line to valley point or valley point to valley point as appropriate. Error in integrations was estimated at ±6% by standard deviations obtained while generating calibration curves.

Acknowledgment. We thank Dr. A. Majumdar for advice on simplex calculations, Mr. R. A. Reamer for extensive NMR characterization of chloro amide **15**, and Miss Marian Spears for typing this manuscript.

Supplementary Material Available: Plots of kinetic data for runs with 0.5 and 5 equiv of DIEA, plot of acid chloride concentration vs time with 5 equiv of DIEA with and without imine present, and ^{13}C NMR spectrum of **13** (6 pages). Ordering information is given on any current masthead page.

Halogenated Adamantanes: Intermolecular Interactions in the Solid State. X-ray Crystal Structures of Difluorodiiodo-, Trifluoroiodo-, and Tetraiodoadamantane

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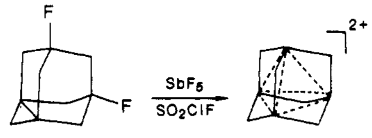
Partial halogen exchange can be achieved selectively from tetraiodoadamantane by using mercuric fluoride. Difluorodiiodo- or trifluoroiodoadamantane are formed in good yields depending on the conditions employed. The X-ray structures of these compounds illustrate the role of anisotropic intermolecular halogen–halogen interactions in the formation of ordered crystalline phases. Tetraiodoadamantane forms a "super-diamond" lattice with tetragonal symmetry, which has only been precedented in Ermer's recent crystal structure of adamantanetetracarboxylic acid.

Whereas all bridgehead-substituted tetrahaloadamantanes AdX_4 (X = F, Cl, Br, I) are well known,[1] those with mixed halogen subsituents are not. Selective halogenation or partial halogen exchange presents considerable difficulties since in most cases product mixtures are obtained. We were interested in the synthesis of 1,3-didehydro-5,7-difluoroadamantane **1** as a precursor for the nonclassical 1,3-didehydro-5,7-adamantanediyl dication **2**.[2] A number of 1,3-didehydroadamantanes have been synthesized by Pincock and co-workers[3] by bridgehead halogen elimination reactions. Hence, the possible precursors to **1**, difluorodibromo(iodo)adamantane **3** and monofluorotribromo(iodo)adamantane **4**, were prepared from tetrabromoadamantane **5** and tetraiodoadamantane **6**, respectively. X-ray crystallography showed **3b**, **4b**, and **6** to have special solid-state properties. Intermolecular halogen–halogen interactions permit these derivatives to crystallize in an orderly manner.

Results and Discussion

Synthesis of Haloadamantanes. When reacted with silver(I) fluoride in cyclohexane or methylcyclohexane, tetrabromoadamantane **5** as well as tetraiodoadamantane **6** gave product mixtures, AdX_nF_m ($n, m = 0...4, n + m = 4$, X = Br, I), which could be separated by preparative HPLC.[4] However, not only are the yields of the desired compounds, **3** and **4**, unsatisfactory, but also the chromatographic separations are tedious and time consuming. Hence, considerable effort was expended in finding conditions for more selective halogen exchange.

While tetrabromoadamantane **5** did not react with mercuric fluoride in refluxing chloroform, tetraiodoadamantane **6** gave either **3b** or **4b**, depending on the conditions. The latter reacts smoothly with butyllithium in ether/pentane to give **1**, which in turn could be converted to the three-dimensional aromatic didehydroadamantanediyl dication **2**.[2]



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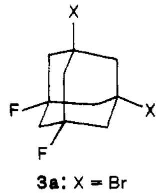
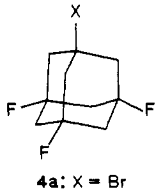


3a: X = Br
3b: X = I



4a: X = Br
4b: X = I

Structures of Haloadamantanes. Tetraiodoadamantane 6. Many symmetrically substituted adamantanes do not form crystals suitable for X-ray structural determination due to the formation of plastic crystalline phases.[1,5] In contrast, the structures of **3b**, **4b**, and **6** could be solved by X-ray diffraction and exhibit interesting solid-state features. Intermolecular I···F and I···I interactions have an ordering influence on the molecules within the crystal lattice and thus help to determine long-range

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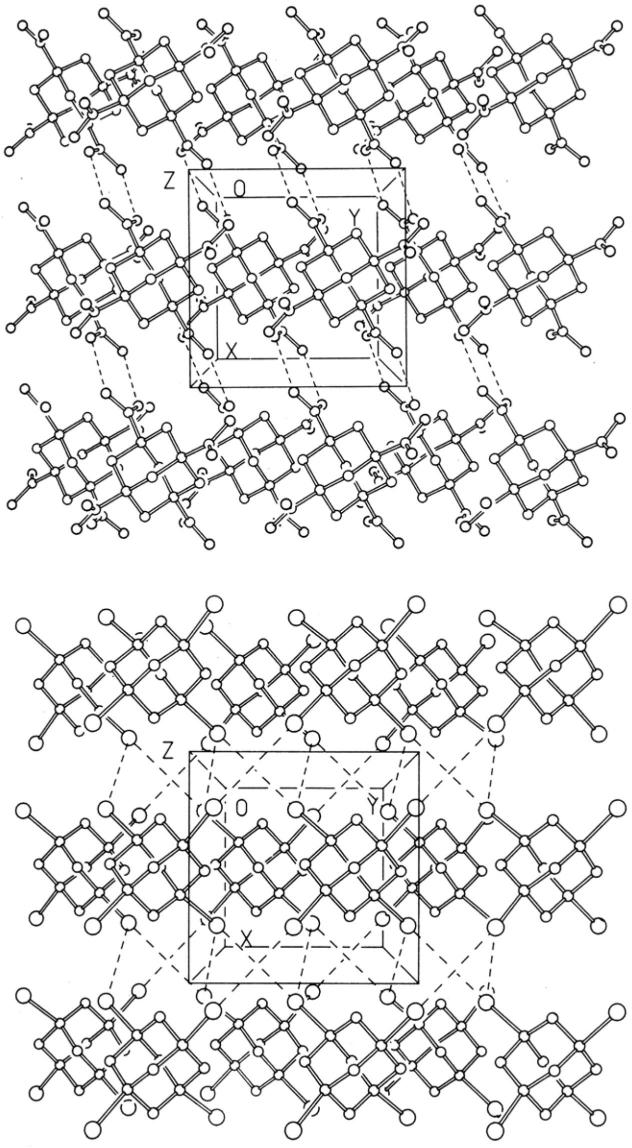

Figure 1. Comparison of crystal packing in tetraiodoadamantane **6** (bottom) and adamantanetetracarboxylic acid **7** (top). Important bond lengths and angles (angstroms and degrees): C–I, 2.16 (3); I···I, 4.093 (6), 4.117 (6); C–I–I, 134.2 (8), 143.7 (8). Crystal coordinates for **7** were taken from ref 7a.

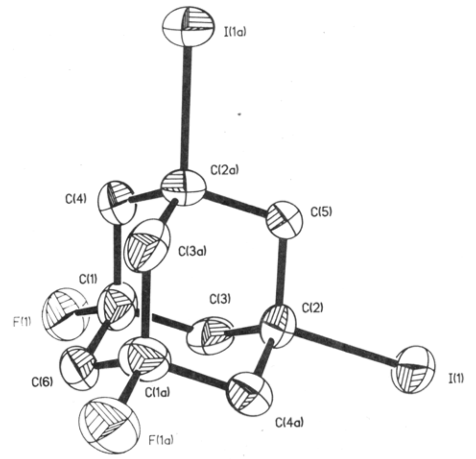

Figure 2. The structure of difluorodiiodoadamantane **3b** in the solid state. Thermal ellipsoids are at the 50% probability level.

Table I. Comparison of Some Iodine–Iodine and Iodine–Fluorine Distances (Angstroms)

	I–I	I–F	I···I	I···F
I_2 (solid)[a]	2.72		3.50, 3.97, 4.27	
IF (gas phase)[b]		1.910 (1)		
IF_7 (solid)[c]		1.83		
$[R_fI\text{–}F\text{–}IR_f]^-$ [d]				2.4–2.5
3b[e]				3.326 (5)
4b[e]			3.73 (1)	3.31 (1)
6[e]			4.093 (6), 4.117 (6)	
van der Waals radii sum[f]			4.3	3.5

[a] Reference 8, p 329. [b] Lovas, F. J.; Tiemann, E. *J. Phys. Chem. Ref. Data* **1974**, *3*, 609. [c] Reference 8, p 333. [d] Reference 11. [e] This work. [f] *CRC Handbook of Chemistry and Physics*, West, R. C., Ed.; CRC Press: Boca Raton, 1983; p D-191.

order. Strong intermolecular interactions have long been known to orient organic molecules into preferred and often predictable packing patterns.[6e,f] Recently, Ermer[7] has reported the fascinating X-ray structures of adamantanetetracarboxylic acid[7a] **7** and 3,3-bis(carboxymethyl)glutaric acid[7b] **8**. Both exhibit "super-diamond" structures in which sections of the diamond lattice connected by hydrogen bonds form interpenetrating "diamondoid" lattices.[7] This results in relatively dense solids with high melting points.[7] The structure of tetraiodoadamantane **6** is completely analogous to Ermer's adamantanetetracarboxylic acid structure.[7a] The highest possible molecular symmetry for **6** is T_d, therefore it could adopt a structure with full cubic symmetry. It crystallizes, however, in the same tetragonal space group ($I4_1/a$) as **7**, which ideally can only have D_{2d} symmetry. Compounds **6** and **7** show similar unit cell dimensions, and in both structures the molecules have crystallographic S_4 symmetry. The packing of adamantanetetracarboxylic acid **7** compared to **6** is somewhat denser. This is reflected in the 10.0 Å distance between the cage centers in **7** compared to 10.7 Å in **6**. Unfortunately the iodine atoms in **6** are severely disordered, and no disorder model could be refined. This results in a high residual electron density in the final fourier difference map (6 e Å^{-3}) and a very poor R value of ca. 0.20. Nevertheless the qualitative similarity to **7** is obvious (Figure 1). The intermolecular iodine–iodine distances in **6** are ca. 4.1 Å and thus are about 0.2 Å shorter than the sum of the van der Waals radii (4.3 Å).

Difluorodiiodoadamantane 3b crystallizes from pentane in the monoclinic space group $C2/c$. The molecules reside in special positions resulting in crystallographic C_2 symmetry (Figure 2). The molecules are associated through I···F interactions (I···F = 3.33 Å). There are no short I···I distances. Figure 3 shows the unit cell and the I···F interactions.

Trifluoroiodoadamantane 4b crystallizes from pentane in the monoclinic space group $C2/c$. There are two independent molecules in the asymmetric unit. The molecules form centrosymmetric tetrameric aggregates with I···I and I···F noncovalent interactions. The I···I distance is 3.73 Å and the I···F distance 3.31 Å, which are both appreciably shorter than the sum of the van der

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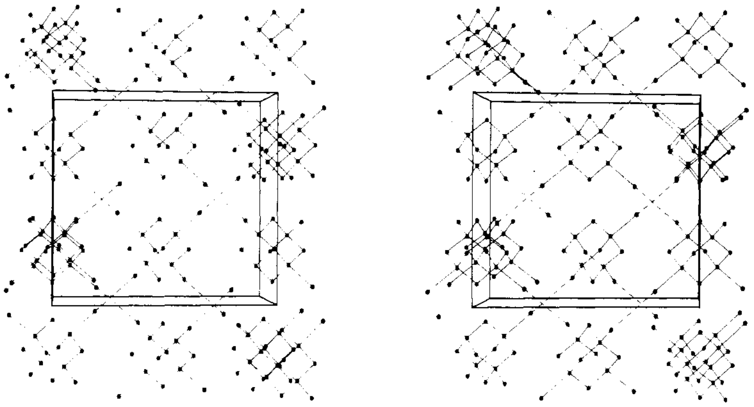

Figure 3. Stereoview of the unit cell of **3b** showing intermolecular iodine–fluorine interactions. Selected bond lengths and angles (angstroms and degrees): I(1)–C(2), 2.177 (6); I(1)–F(1), 3.326 (5); F(1)–C(1), 1.429(8); C(2)–I(1)–F(1), 171.5(2); I(1)–F(1)–C(1), 118.1(4).

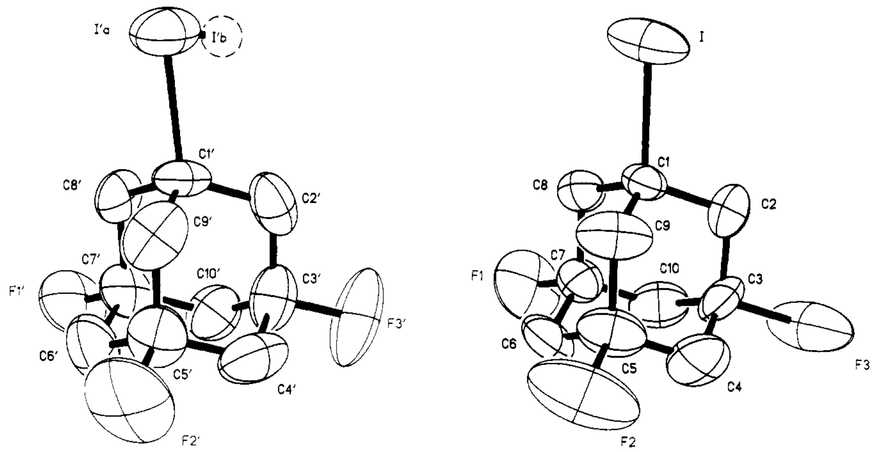

Figure 4. The two independent formula units of trifluoroiodoadamantane **4b**. Thermal ellipsoids are at the 50% probability level. One iodine atom was refined in two positions, I'a and I'b, with site occupation factors of 0.724 and 0.276, respectively. Although disorder of F3 is indicated by very large temperature factors and a very unusual C–F bond length (1.583 (19) Å), no disorder model could be refined. An attempt to refine partial occupancy of I and F3 did not lead to a significant deviation of the site occupation factors from unity.

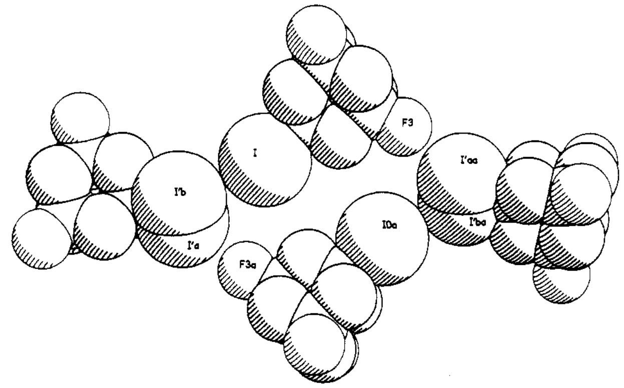

Figure 5. Space-filling model of the tetrameric aggregates in **4b**. Selected bond lengths and angles (angstroms and degrees): C(1)–I, 2.185; I–I('b), 3.731 (14); I('b)–C(1'), 2.17 (20); C(1')–I('a), 2.195 (13); I('a)–C(3a), 3.312 (14); F(3a)–C(3a), 1.583 (19); C(1)–I–I('b), 157.6 (4); C(1')–I('b)–I, 138.0(6); C(1')–I('a)–F(3a), 147.3(5); C-(3a)–F(3a)–I('a), 157.6 (10).

Waals radii (4.3 and 3.5 Å, respectively). Figure 4 shows the two independent formula units, Figure 5 shows the tetrameric units, and Figure 6 gives a stereo view of the unit cell.

Short intermolecular halogen–halogen contacts in the solid state are well known.[6] Elemental chlorine, bromine, and iodine adopt layer structures with relatively short intermolecular distances, well within the sum of the van der Waals radii. Table I includes data for elemental iodine and pertinent comparisons in relation to the nonbonded distances we have observed.

Many crystalline organochlorine compounds exhibit short halogen–halogen distances. This has been described as the "chloro effect" and has been used to devise novel solid-state reactions.[6d] The Cl···Cl distances in hexachlorobenzene are 3.51 and 3.72 Å; these intermolecular interactions have an important influence upon crystal packing. In triphenylbromomethane the intermolecular bromine–bromine distance is 3.20 Å.[9] In α-ICl there are very short I···Cl and I···I contacts (I···Cl = 3.00 Å, I···I = 3.08 Å, vs I-Cl = 2.44 Å).[10]

Very recently, X-ray structures of fluorine-bridged carbanions containing a $[R_f\text{–I–F–I–}R_f]^-$ moiety (R_f = polyfluorinated aryl group) have been published.[11] The I–F bond distances in the central I–F–I unit, although over 0.5 Å longer than those in IF itself, are approximately 1.0 Å shorter than the sum of the van der Waals radii (3.5 Å, see Table I). According to Farnham et al.[11] these distances reflect (formally) hypervalent interactions in a five-center six-electron bonding arrangement. The iodine–fluorine (and iodine–iodine) contacts we report here are longer but are still shorter than the sum of the van der Waals radii (Table I). Halogen–halogen interactions must be strong enough to produce ordered structures, in our cases for molecules which exhibit relatively high molecular sym-

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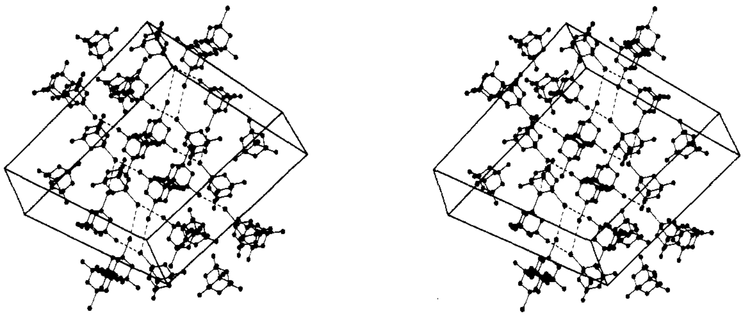

Figure 6. Stereoview of the unit cell of **4b** with intermolecular interactions indicated.

metry (point groups T_d, C_{3v}, and C_{2v}, respectively).

Conclusion

The significance of the results presented above has been well summarized by a referee: "Intermolecular halogen–halogen interactions have long been known to direct molecules into preferred packing patterns, but this is the first evidence that such interactions also help to determine long-range order."

Experimental Section

1,3-Difluoro-5,7-diiodoadamantane (3b). Tetraiodoadamantane **6**[12] (11.5 g, 18 mmol) and mercuric fluoride (10.7 g, 45 mmol) were refluxed in dry chloroform under nitrogen for 4 days. The mixture was sonicated in an ultrasound bath for 1 out of every 12 h. After filtration, the solvent was removed. The residue was redisolved in pentane, filtered through a short silica gel column, and crystallized slowly from pentane. Compound **3b**, 4.4 g (58%), was obtained as colorless crystals, mp 132–134 °C.[13] Anal. Calc for $C_{10}H_{12}F_2I_2$: C, 28.33; H, 2.85. Found: C, 28.25; H, 2.88.

1,3,5-Trifluoro-7-iodoadamantane (4b). Tetraiodoadamantane **6** (19.2 g, 30 mmol) and mercuric fluoride (25.1 g, 105 mmol) were refluxed under nitrogen in dry chloroform for 7 days. Sonication was carried out intermittantly every 12 h. After workup as for **3b** above, 6.7 g of **4b** (70.7%) was obtained from pentane as colorless crystals, mp 72–73 °C.[13] Anal. Calc for $C_{10}H_{12}FI_3$. C, 38.00; H, 3.83. Found: C, 37.80; H, 3.60.

X-ray Crystallography. Crystals of **3b**, **4b**, and **6** were sealed into glass capillaries and mounted on a Nicolet R3m/V diffractometer (Mo Kα radiation, λ = 0.71073, graphite monochromator). Initial investigations revealed the crystal systems to be monoclinic and tetragonal, respectively. Final lattice parameters were determined from least-squares refinement of the angular settings of 18 strong, accurately centered reflections. The data were corrected for crystal decay and Lorentz and polarization effects and converted into structure factors. An empirical absorption correction was applied for **3b** and **6**. Crystal data for **3b**: colorless columns from pentane; crystal size, 0.6 × 0.4 × 0.4 mm^3; space group, $C2/c$; a = 12.575 (4), b = 11.740 (4), and c = 8.373 (3) Å; β = 95.75 (3)°; V = 1230 Å^3, ρ_x = 2.29 g cm^{-3} (Z = 4); T = 293 K; ω scan with 3 to 15°/min in ω; reflections collected, 4430 (4° < 2θ < 64°); unique reflections, 2145; observed reflections, 1725 ($F > 6\sigma(F)$); solution, direct methods (SHELXTL PLUS); refinement, full matrix least squares; non-hydrogen atoms anisotropic, hydrogen atoms were included using a riding model; R = 0.055, R_w = 0.061; data/parameter: 22.1:1. **4b**: colorless columns from pentane; crystal size, 0.4 × 0.3 × 0.2 mm^3; space group, $C2/c$; a = 23.949 (7), b = 7.334 (2), c = 26.000 (7) Å; β = 93.43 (2)°, V = 4558 Å^3; ρ_x = 1.84 g cm^{-3} (Z = 16); T = 293 K; ω scan with 3 to 15°/min in ω; reflections collected, 4229 (4° < 2θ < 48°); unique reflections, 3575; observed reflections, 2266 ($F > 3\sigma(F)$); solution, direct methods (SHELXTL PLUS); refinement, full matrix least squares; non-hydrogen atoms anisotropic, hydrogen atoms were included using a riding model; R = 0.082, R_w = 0.086; data/parameter, 8.6:1. **6**: pale yellow cubes from toluene; crystal size 0.6 × 0.5 × 0.5 mm^{-3}; space group, $I4_1/a$; a = 7.177 (1), c = 28.466 (6) Å; V = 1466 Å^3; ρ_x = 2.90 g cm^{-3} (Z = 4); T = 200 K; ω scan with 3 to 15°/min in ω; reflections collected, 3468 (4° < 2θ < 60°); unique reflections, 1024; observed reflections, 903 ($F > 4\sigma(F)$); solution, direct methods (SHELXTL PLUS); refinement, full matrix least squares; iodine atoms anisotropic, carbon atoms isotropic, hydrogen atoms were not included; R = 0.203, R_w = 0.226; data/parameter: 45.1:1.

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Registry No. **3b**, 109637-48-1; **4b**, 109614-03-1; **6**, 40950-19-4; HgF_2, 7783-39-3.

Supplementary Material Available: Tables of fractional atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for **3b**, **4b**, and **6** (11 pages); observed and calculated structure factors for **3b**, **4b**, and **6** (25 pages). Ordering information is given on any current masthead page.

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[13] Spectroscopic data for **3b** and **4b** have been reported previously (ref 2).