter velocity was 10 nm s^{-1} .

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