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The Solid-State Polymerization of 3,5-Dihalo-4-aminobenzoylchlorides: New Structural Perspectives

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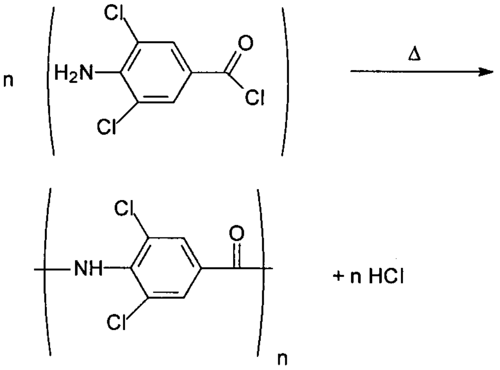
Abstract—Heating 3,5-dihalo-4-aminobenzoylchlorides affords the analogous solid polybenzamides. X-Ray structure determinations of 3,5-dichloro-, 3,5-dibromo- and 3,5-diiodo-4-aminobenzoylchlorides reveal that all three structures contain infinite hydrogen-bonded chains of monomers in a head-to-tail arrangement (graph set notation **C(8)**), with amine-to-carbonyl carbon atom distances <4 Å. The proposal that the chain directions represent reaction pathways for the solid-state polymerization of the monomers is consistent with refractive index measurements made by Morgan over two decades ago.

Introduction

Solid-state polymerization reactions remain among the most interesting—and often most difficult to design or engineer—of all solid-state reactions. Among the most outstanding recent examples are the elegant studies of Lauher and Fowler on the synthesis of a poly(triacetylene)[1] and the studies by Matsumoto, Sada, Tashiro and coworkers on single-crystal polymerizations of muconate esters and salts.[2] The geometric criteria for these processes are clearly established, thus both facilitating and stimulating further design and synthesis. As solid-state chemists, we know considerably less about solid-state reactions that, at least as a class, may be effected only by thermal excitation. The best-characterized examples in this class include the single crystal polymerization of dihalobis(tris-2-cyanoethylphosphine)nickel complexes[3] and the single crystal polymerization of S_2N_2 to $(SN)_x$.[4] Although the importance of designing and characterizing new systems cannot be denied, there is still much to learn from a return to extant examples in the literature.

Polybenzamides (PBA) are an important class of macromolecules, well known for their chain stiffness and thermal stability.[5,6] High molecular weight PBA have been prepared by the following methods: reaction at low temperature in an organic solvent,[7] interfacial procedures which utilize water-miscible organic solvents,[8] and crystalline state polymerization at high temperature.[9,10] However, high molecular weight polymers of chlorine-substituted PBA could not be produced by solution methods.[9] In a typical liquid state polymerization, side reactions, air oxidation and solubility problems can prevent formation of high polymers. Morgan was able to prepare high molecular weight chlorine-substituted PBA by thermally induced polymerization in the crystalline phase.



Through measurements of refractive index, Morgan showed that thermal solid-state polymerization of 3,5-dichloro-4-aminobenzoylchloride **1** resulted in a highly crystalline polymer, and that the polymer chains are oriented perpendicular to the long needle axis.[9] Hence, despite loss of a gas from the crystal, considerable retention of crystallinity was observed. While loss of a gas from a crystalline solid would likely lead to (at best) a polycrystalline sample or an amorphous phase, the additional information regarding polymer orientation suggested that a study of the structure–reactivity relationships for **1** and/or related compounds would be highly rewarding. We report here (i) the crystal and molecular structures of the 3,5-dichloro-, 3,5-dibromo- and 3,5-diiodo-4-aminobenzoylchlorides (**1a**, **2** and **3**, respectively), (ii) the interrelationships among these structures, (iii) an analysis of probable structure–reactivity relationships and (iv) a survey of solid-state reactivity.

Keywords: 3,5-dihalo-4-aminobenzoylchlorides; solid-state polymerization; refractive index; crystal structure.

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Table 1. Percent conversion vs time and temperature

Monomer	Time (h)	Temperature (°C)	Conversion (%)
1	62.5	67	20.44
	62.5	125	73.15
	43	150	88.91
	23	190	90.27
3	43	125	89.27

Results and Discussion

Solid-state polymerization of aminobenzoylchlorides 1–3

Heating compounds **1–3** for extended periods leads to release of gaseous HCl and concomitant formation of the corresponding poly(1,4-benzamide), in agreement with the results of Morgan for **1**.[9] Results shown in Table 1 are based on weight difference experiments, and indicate, as expected, that polymerization rate increases with temperature, and that compound **3** is more reactive, although the difference is not striking. The progress of the reaction was also followed by monitoring the IR spectra of the solids; results were consistent with observations from the weighing experiments. It was also noted that, while monomers **1** and **2** were stable under ambient laboratory conditions, compound **3** was much more sensitive to hydrolysis. X-ray diffraction experiments indicated 42.4% decomposition of the crystal during ca. 36 h X-ray exposure. While the observed decomposition may also be X-ray induced, it was not investigated further.

X-Ray structure determination of compounds 1a, 2 and 3

In order to provide information on the structural basis for solid-state polymerization, the structures of compounds **1a**, **2** and **3** were determined. Data for the X-ray structure determinations are presented in Table 2. The dichloro derivative was obtained in two polymorphic forms. The polymorphism was first discovered when several crystals were mounted and examined by Weissenberg photography. Polymorph **1a** crystallizes in the orthorhombic system, space group *Pna2₁* (Table 2). Polymorph **1b** also crystallizes in the orthorhombic system, with a=25.178(5), b=17.708(4) and c=3.785(1) Å. Note (Table 2) that this unit cell is identical within experimental error to that of **1a**, except that the a-axis is twice the value of a in polymorph **1a**. If we choose the axes to correspond in this manner, then the possible space groups, based upon systematic absences, will be $Pn2_1a$ or *Pnma*; the nonstandard, noncentrosymmetric group $Pn2_1a$ was later confirmed as the correct choice, as described below. The nonstandard setting was chosen in order to preserve the correspondence between axial dimensions.

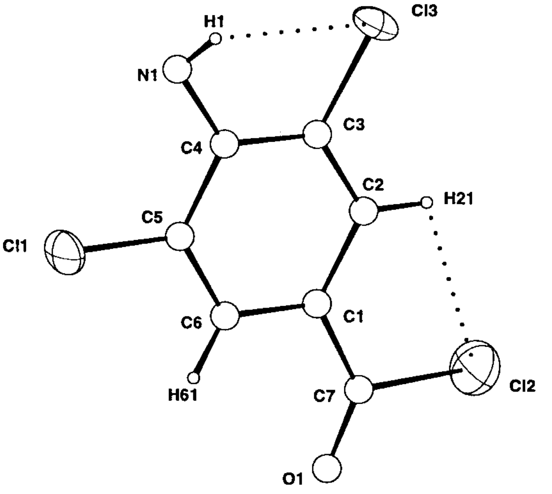

Figure 1. Molecular structure of **1a**.

Polymorphs **1a** and **1b** may be examples of *concomitant polymorphism*;[11] however, we did not investigate the phenomenon thoroughly. When crystals of **2** were grown and studied, we discovered that **2** and **1b** have very similar cell constants, as well as identical space groups. It is thus extremely likely that these two phases are isomorphous.[12] Crystals of **1b** were not suitable for a complete structure analysis, but the structure is presumed to be identical to that of **2**, as described below. The molecular structures of **1a**, **2** and **3** are shown in Figs. 1–3. There are two molecules of **2** in the asymmetric unit. All H atoms were located except for one of the H atoms attached to N(1) in compounds **1a** and **2**. Each of the three molecules exhibit two weak intramolecular hydrogen bonds (C–H···Cl and N–H···X): (a)

Table 2. Data for the X-ray diffraction studies of **1a**, **2** and **3**

Formula	**1a**, $C_7H_4ONCl_3$	**2**, $C_7H_4ONClBr_2$	**3**, $C_7H_4ONClI_2$
a (Å)	12.599(3)	25.759(5)	7.982(2)
b (Å)	17.691(4)	17.924(3)	8.327(2)
c (Å)	3.791(1)	3.902(1)	8.857(2)
α (°)	90	90	91.18(2)
β (°)	90	90	112.83(2)
γ (°)	90	90	111.81(2)
V (Å^3)	845.0	1801.6	494.3
Z	4	8	2
Formula wt	224.48	313.39	407.38
Space group	$Pna2_1[C_{2v}^9$; No. 33]	$Pn2_1a[C_{2v}^9$; No. 33]	$P\bar{1}[C_i$, No. 2]
T (°C)	294(1)	294(1)	294(1)
λ (Å)	0.71073	0.71073	0.71073
ρ_{calc} (g cm^{-3})	1.765	2.312	2.737
μ (mm^{-1})	1.032	9.161	6.522
Trans. factors	–	0.25–0.58	–
R ($I/\sigma(I)\geq1.96$)[a]	0.0929	0.0545	0.0543
R_w ($I/\sigma(I)\geq1.96$)[a]	0.0698	0.0485	0.0583

[a] $R=\sum||F_o|-|F_c||/\sum|F_o|$; $R_w=\{\sum w[|F_o|-|F_c|]^2/\sum w|F_o|^2\}^{1/2}$.

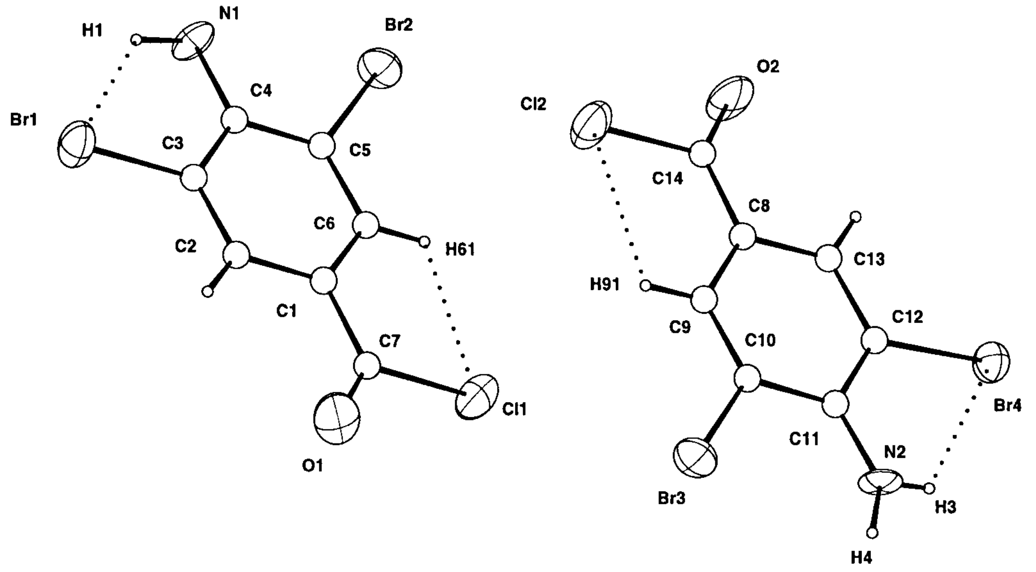

Figure 2. Molecular structure of **2**. Figs. 1–3 show intramolecular hydrogen bonds as well as 50% probability ellipsoids for atoms refined using ADP's.

$C–H_{ortho}\cdots Cl$ [C···Cl, 3.03–3.07 Å; C–H···Cl, 107–108°] and (b) N–H···Cl [N···Cl, 2.99 Å; N–H···Cl, 114°]; N–H···Br [N···Br, 3.09–3.12 Å; N–H···Br, 122–125°]; N–H···I. [N···I, 3.24 Å; N–H···I, 125°]. The similarity in internal interactions in these molecules leads to nearly identical features in their molecular structures. Bond lengths and angles (Table 3) lie within normal ranges for all three compounds. The dihedral angles between the phenyl rings and the –C(O)Cl moieties are 4.1° in **1a**, 3.8 and 2.3° for the two molecules in **2**, and 2.1° in **3**.

The solution of the structure of compound **1a** was complicated by a disorder, as shown in Fig. 4. The major and minor components of the disorder are related by a mirror operation perpendicular to the crystallographic *c*-axis in space group *Pna2₁*. As shown in Fig. 4, atom Cl(2) lies on the pseudo-mirror place, and atoms C(3) and C(2) are very near to the mirror. The refined occupancy of the major component is 0.753(8); this precludes *Pnam* as a possible spacegroup, since the occupancies would then be required to be equal. In order to improve clarity, only one of the two components is shown in Fig. 1 and other figures depicting this structure. However, the discussion applies to the structural properties of *either* component.

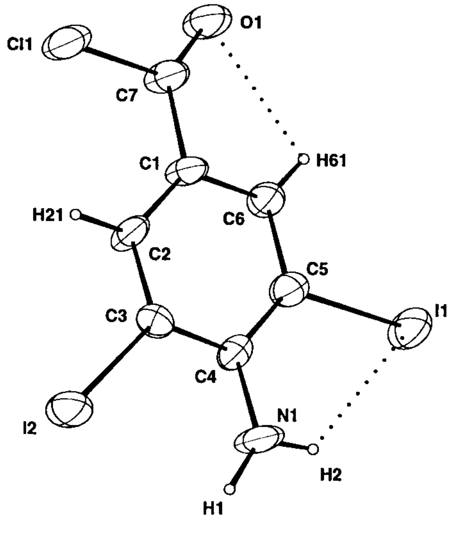

Figure 3. Molecular structure of **3**.

Table 3. Selected bond lengths (Å) and angles (°) for **1a**, **2** and **3**

3,5-Dichloro-4-aminobenzoylchloride **1a**			
Cl(1)–C(5)	1.730(13)	O(1)–C(7)	1.175(15)
Cl(2)–C(7)	1.827(13)	N(1)–C(4)	1.361(15)
Cl(3)–C(3)	1.730(12)	C(1)–C(7)	1.445(17)
C(2)–C(1)–C(7)	123.9(11)	Cl(1)–C(5)–C(4)	119.5(9)
C(6)–C(1)–C(7)	116.1(11)	Cl(1)–C(5)–C(6)	119.0(10)
Cl(3)–C(3)–C(2)	119.5(9)	Cl(2)–C(7)–O(1)	117.5(10)
Cl(3)–C(3)–C(4)	117.9(9)	Cl(2)–C(7)–C(1)	114.4(10)
N(1)–C(4)–C(3)	123.3(11)	O(1)–C(7)–C(1)	128.1(13)
N(1)–C(4)–C(5)	119.3(11)		
3,5-Dibromo-4-aminobenzoylchloride **2**			
Br(1)–C(3)	1.899(15)	Cl(2)–C(14)	1.830(18)
Br(2)–C(5)	1.901(14)	O(1)–C(7)	1.19(2)
Br(3)–C(10)	1.845(15)	O(2)–C(14)	1.21(2)
Br(4)–C(12)	1.871(12)	N(1)–C(4)	1.365(18)
Cl(1)–C(7)	1.793(18)	N(2)–C(11)	1.346(17)
C(1)–C(7)	1.47(3)	C(8)–C(14)	1.42(2)
C(2)–C(1)–C(7)	117.8(15)	C(9)–C(8)–C(14)	126.1(15)
C(6)–C(1)–C(7)	122.3(15)	C(13)–C(8)–C(14)	115.2(15)
Br(1)–C(3)–C(2)	118.5(12)	Br(3)–C(10)–C(9)	119.9(12)
Br(1)–C(3)–C(4)	118.3(12)	Br(3)–C(10)–C(11)	118.4(11)
N(1)–C(4)–C(3)	123.4(15)	N(2)–C(11)–C(10)	121.7(13)
N(1)–C(4)–C(5)	119.5(15)	N(2)–C(11)- C(12)	121.4(12)
Br(2)–C(5)–C(4)	118.8(11)	Br(4)–C(12)–C(11)	121.2(9)
Br(2)–C(5)–C(6)	119.8(10)	Br(4)–C(12)–C(13)	117.9(10)
Cl(1)–C(7)–O(1)	116.0(14)	Cl(2)–C(14)–O(2)	115.1(13)
Cl(1)–C(7)–C(1)	116.6(13)	Cl(2)–C(14)–C(8)	115.1(13)
O(1)–C(7)–C(1)	127.4(16)	O(2)–C(14)–C(8)	129.8(16)
3,5-Diiodo-4-aminobenzoylchloride **3**			
I(1)–C(5)	2.088(8)	O(1)–C(7)	1.17(1)
I(2)–C(3)	2.094(8)	N(1)–C(4)	1.36(1)
Cl(1)–C(7)	1.813(9)	C(1)–C(7)	1.47(1)
C(2)–C(1)–C(7)	123.7(7)	I(1)–C(5)–C(4)	120.0(6)
C(6)–C(1)–C(7)	116.4(7)	I(1)–C(5)–C(6)	118.0(6)
I(2)–C(3)–C(2)	117.4(6)	Cl(1)–C(7)–O(1)	117.2(6)
I(2)–C(3)–C(4)	120.0(6)	Cl(1)–C(7)–C(1)	114.5(6)
N(1)–C(4)–C(3)	121.2(7)	O(1)–C(7)–C(1)	128.4(8)
N(1)–C(4)–C(5)	122.0(7)		

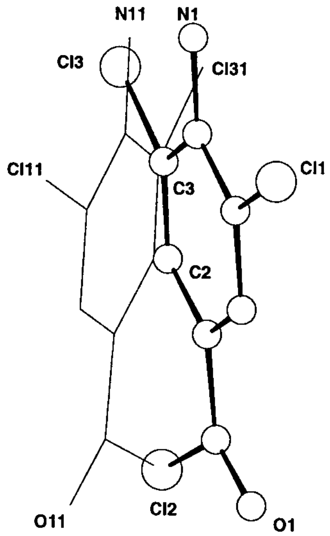

Figure 4.

Crystal structures of compounds 1a, 2 and 3

The packing of compound **1a** is shown in Fig. 5. The crystal structures of compounds **1a**, **1b** and **2** have the well-known β-type structure, with a short stacking axis (or lattice constant) of ≈3.7–3.9 Å.[13] This arrangement is common for aromatics with pendant chlorine (and sometimes bromine) atoms. The structure of **1a** consists of interleaved one-dimensional chains of head-to-tail hydrogen-bonded molecules (graph set notation **C(8)**).[14] Although one H atom on N(1) could not be located, the other H atom is clearly involved in a hydrogen bond to the carbonyl oxygen atom of the next molecule in the chain (Fig. 5; N(1)–H(1)···O(1)[$-1/2-x$, $1/2+y$, $1/2+z$]: N···O, 3.18 Å, N–H···O, 133°). The hydrogen bond is weaker than those in compound **2**, since the same H atom is also involved in the internal interaction shown in Fig. 1. The molecules in each chain are twisted by 47.2° (dihedral angle between NC_6 and C(O)Cl planes). The packing of compound **2** is shown in Fig. 6; there are two symmetry-independent **C(8)** chains in the unit cell. Although one H atom on N(1) could not be located, it is likely that N(1) and N(2) are involved in hydrogen bonds to the carbonyl oxygen atoms of the next molecule in the chain. In each chain molecules are connected by N–H···O hydrogen bonds (N(2)–H(4)···O(2)[$1-x$, $1/2-y$, $1-z$]: N···O, 3.04 Å, N–H···O, 161°; N(1)–'H(2)'···O(1) [$1/2-x$, $y-1/2$, $1/2+z$]: N(1)···O(1), 3.09 Å). The molecules in each chain are not coplanar, but are twisted by 14.1° for the chain connected by N(2)–H(4)···O(2) hydrogen bonds (leftmost in Fig. 6), and by 47.5° for the chain connected by N(1)–'H(2)'···O(1) hydrogen bonds (next chain to right in Fig. 6). This pattern alternates, with the next chain again having molecules twisted by 14.1°, then 47.5°, after which the pattern is repeated infinitely owing to unit cell translation along *a*. The crystal structure of compound **3** does not have a β-type packing arrangement. However, inspection of the crystal structure of compound **3** (Fig. 7) also reveals a head-to-tail hydrogen-bonded arrangement, with an infinite series of N(1)–H(1)···Cl(1) [$x-1$, y, $z-1$] interactions (N(1)–Cl(1), 3.49 Å; N(1)–H(1)···Cl(1), 145°). In this case, since the molecules in the **C(8)** chain are related by translation, all molecules are parallel. Within these chains, the N···O distance (3.06 Å) is as short as that observed in **2**, but the N(1)–H(2)···O(1) angle (106°) is indicative of a relatively weak interaction. The rather striking similarity of the arrangements in **1a**, **2** and **3** leads us to conclude that either N–H···O or N–H···Cl hydrogen bonds will direct

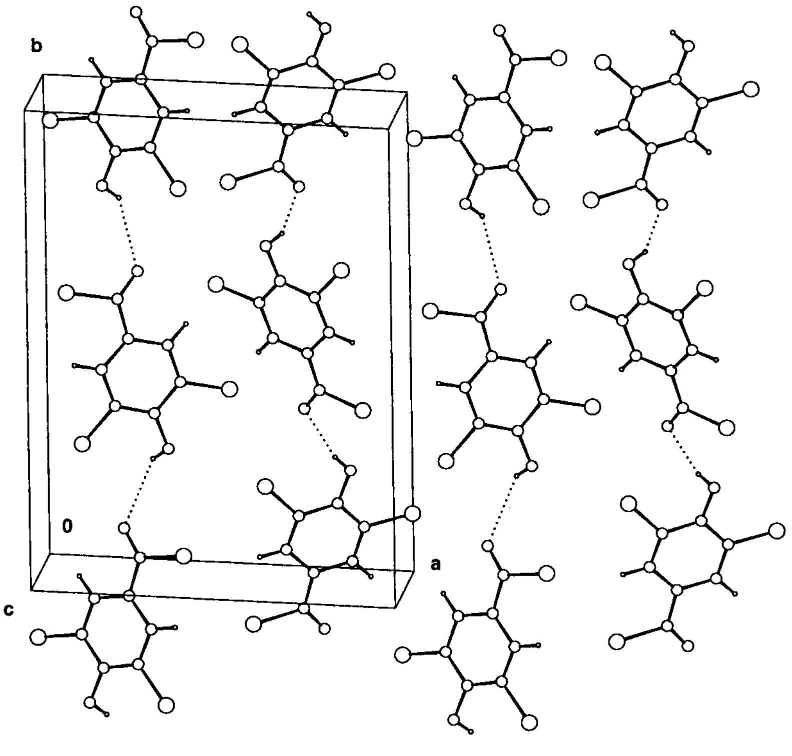

Figure 5. View of the packing of **1a**, showing chains of N–H···O hydrogen bonds.

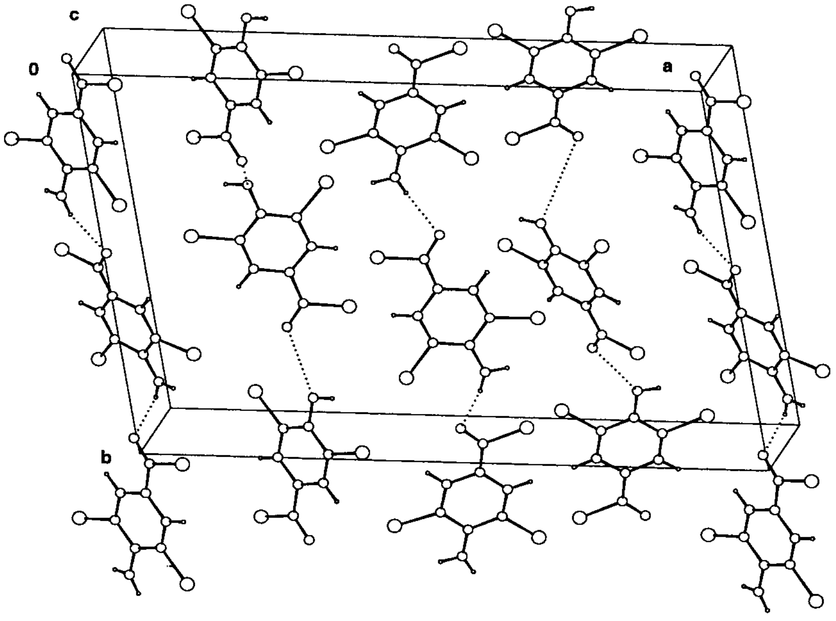

Figure 6. View of the packing of **2**, showing chains of N–H···O hydrogen bonds.

the packing of aminobenzoyl chlorides to a head-to-tail arrangement, which favors short N···O contacts and likely solid-state reactivity. A search of the Cambridge Structural Database, Version 5.18 (October 1999) revealed 33 compounds containing an acid chloride group.[15] None of these, however, also contained an amino moiety. We thus have no molecules with which to compare these unique structures, but it seems likely that there will be persistent interactions of this kind in aminoaroylchlorides. While in-plane attack is not preferred, the only pathways with infinite, short amine-carbonyl carbon contacts are those shown in Figs. 5–7.

Consistent with this hypothesis, the assignment of reaction pathways for **1a** and **2** is consistent with the observed optical properties of the polymer. In any case, thermal reactions may involve rearrangements of groups at distances well over 5 Å.[3,16]

Polymorphism of 1a, 1b and 2

The structural relationship between polymorphs **1a** and **1b** may be understood by examining the interleaving of the hydrogen bonded chains in **1a** and **2** (isomorphous with **1b**). The difference between the interleaving of the chains in **1a** and **2** is shown in Fig. 8. The figure shows the nearly linear chains of **1a** (above), with a repeating 47.2° twist, and, similarly, the nearly linear, but symmetry-independent chains in **2** (below), with alternating approximately parallel (14.1°)—then twisted (47.5°) chains. The chains with the 47.5° twist closely resemble the chains in **1a**. It seems likely that **1a** and **1b** have similar lattice energies, and a search for

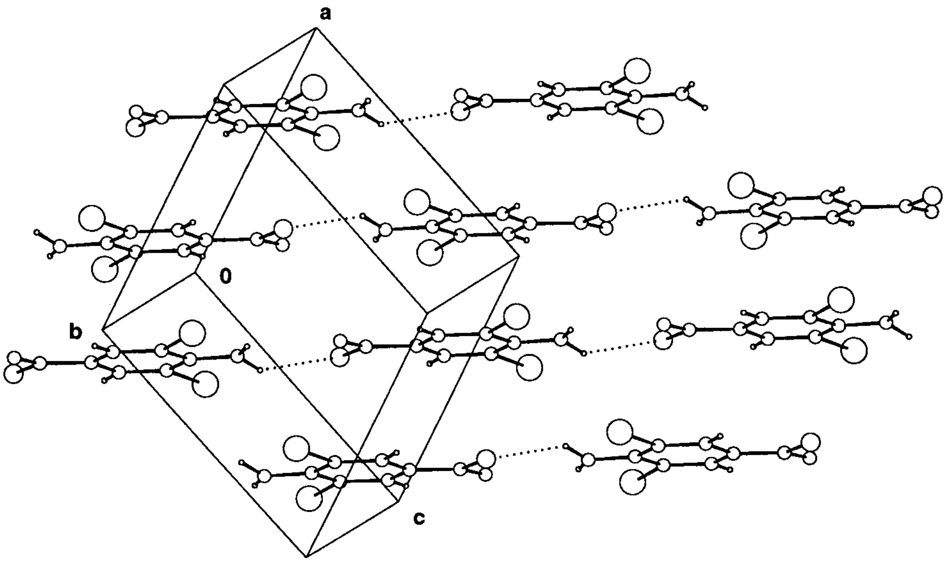

Figure 7. Packing of **3** showing N–H···Cl hydrogen bonds.

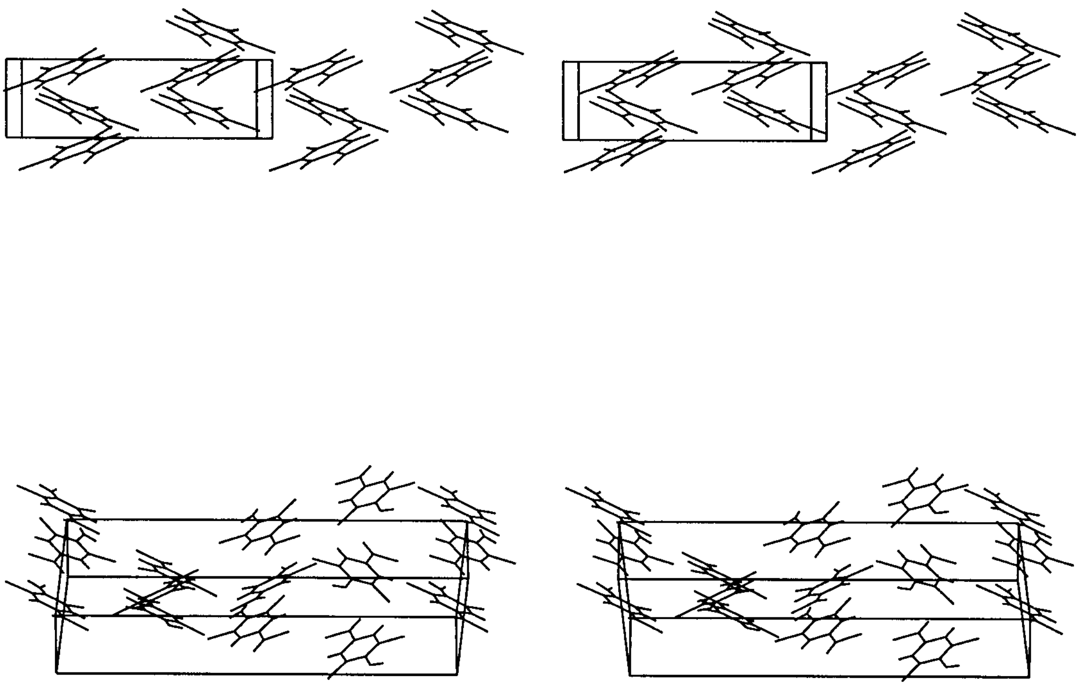

Figure 8. Stereo views of the hydrogen-bonded **C(8)** chains in **1a** (upper stereo pair) and **2** (lower stereo pair).

a polymorph of **2** isomorphous with **1a** might yield positive results. However, we did not discover such a polymorph in our studies.

In conclusion, the polymeric product from the solid-state polymerization of 3,5-dichloro-4-aminobenzoylchloride **1a** has been shown to possess some degree of crystallinity by powder diffraction. Additionally, Morgan demonstrated that the polymer chains grow perpendicular to the needle axis.[9] Oscillation and Weissenberg photographs of 3,5-dichloro- and 3,5-dibromo-4-aminobenzoylchloride indicate that the long needle axis of these crystals corresponds to the crystallographic *c*-axis. Thus, from Morgan's observations we expect the reaction to occur in the *ab*-plane. Figs. 5 and 6, which depict the packing in *ab* crystal planes, along with the putative reaction pathways, support Morgan's observation. Thus, the probable reaction pathway in these materials is 'set up' by **C(8)** hydrogen-bonded chains in each material. The **C(8)** chains lead to both short amine–carbonyl intermolecular contacts and a facile solid-state polymerization to polybenzamides.

Experimental

General

Infrared spectra in the range 4000–200 cm^{-1} were recorded as KBr pellets (3% concentration) on a Perkin–Elmer 683 spectrophotometer. The 1601 cm^{-1} stretch of polystyrene was used as a reference. Melting points were measured using a Fisher Digital Melting Point Analyzer Model 355. A Phillips-Norelco X-ray generator with a Cu K_α source operated at 40 kV and 15 mA was used with Debye-Scherrer and Weissenberg cameras. 3,5-Diiodo-4-aminobenzoic acid and 3,5-dichloro-4-aminobenzoic acid were obtained from Pfaltz and Bauer, Inc; *p*-aminobenzoic acid was obtained from Aldrich Chemical Company.

Purification of carboxylic acids

Carboxylic acids were purified according to the procedure of Perrin et al.[17] The acid was dissolved in 1 M aqueous KOH, decolorizing carbon was added, and the solution was stirred for 15 min. The acid was precipitated from the filtered solution with 2 M aqueous HCl and dried at 80°C.

3,5-Dibromo-4-aminobenzoic acid.[18] To 1.00 g (7.29 mmol) of *p*-aminobenzoic acid dissolved in a minimum of ethanol (~15 mL), a brominating solution (15.00 g (0.13 mol) of KBr in 100 mL of water plus 10.00 g (0.063 mol) bromine) was added dropwise, with constant stirring. The yellow color of the brominating solution continued to disappear until a white fluffy precipitate separated from the solution. The addition of brominating solution was continued until no more product precipitated. A 50 mL portion of water was added; the product was filtered off and washed with a dilute solution of sodium bisulfite followed by water. Recrystallization from ethanol afforded 0.80 g (2.72 mmol, 37.3%) of colorless needles which did not melt below 300°C.

Preparation of 3,5-dihalo-4-aminobenzoylchlorides. All 3,5-dihalo-4-aminobenzoylchlorides were prepared analogously using the following procedure.[19] For example, to a 50 mL round bottom flask fitted with a condenser were added 20 mL of chlorobenzene (Aldrich Chemical Co.) and 2.00 g (9.71 mmol) of 3,5-dichloro-4-aminobenzoic acid. The suspension was held at 90°C in a sand bath. Over a period of 10 min, 3.00 g (14.4 mmol) of phosphorus pentachloride was slowly added to the hot solution which was stirred until it became clear. Slow cooling yielded colorless crystalline needles. The product was then recrystallized from 15 mL of benzene giving 1.50 g (6.68 mmol, 68.8%) of 3,5-dichloro-4-aminobenzoylchloride **1**, m.p.=162°C. (m.p. 3,5-dibromo-4-aminobenzoylchloride 2, 180°C; m.p. 3,5-diiodo-4-aminobenzoylchloride 3, 190°C (decomp.)). The melting point test must be done rapidly because these products tend to polymerize and the polymerized products do not melt. 3,5-Dibromo- and 3,5-dichloro-4-aminobenzoylchloride crystallize as needles elongated along the *c*-axis, but 3,5-diiodo-4-aminobenzoylchloride crystallizes as thin plates. The 3,5-dichloro- derivative crystallizes in two polymorphic modifications. The crystal structure of modification **1b** is isomorphous with the determined structure of the 3,5-dibromo-derivative. The other polymorph **1a** has a similar unit cell to that of **1b**, but with *a* equal to one-half of the value for **1b** and **2**. Both modifications were crystallized from benzene, and the overwhelming majority of crystallizations yielded modification **1b**; production of crystals of **1a** appeared to be a fortuitous occurrence. No reliable synthesis for the preparation of modification **1a** could be created. Cell constants for modification **1b** were determined from 11 reflections and refined 2θ, ω, χ values in the range $9\leq|2\theta|\leq13°$ (λ(Mo K_α=0.71073 Å): a=25.178(5), b=17.708(4), c=3.785(1) Å, and V=1687.79 Å^3; for **1a**, the cell constants were (12±(hkl) and refined 2θ, ω, χ values in the range $11\leq|2\theta|\leq23°$): a=12.599(3), b=17.691(4), c=3.791(1) Å, and V=845.0 Å^3. X-Ray powder diffraction for **1b**: (Å) 6.03m, 5.18w, 4.32m, 4.22s, 4.07s, 3.99w, 3.50s, 3.31ms, 3.20ms, 3.14s, 3.02m, 2.92m, 2.82ms, 2.75ms, 2.54m, 2.46s, 2.40m, 2.33w, 2.23w, 2.03s, 1.87w, 1.80w.

Thermal polymerization of crystalline 3,5-dihalo-4-aminobenzoylchlorides

The crystalline solid was placed in a 1 cm test tube equipped with a side arm. The test tube was heated in a bath of silicone oil and maintained at a constant temperature under dry nitrogen. Depending on the particular experiment the temperature was kept between 95 and 300°C. The contents of the tube became opaque but did not melt. The solid polymer retained the habit of the monomer crystals. In the case of the 3,5-diiodo-derivative, the contents also turned brown. The reason for the color change in the case of the 3,5-diiodo-derivative may indicate decomposition, with partial release of iodine. The reaction could be followed by changes in infrared spectra. The monomer IR spectra show the characteristic doublets of a primary amine. One absorption band of the doublet is near 3500 cm^{-1}, and the other is near 3400 cm^{-1}. A strong absorption near 1740 cm^{-1} due to the C═O stretching frequency is typical of conjugated acid chlorides. The spectra of the polymers show reduced intensity of the primary amine doublet and the growing in of a broad absorption due to the N-arylated amide proton of the polymer, along with replacement of the strong C═O stretch of the acid chlorides near 1740 cm^{-1} by a band characteristic of amides at ~1660 cm^{-1}. The polymerization could be followed more quantitatively by weighing a heated sample after specific times. Owing to the loss of HCl(g), the weight difference may be used to calculate percent conversion. Table 3 illustrates time–temperature-conversion data for compounds **1** and **3**. X-Ray powder patterns taken of poly(3,5-dichloro-*p*-benzamide) derived from the solid-state reaction of **1a** indicate that the polymers are partially crystalline. The powder pattern of the polymer has only four lines (at 6.37, 5.45, 3.73 and 2.75 Å), but these are distinct from the powder pattern of the monomer (vide supra).

X-Ray structure determination

After preliminary studies of **1a**, **2** and **3** by oscillation and Weissenberg techniques, fresh crystals of each were mounted on a Pyrex fiber affixed to a brass pin, then transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2_1 diffractometer. Routine operations were performed as described previously;[20] other operations are described below. The structures were solved using the heavy-atom method; preliminary computational work was carried out using the Enraf-Nonius MOLEN software package.[21] Final refinement was carried out using the Oxford University CRYSTALS package;[22] drawings were produced using CAMERON.[23] The structure analysis of **1a** was complicated by disorder of the molecule about a pseudo-mirror plane at z=0 in $Pna2_1$. Atom Cl(2) was sited on the pseudo-mirror plane, and refined at full occupancy. Other atoms in each component were constrained to have the same occupancy, with the occupancies of both components constrained to sum to 1.0; the final value for the major component was 0.753(8). The minor component was constrained to be related to the major component by the pseudo-mirror; isotropic displacement parameters in the major and minor components were constrained to be equal. The C(7)–Cl(2) distance was restrained to 1.79(3) Å, and the C–C distances in the phenyl moiety were restrained to 1.397(50) Å. The phenyl group was restrained to be planar within 0.05 Å. The final refinement included anisotropic displacement parameters for the major component Cl atoms, and isotropic displacement parameters for other nonhydrogen atoms. The coordinates of the H atom attached to N were refined (U_{iso} fixed at 0.05); phenyl H atoms were fixed at calculated positions (494 data for which $I>1.96\sigma(I)$; 70 parameters). The enantiopole parameter could not be successfully refined using the present data set. The final refinement for **2** was carried out using anisotropic displacement parameters for Br, N, O and Cl; C atoms were refined using isotropic displacement parameters (1256 data for which $I>1.96\sigma(I)$; 156 parameters). Phenyl hydrogen atoms were included at fixed positions. H atoms attached to N were restrained (N–H, 0.88(5) Å; H–N–H, 109.5(5), ΔU_{iso} (N(1)–H(1)=0.0(5)). Only one of the two H atoms attached to N(1) could be located. The absolute polarity of the crystal could not be established; a value of 0.43(8) for the enantiopole parameter was obtained. For **3**, a linear decay correction (42.4% maximum) was applied to the data. The final refinement was carried out using anisotropic displacement parameters for all nonhydrogen atoms (1445 data for which $I>1.96\sigma(I)$; 118 parameters). Phenyl hydrogen atoms were included at fixed positions, while H atoms attached to N were restrained (N–H, 0.88(5) Å; H–N–H, 109.5(5)). Coordinates for the structures of **1a**, **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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