J. Am. Chem. Soc. 1989, 111, 6757-6764

Other products listed in Chart I were identified upon comparison of their NMR and/or MS spectra with those of authentic samples; ^{13}C NMR chemical shifts agreed within ±0.1 ppm with literature data.[61,65]

Kinetic Measurements. In the majority of cases, absolute rates were determined under pseudo-first-order conditions, with the dioxirane in large excess over the hydrocarbon initial concentration. At zero time an aliquot (0.2 mL) of a thermostated solution of the given hydrocarbon (usually 0.15–0.20 M), also containing the calibration standard Freon A112 (see above), was added to 2 mL of a 0.3–0.4 M dioxirane **1b** solution (also thermostated). Aliquots (10 μL) of the reaction solution were withdrawn periodically, quenched with 0.1 mL of ca. 0.15 M n-Bu$_2$S or p-MeC$_6$H$_4$SMe in CH$_2$Cl$_2$, and the samples analyzed by GLC. Linear ln (C_0/C) vs time plots were obtained for hydrocarbon consumption to over 70% reaction, yielding k_1 (s^{-1}); from this, and the known dioxirane initial concentration (iodometric titre), k_2 (M^{-1} s^{-1}) values could be estimated (Table II). In competition kinetics essentially the same procedure was followed, but now two hydrocarbons (A and B) in the same solution, were allowed to react with excess dioxirane, making ([A]$_0$ + [B]$_0$) $\ll$ [dioxirane]$_0$). Aliquots were withdrawn (and quenched) within the first 15–30% of reaction; GLC analyses of these allowed to obtain relative rate (k_r) data as k_A/k_B = log ([A]/[A]$_0$)/(log ([B]/[B]$_0$). In each experiment, at least three values were measured and averaged (estimated error $\leq \pm 8\%$).

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Cyano--Halogen Interactions and Their Role in the Crystal Structures of the 4-Halobenzonitriles

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Abstract: A survey of 73 intermolecular cyano--halogen contacts retrieved from 124 crystal structures in the Cambridge Structural Database has revealed that short C≡N--X contacts are commonly found when X = Cl and Br, with the linearity of the C≡N--X angle being a particularly prominent feature when X = Br. These contacts arise due to halogen polarizability and are also found when X = I. The crystal packing of several simple halogen–cyano compounds may be rationalized on the basis of a linear secondary motif built up via these C≡N--X contacts. These structures may be nominally visualized in terms of parallel or antiparallel alignment of the linear motifs. However, a closer examination of some of the "model" structures evoked serious questions about their reliability, and thus the crystal structures of 4-chloro-, 4-bromo-, and 4-iodobenzonitrile were reinvestigated. 4-Chlorobenzonitrile exists as two polymorphs, the previously reported centrosymmetric form ($P2_1/c$, Z = 4) with antiparallel chains of molecules linked by linear C≡N--Cl contacts [N--Cl, 3.350 (2) Å] and a new noncentrosymmetric, polar form (Pc, Z = 2) with parallel, zigzag chains [N--Cl, 3.370 (4) Å; C≡N--Cl, 87.7 (3)°]. In the centrosymmetric form, the alignment of the linear chains is variable and often less than perfect, leading to unusual features in the diffraction pattern and to a crystal structure that is partially "disordered" (C≡N versus Cl). In contrast, the crystal structure of the noncentrosymmetric form is not disordered. The centrosymmetric form converts to the noncentrosymmetric form upon grinding; this interconversion has been followed by X-ray powder diffraction and Second Harmonic Generation techniques. 4-Bromobenzonitrile exists only as a noncentrosymmetric, polar form (Am, Z = 2) with parallel chains of molecules connected by short, linear C≡N--Br contacts of 3.249 (5) Å. Some disordering of the Br and C≡N groups was noted here, indicating again that the alignment of the chains is not perfect. In the structure of 4-iodobenzonitrile, the linear chains have very short C≡N--I contacts of 3.127 (4) Å and pack in an ordered, antiparallel fashion in a centrosymmetric space group ($I2/a$, Z = 4). However, there is no evidence of misalignment of linear motifs here. The crystallographic anomalies encountered in this study emphasize that the tertiary interactions that link secondary motifs in organic solids may be very subtle, rendering difficult the deliberate design or engineering of their crystal structures.

The stabilizing role of weak intermolecular interactions in the crystal structures of molecular solids has elicited much recent interest.[1-5] An appreciation of interactions such as C–H--O, C–H--N, C–H--halogen, halogen--halogen, halogen--O, halogen--S, N--S, and S--S may be quite useful in efforts at predicting and designing new crystal structures.[6-12] Although such heteroatom interactions are very weak, they are directional in nature and are therefore able to steer or direct molecules to predictable packing modes characterized by recurring geometrical patterns. Construction of such molecular patterns is accordingly a convenient first step in crystal engineering. Of course, the dissection of a three-dimensional crystal structure into modular units is a subjective exercise, but it is convenient to define these secondary units

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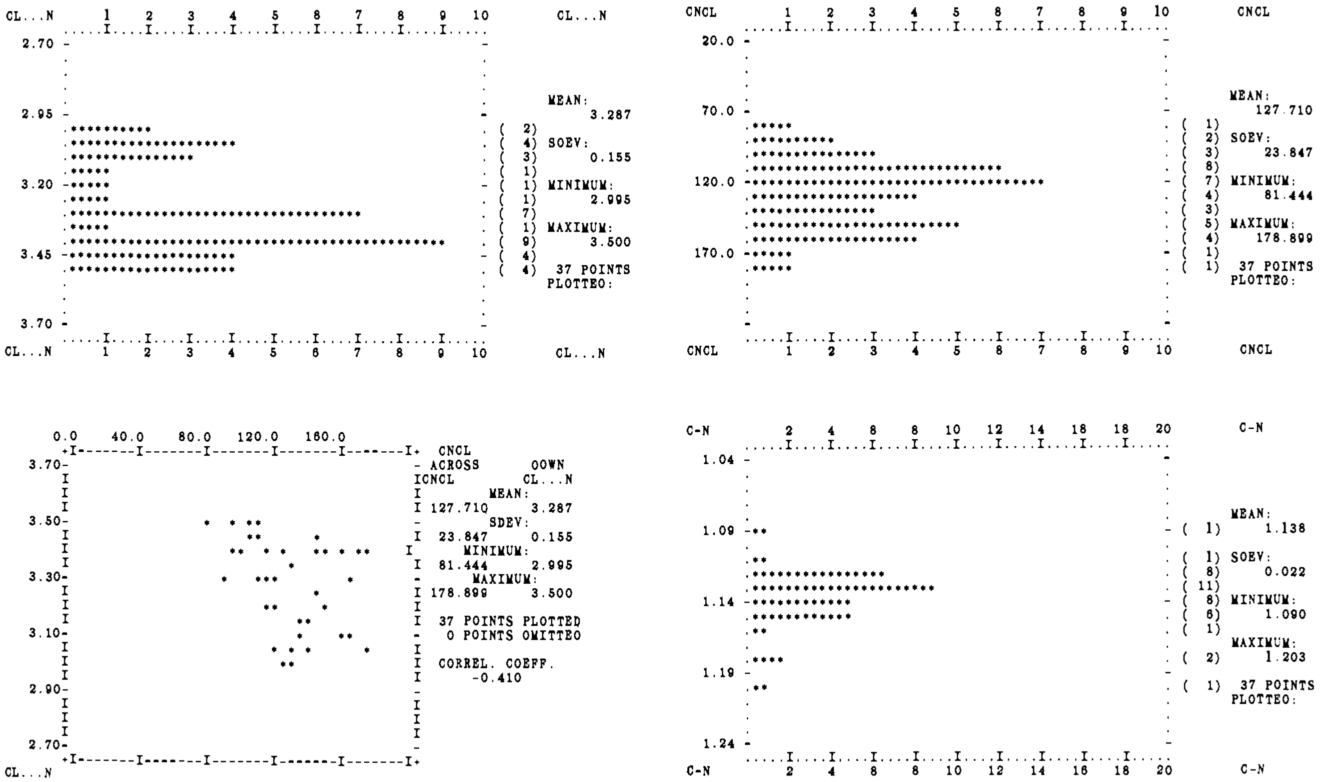


Figure 1. Some geometrical parameters for CN--Cl contacts retrieved from the Cambridge Database. From top left clockwise, histogram of N--Cl lengths, histogram of C≡N--Cl angles, histogram of C≡N lengths, scatter plot of N--Cl length versus C≡N--Cl angle.

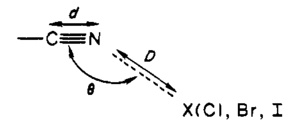
in terms of directional heteroatom interactions and to synthesize them with isotropic van der Waals forces to yield the tertiary or complete crystal structure.

Charting these patterns of heteroatom interactions has been greatly facilitated by the Cambridge Structural Database,[13,14] the third and most recent version of which may be used to define intermolecular connectivities. The database now contains more than 70 000 entries, and it is possible to evaluate structural conjectures critically because of the availability of statistically significant amounts of data. In this paper, we have examined the geometrical characteristics of the C≡N--X (X = Cl, Br, I) interaction in organic crystals and have reexamined the prototype compounds, 4-chloro-, 4-bromo-, and 4-iodobenzonitrile whose crystal structures are subtle despite the obvious simplicity of their molecular structures.

This study was prompted by the observation that crystalline powders of 4-chlorobenzonitrile exhibit a weak and variable Second Harmonic Generation (SHG), which is seemingly incompatible with its centrosymmetric space group, while the crystal structure of 4-bromobenzonitrile does not fully account for some of its physical properties. These observations were part of a larger screening program aimed at the identification of new crystalline materials for nonlinear optics. While it was possible in this program to identify several compounds with promising optical properties, it was felt that a systematic study of the intermolecular interactions in these crystals would lead to a better understanding of, and ultimately to a predictive control of, the packing of secondary motifs in such molecular crystals.

Results and Discussion

(a) Cyano--Halogen Interactions. The existence of short C≡N- -X contacts was first postulated by Hassel[15,16] and much early work was reviewed by Britton,[17,18] who determined the crystal structures of several simple cyano–halogen compounds. There is some question as to whether a van der Waals radius of 1.50 (Pauling), 1.55 (Bondi), or 1.57 Å (Kitaigorodskii) for nitrogen is a systematically underestimated value because of the frequent occurrence of weak but specific heteroatom contacts, such as the N--X ones discussed here. One of the advantages of working with the Cambridge Database is that it is not necessary to prejudge the issue with an arbitrary choice of atomic radii. Rather, a comparative survey of structural data should reveal what is and what is not a significant intermolecular interaction. This is a more flexible approach, expected to discriminate between directional forces, chemical forces, and isotropic close-packing effects.



Retrieval from the Dec 1988 update of the Cambridge Database (version 3.3; 69691 entries) of error-free (0.02-Å level), diffractometer-data crystal structures of cyano compounds containing chlorine either in the same molecule or in a distinct molecule (solvates, complexes, etc.) resulted in 76 entries. A similar search for cyano–bromo compounds resulted in 48 entries. Only 16 such cyano–iodo compounds were obtained. The program GSTAT88 was used to calculate all independent intermolecular C≡N--Cl contacts less than 3.5 Å. There were 37 such contacts, and Figure 1 shows histograms of the N--Cl (*D*) and C≡N (*d*) distances and the C≡N--Cl angle (*θ*). A scatterplot of *D* versus *θ* is also given. Figure 2 is a graphical representation of the corresponding analysis for 36 C≡N--Br contacts less than 3.8 Å.

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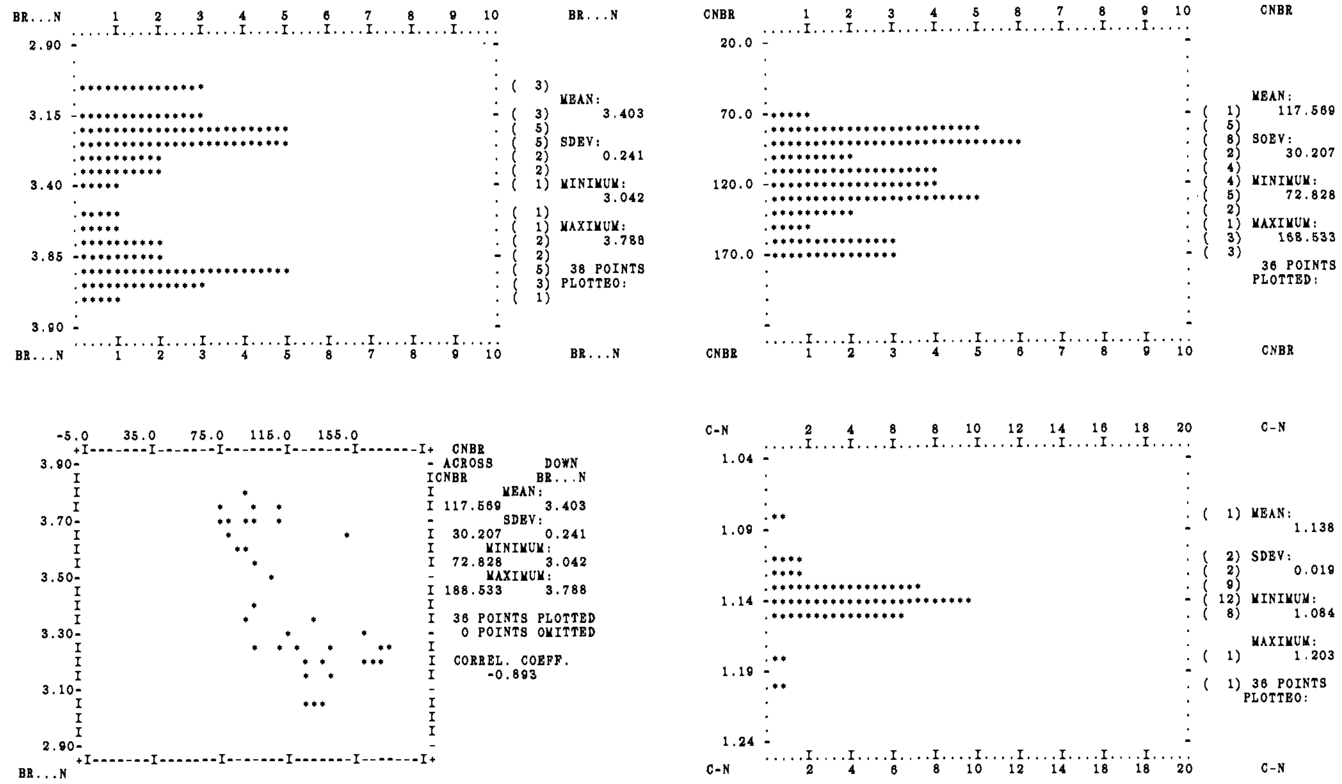

Figure 2. Some geometrical parameters for CN--Br contacts retrieved from the Cambridge Database. From top left clockwise, histogram of N--Br lengths, histogram of C≡N--Br angles, histogram of C≡N lengths, scatterplot of N--Br length versus C≡N--Br angle.

Figure 1 shows that, even if conservative values of the van der Waals radii (N, 1.50 Å; Cl, 1.75 Å) are used, a significant number of C≡N--Cl contacts would have to be considered "short". The histogram of these contacts in fact reveals the existence of two maxima, the first at around 3.40 Å corresponding to a "normal" N--Cl contact and the second at around 3.00 Å corresponding to a short contact. Perhaps, the presence of the maximum at 3.40 Å indicates that the van der Waals radii of either or both N and Cl used above are slightly underestimated. However, it should be emphasized that any of these isotropic radii are empirical quantities that permit only an approximate rationalization of nonbonded distances in crystals. This is true even for the various anisotropic radii that have been proposed for these atoms.[19,20] We feel that the use of any one consistent set of radii is adequate. What are of more significance are the chemical factors that lead to these anomalously short N--Cl distances.

The histogram of the C≡N--Cl angle (Figure 1) is seemingly featureless and shows that the variation in this angle is between 80° and 180°. There has been some discussion regarding the linearity of this C≡N--Cl contact. It has been argued[21] that, if the contact is of the type $^{+}X\text{-}C{\equiv}N^{-}\text{--}{}^{+}X\text{-}C{\equiv}N^{-}$, a linear arrangement should be preferred but that, if it were of the type $^{+}X\text{-}C^{-}{=}N\text{—}X^{+}\text{-}C^{-}{=}N$, the contact should be bent with an optimal C≡N--Cl angle of 120°. The scatterplot of N--Cl distance versus C≡N--Cl angle shows, in fact, that the shorter contacts are in general more linear.

The corresponding statistics for C≡N--Br contacts offer much additional insight. The trends described above for C≡N--Cl contacts, some of which might be considered uncertain, are now unequivocal. There is no doubt about the existence of two maxima in the histogram of N--Br nonbonded distances; the normal and short contacts are distinct and well-separated. The first maximum corresponds to the normal contact and peaks at around 3.70 Å because of the larger size of the Br atom relative to Cl. The second maximum occurs at around 3.20 Å, which is almost the same as that obtained for N--Cl contacts. It is significant that the shorter N--Cl and N--Br contacts are of almost equal lengths despite the differing sizes of Br and Cl. These observations support the view that the longer N--Cl and N--Br contacts are indeed normal or of the van der Waals type while the shorter ones are the result of atomic polarization. In fact, a similar situation arises when comparing Br--Br and Cl--Cl contacts. The shortest intermolecular Cl--Cl contact in crystalline Cl_2 is 3.27 Å, but the corresponding shortest Br--Br contact in the isomorphous, crystalline Br_2 is as short as 3.31 Å.[22]

While the histogram of the C≡N--Br angle is again not very informative, displaying an overall angular variation between 70° and 180°, the scatterplot of C≡N--Br angle versus N--Br distance separates the two populations and shows clearly that the shorter contacts ($D < 3.30$ Å) are invariably associated with a greater degree of linearity ($\theta > 120°$). There is but a lone outlier (BRMALN; bromomalononitrile)[23] with N--Br = 3.65 Å and C≡N--Br = 149.1°. Significantly, this crystal structure has a second N--Br contact with a distance of 3.26 Å and an angle 108.2°. Neither of these contacts conforms to the trends described above, and it is possible that the small molecular size of this compound imposes additional constraints on the packing. Quantitatively too, the correlation of nonbonded distance N--X with angle C≡N--X is much more satisfactory for Br (−0.693) than it is for Cl (−0.410), revealing the importance of atomic polarizability in establishing these contacts. Unfortunately, the number of iodo–cyano compounds with sufficient precision does not enable an extension of this aspect of the study to iodo compounds.

These results on the geometrical preferences of N--Cl and N--Br compounds help in rationalizing many earlier crystallographic observations. The sheet structure of 2,4,6-trichlorobenzonitrile, CLBECN01, is stabilized by short N--Cl contacts of 3.22 Å accounting for the adoption of a 4-Å short axis by this compound.[24] The importance of molecular polarization in N--X contacts is reflected in the fact that short N--Cl contacts are observed in

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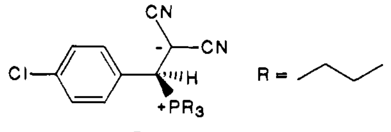
Table I. Symmary of the Crystallographic Information for the 4-Halobenzonitriles

	IBzCN	BrBzCN	ClBzCN		
			form I		
			good crystal	anomalous crystal	form II
formula	C_7H_4IN	C_7H_4BrN	C_7H_4ClN	C_7H_4ClN	C_7H_4ClN
formula wt	229.02	182.02	137.57	137.57	137.57
crystallization method	sublimation	sublimation	sublimation	sublimation	ethanol solution
color	colorless	colorless	colorless	colorless	colorless
size, mm	0.06 × 0.19 × 0.39	0.24 × 0.11 × 0.45	0.24 × 0.45 × 0.45	0.19 × 0.32 × 0.40	0.09 × 0.33 × 0.45
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$I2/a$	Am	$P2_1/c$	$P2_1/c$	Pc
a, Å	8.961 (2)	4.097 (1)	4.038 (1)	4.028 (1)	3.937 (1)
b, Å	10.575 (2)	8.538 (2)	16.657 (2)	16.660 (5)	6.474 (1)
c, Å	7.679 (2)	9.490 (2)	9.504 (1)	9.500 (2)	12.438 (3)
β, deg	104.01 (2)	90.83 (1)	90.05 (1)	90.09 (1)	90.05 (2)
V, Å^3	706.0	331.9	639.3	637.5	317.0
T, °C	−100	−100	−100	−100	−100
Z	4	2	4	4	2
ρ_{calc}, g cm^{-3}	2.154	1.821	1.429	1.433	1.441
μ, cm^{-1}	43.90	60.29	4.89	4.90	4.93
data collected	1832	854	1756	3458	1695
octants	$\pm h,+k,+l$	$\pm h,-k,\pm l$	$-h,-k,\pm l$	$-h,\pm k,\pm l$	$\pm h,\pm k,-l$
transmission factors	0.46–0.77	0.23–0.34			
σ cutoff	3.0	3.0	2.0	2.0	3.0
unique data	754	797	993	881	636
parameters	52	55	98	98	96
R, R_w	0.018, 0.022	0.028, 0.033[a]	0.043, 0.047	0.039, 0.046	0.034, 0.040[b]
max residual density, e Å^{-3}	0.98	1.05	0.28	0.33	0.25
located near	I	Br	C(7), N	C(1), Cl	Cl

[a] Enantiomorphic structure refined to $R = 0.036$, $R_w = 0.045$. [b] Enantiomorphic structure refined to $R = 0.035$, $R_w = 0.041$.

chlorocyanoacetylene[25] but not in dichlorofumaronitrile.[26] In the phosphorus ylide, BYMBPY, the carbon attached to the cyano



BYMBPY

group bears a formal negative charge, stabilizing the N--Cl contact of 3.29 Å.[27] The crystal structure of the 2,5-Cl_2TCNQ/TTF complex, BABCIQ, is but a slight perturbation of the TCNQ/TTF structure, but the perturbation is such that an intermolecular N--Cl contact of 3.41 Å is formed.[28] The distinction between the abilities of Br and Cl to form short contacts to cyano groups is borne out in the crystal structures of tricyanobromomethane and tricyanochloromethane.[29] While the former compound exhibits very short N--Br contacts of 3.03 Å, the latter compound is isomorphous with 1,1,1-tricyanoethane.[29] The existence of such a chloro–methyl exchange is clear evidence that the chloro group behaves in a space-filling manner, that is, according to its volume, size, and shape.[30–32] In contrast, the completely different crystal structure of the bromo compound is controlled by directional N--Br interactions.

(b) Crystal Structures of the 4-Halobenzonitriles. The structures of 4-chloro-(ClBzCN),[33] 4-bromo- (BrBzCN),[34] and 4-iodobenzonitrile (IBzCN)[35] were originally determined by Britton. These analyses are of limited accuracy. As in the case of the cyanogen halides[21] and the halocyanoacetylenes,[25] these structures are characterized by a linear array of molecules strung together by short N--X (X = Cl, Br, I) interactions. Not surprisingly, such N--X contacts are not observed in the structure of 4-fluorobenzonitrile (FBzCN).[36] These studies showed the presence of nonbonded N--X contacts of 3.31, 3.27, and 3.18 Å for ClBzCN, BrBzCN, and IBzCN, respectively. It is very convenient to identify this linear molecular array as the secondary motif in these structures. The tertiary structure may be considered as arising from a close packing of these linear rods. This may be accomplished in one of two ways. The linear arrays are arranged in either a parallel (BrBzCN, low-temperature iodocyanoacetylene) or an antiparallel fashion (ClBzCN, IBzCN, cyanogen chloride, cyanogen bromide, monoclinic iodocyanoacetylene). The parallel arrangement is associated with noncentrosymmetry and crystal polarity, while the antiparallel arrangement is centrosymmetric.

We noted that the crystal structures of ClBzCN, BrBzCN, and IBzCN appeared to suffer from numerous problems, some of which were pointed out by Britton et al. In all cases, the refinements were poor (high R indices); in no case could the hydrogen atoms be located and refined. In BrBzCN, the C–N bond length had to be constrained, while in IBzCN the bond distances associated with the CN group were abnormal (C–C short, C–N long) but were explained as due to a large contribution of the $^{+}I(C_6H_4){=}C{=}N^{-}$ resonance form. This latter structure was refined using visually determined intensities and was therefore considered to be unreliable; however, a confirmation of the presence of this resonance form would have been extremely interesting. Furthermore, we discovered that a powdered sample of ClBzCN had a weak and variable SHG signal, not possible if the structure were truly centrosymmetric (reported space group $P2_1/c$). Finally, crystals of ClBzCN, grown by sublimation, did not show $2/m$ symmetry but did exhibit a variety of habits including many with curved faces and/or very thin needles protruding from the corners of some of the larger crystals. These perplexing observations caused us to reexamine the crystal structures of these three compounds.

Crystal Structure of 4-Iodobenzonitrile. The refinement of this structure with low-temperature data was perfectly straightforward; even the hydrogen atoms were refined to yield acceptable positional

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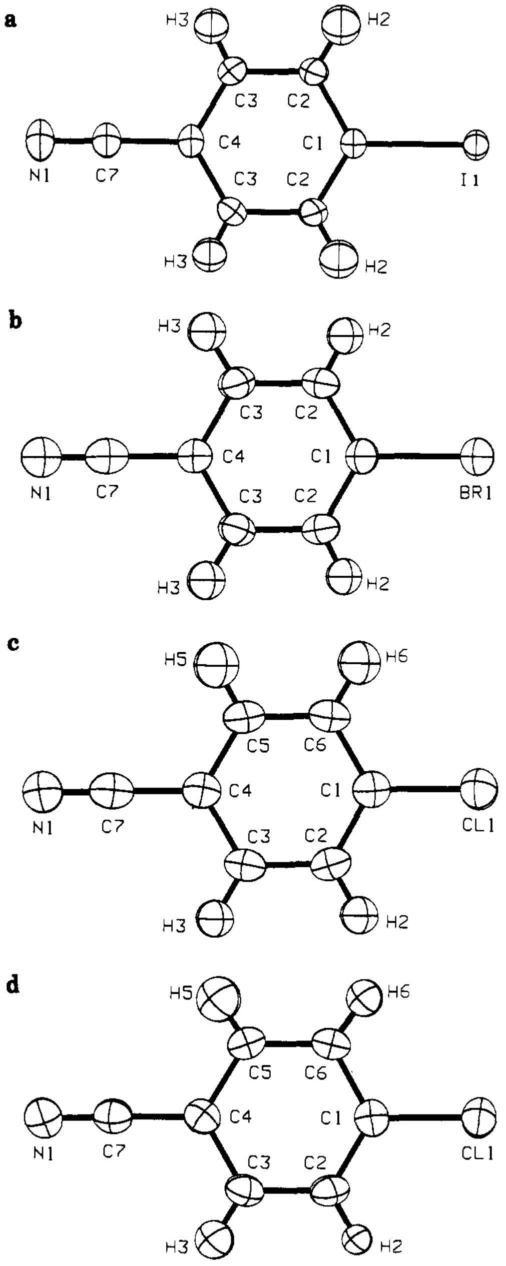

Figure 3. ORTEP drawings of the molecules with their atom-numbering schemes. (a) 4-Iodobenzonitrile, space group *I*2/*a*. The molecule has crystallographic 2-fold symmetry. (b) 4-Bromobenzonitrile, space group *Am*. The molecule has crystallographic mirror symmetry perpendicular to the molecular plane. (c) 4-Chlorobenzonitrile, form I, space group *P*2₁/*c*. (d) 4-Chlorobenzonitrile, form II, space group *Pc*.

and thermal parameters. The packing is that described earlier by Schlemper and Britton,[35] i.e., antiparallel chains along the crystallographic 2-fold axis. The I--N contact, 3.127 (4) Å, is very short. However, the unusual bond lengths originally found for the nitrile group (C–C, 1.370 (12) Å; C–N, 1.199 (12) Å), which suggested a major contribution from the $^+I(C_6H_4)=C=N^-$ resonance form, were not substantiated. The C–C and C–N bond lengths were found to be completely normal: 1.438 (5) and 1.142 (6) Å.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for the 4-Halobenzonitriles

atom	*X*	*Y*	*Z*	B_{iso}
(a) 4-Iodobenzonitrile, IBzCN				
I(1)	0.25	0.52751 (2)	0.0	2.0 (1)^a
N(1)	0.25	−0.1768 (3)	0.0	3.2 (1)^a
C(1)	0.25	0.3295 (3)	0.0	1.8 (1)^a
C(2)	0.1208 (3)	0.2644 (3)	−0.0945 (3)	2.1 (1)^a
C(3)	0.1209 (3)	0.1332 (3)	−0.0942 (3)	2.2 (1)^a
C(4)	0.25	0.0672 (3)	0.0	2.1 (1)^a
C(7)	0.25	−0.0688 (4)	0.0	2.4 (1)^a
H(2)	0.035 (4)	0.307 (4)	−0.157 (5)	3.6 (8)
H(3)	0.041 (4)	0.098 (4)	−0.158 (4)	2.8 (7)
(b) 4-Bromobenzonitrile, BrBzCN				
Br(1)	0.0	0.0	0.5	3.0 (1)^a
N(1)	0.7984 (15)	0.0	−0.1702 (6)	4.0 (1)^a
C(1)	0.2018 (13)	0.0	0.3212 (5)	2.5 (1)^a
C(2)	0.2784 (10)	0.1412 (4)	0.2581 (4)	2.8 (1)^a
C(3)	0.4396 (10)	0.1417 (5)	0.1309 (4)	2.9 (1)^a
C(4)	0.5157 (16)	0.0	0.0665 (6)	2.5 (1)^a
C(7)	0.6824 (18)	0.0	−0.0681 (7)	3.3 (2)^a
H(2)	0.252 (11)	0.233 (6)	0.298 (5)	2.9 (9)
H(3)	0.506 (12)	0.241 (6)	0.087 (5)	3.3 (9)
(c) 4-Chlorobenzonitrile, ClBzCN, Form I, Good Crystal				
Cl(1)	0.36139 (15)	0.12847 (5)	−0.05359 (6)	3.5 (1)^a
N(1)	−0.4473 (5)	0.1207 (2)	0.6038 (2)	4.0 (1)^a
C(1)	0.1697 (5)	0.1271 (2)	0.1109 (2)	2.7 (1)^a
C(2)	0.1011 (9)	0.0536 (2)	0.1729 (4)	3.0 (1)^a
C(3)	−0.0632 (9)	0.0514 (2)	0.3006 (4)	3.0 (1)^a
C(4)	−0.1527 (5)	0.1237 (2)	0.3650 (2)	2.7 (1)^a
C(5)	−0.0777 (9)	0.1965 (2)	0.3024 (4)	3.0 (1)^a
C(6)	0.0830 (9)	0.1986 (2)	0.1742 (4)	3.0 (1)^a
C(7)	−0.3213 (6)	0.1221 (2)	0.5001 (3)	3.3 (1)^a
H(2)	0.173 (8)	0.004 (2)	0.133 (3)	3.0 (6)
H(3)	−0.131 (8)	−0.002 (2)	0.343 (3)	3.0 (6)
H(5)	−0.118 (9)	0.247 (2)	0.348 (4)	4.4 (8)
H(6)	0.112 (8)	0.251 (2)	0.124 (3)	3.9 (8)
(d) 4-Chlorobenzonitrile, ClBzCN, Form I, Anomalous Crystal				
Cl(1)	0.36133 (18)	0.12824 (7)	−0.05405 (8)	3.2 (1)^a
N(1)	−0.4441 (6)	0.1211 (3)	0.6023 (3)	3.5 (1)^a
C(1)	0.1695 (6)	0.1264 (3)	0.1118 (3)	2.3 (1)^a
C(2)	0.1008 (14)	0.0535 (3)	0.1719 (7)	2.6 (1)^a
C(3)	−0.0638 (14)	0.0516 (3)	0.3023 (8)	2.8 (1)^a
C(4)	−0.1526 (6)	0.1232 (3)	0.3662 (3)	2.3 (1)^a
C(5)	−0.0772 (13)	0.1969 (3)	0.3021 (7)	2.5 (1)^a
C(6)	0.0822 (14)	0.1987 (3)	0.1768 (8)	2.6 (1)^a
C(7)	−0.3225 (7)	0.1221 (3)	0.5030 (3)	3.1 (1)^a
H(2)	0.175 (8)	0.006 (2)	0.141 (3)	1.3 (6)
H(3)	−0.138 (7)	0.002 (2)	0.336 (3)	1.0 (6)
H(5)	−0.089 (12)	0.252 (4)	0.368 (5)	7.0 (15)
H(6)	0.092 (10)	0.255 (3)	0.115 (4)	5.0 (12)
(e) 4-Chlorobenzonitrile, ClBzCN, Form II				
Cl(1)	0.5	−0.1897 (2)	0.0	3.2 (1)^a
N(1)	−0.2860 (10)	0.5660 (6)	0.3255 (3)	3.7 (1)^a
C(1)	0.3068 (9)	−0.0031 (6)	0.0797 (3)	2.4 (1)^a
C(2)	0.2409 (10)	0.1896 (7)	0.0373 (3)	2.8 (1)^a
C(3)	0.0829 (10)	0.3364 (6)	0.1012 (3)	2.8 (1)^a
C(4)	−0.0068 (10)	0.2877 (6)	0.2068 (3)	2.5 (1)^a
C(5)	0.0624 (11)	0.0915 (7)	0.2479 (4)	2.7 (1)^a
C(6)	0.2185 (11)	−0.0535 (7)	0.1842 (4)	2.7 (1)^a
C(7)	−0.1660 (11)	0.4422 (6)	0.2737 (4)	2.9 (1)^a
H(2)	0.326 (9)	0.230 (6)	−0.029 (3)	2.0 (8)
H(3)	0.052 (12)	0.475 (7)	0.075 (4)	3.3 (9)
H(5)	−0.013 (14)	0.064 (8)	0.310 (5)	4.2 (12)
H(6)	0.294 (11)	−0.182 (7)	0.207 (4)	2.8 (9)

[a] Refined with anisotropic thermal parameters.

Crystal Structure of 4-Bromobenzonitrile. The refinement of this structure also proceeded uneventfully. The unit cell was defined to facilitate the comparison between this structure and that of the chloro analogue; hence, the space group is given as *Am* instead of *Cm*. The crystal structure is essentially that determined by Britton et al.[34] except that the bond distances and angles are much improved (see Table II; atom numbering is shown in Figure 3). The molecules, which reside across crystallographic mirror planes, form chains through short N--Br contacts (N--Br, 3.249 (5) Å; C–N--Br, 168.8 (3)°), which then stack so that all of the CN groups point in the same direction (parallel packing). The C–N bond, 1.085 (9) Å, is much shorter than the expected value, 1.138 Å, which is the mean value of the 36 nitrile groups displayed in Figure 2. A plausible explanation for this shortening is a small amount of disorder between the Br and CN groups. This disordering, particularly if it involved the reversal of an entire layer (antiparallel packing), would also explain the streaks seen by

Britton et al., along the b^* axis of their Weissenberg photographs and the anomalous pyroelectric measurements of this compound reported recently by Weiss et al.[37]

Crystal Structure of Form I of 4-Chlorobenzonitrile. Crystals of this form were grown by sublimation. As described above, they exhibited a wide variety of habits but lacked the expected $2/m$ symmetry. Although the different habits could have been an indication of polymorphism, a powder diffraction pattern of the combined sublimate proved that all the crystals (within the detection limits of 2–3%) had the same structure, i.e., that determined by Britton et al.[33] The crystal initially selected for study was an irregular block, and while the initial examination of the crystal on the diffractometer suggested that it was an acceptable single crystal, several unusual features were noted during the data collection, which ultimately led to a more careful examination of the crystal. The most noticeable feature was that a number of the low-angle peaks were not centered in the data-collection profiles. Careful ω scans of these reflections revealed that their widths were both variable and often much larger than scans of normal reflections: abnormal (0,–1,–1) and (0,–3,–1) reflections had widths of 0.67 and 0.36 deg, respectively, while a normal (0,–2,–1) reflection measured 0.25 deg. Also, careful centering of these reflections yielded calculated indices in which the k value deviated slightly from an integer value: for example, the (0,–1,–1) and (0,–3,–1) reflections were calculated as (0.00,–0.97,–1.00) and (0.00,–3.02,–1.00), respectively. Having no immediate explanation for this behavior, a search was begun to find a better crystal. Eventually, one was found. The data collection and structure refinement on this new crystal appeared to proceed in an uncomplicated fashion and resulted in the structure shown in Figure 3 and 4. The packing is that described by Britton et al., i.e., rows of molecules with N--Cl contacts which pack in an antiparallel fashion with two layers having their CN groups pointing first in one direction and then two layers in which the CN groups point in the opposite direction.

The major difference between the unit cell of this structure and that of BrBzCN is that the b axis has doubled in length to accommodate the antiparallel layers. The crystallographic mirror plane that existed in the BrBzCN (space group Am) becomes a pseudomirror plane in ClBzCN at $y = 0.125$. The remnant of the A centering is also seen in ClBzCN data: when k is even and $k/2 + 1 = 2n$, the intensities tend to be very strong; when k is even and $k/2 + 1 = 2n + 1$, the intensities are very weak; for the remaining reflections where k is odd, the intensities are intermediate in value. Basically, the even k reflections derive their intensity from the "average" structure, one in which the Cl and CN groups would be totally disordered, while the odd k reflections have intensity primarily because of the antiparallel stacking of the layers of molecules. Once this is appreciated, the unusual observations about the first crystal take on more significance, for it is the odd k reflections that are anomalous, with the calculated indices thus suggesting that some contribution to the intensities of the odd reflections may come from a modulation of the layers stacked along b.

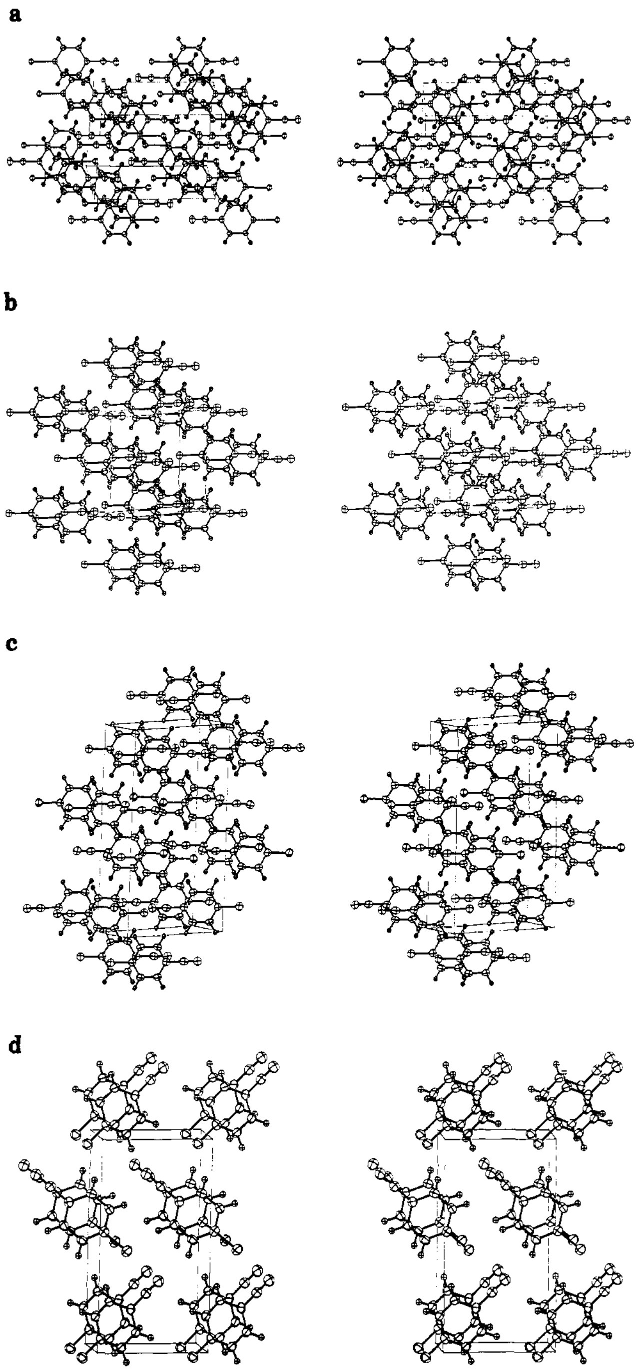

Figure 4. Packing diagrams for the four crystal structures. (a) 4-Iodobenzonitrile, antiparallel structure. The molecules reside on crystallographic 2-fold axes parallel to the b axis (horizontal). The view is perpendicular to the molecular plane. (b) 4-Bromobenzonitrile, parallel structure. The view is nearly parallel to the crystallographic mirror planes which are perpendicular to the b axis (vertical). (c) 4-Chlorobenzonitrile, form I, antiparallel structure. The view is similar to that of the 4-bromobenzonitrile shown in (b). The b axis is again vertical, but what were crystallographic mirror planes are now pseudomirror planes. (d) 4-Chlorobenzonitrile, form II, parallel structure. The view is approximately parallel to the a axis, the 3.937-Å "stacking" axis. The b axis is horizontal.

A comparison of the refinement results for the two crystals is also interesting. The good crystal refined well in spite of potential problems from the pseudomirror plane which divides the molecule: the largest correlation coefficient was 0.63, relating the z values of C(2) and C(6). The only suggestion of any disordering among the Cl and CN groups is the somewhat short C–N bond, 1.110 (3) Å (mean nitrile distance for 38 groups is 1.138 Å as shown in Figure 1), and a small peak, 0.28 e Å^{-3}, located between C and N atoms of the nitrile group. The latter may not be significant because every C–C bond had a small peak in the center of it; these peaks undoubtedly represent bonding density. Although not reported here, it is worth noting that a wide variety of refinements were actually carried out on the data (e.g., using all reflections, using unit weights, etc.) in order to see if the C–N distance would lengthen to its normal value and to test for correlation effects. In all cases, the C–N distances remained short and the potentially correlated distances did not vary by more than one standard deviation. The data from the anomalous crystal did not refine as well. First, in spite of collecting four quadrants of data and averaging them, there were fewer observed reflections; more significantly, it was the odd reflections that were lost. Consequently, the pseudomirror became more important, and correlation

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[37] Fleck, S.; Weiss, A. *Z. Naturforsch* **1987**, *42a*, 645. We thank Prof. D. Y. Curtin for drawing our attention to this paper and for an informative discussion.

coefficients were much higher (up to 0.86). This probably explains why the hydrogen atoms did not refine particularly well. The most noteworthy difference in the two structures is the C≡N bond length; for the anomalous crystal, it is very short, 1.064 (4) Å. All these observations strongly indicate that there is much more disorder among the Cl and CN groups here than in the case of the good crystal. The study of the anomalous crystal clearly suggests that the stacking of the layers of molecules in a truly antiparallel fashion is often much less than perfect for this compound.

Crystal Structure of Form II of 4-Chlorobenzonitrile. Measurement of the SHG signal on freshly sublimed crystals yielded no signal, as one would expect for a centrosymmetric crystal. Crystals taken directly from a commercial sample (Aldrich) did, however, produce an SHG signal. This puzzle was resolved when time-dependent X-ray powder diffraction studies were carried out on a freshly sublimed and ground sample: clear evidence of a phase transformation was found. It was eventually shown (see section c) that this new polymorph had the same structure as crystals grown from an ethanol solution and is now referred to as form II.

Many of the crystals grown from ethanol had striations and other visible defects. It took considerable effort to isolate a piece that was optically acceptable, and even it had ω scans that were broad and often structured. In spite of this problem, the structure was easily solved and refined. This noncentrosymmetric structure is a variant of the BrBzCN structure in that all the CN vectors are not parallel but point in a zigzag fashion in the same direction (Figure 4d). There are N--Cl contacts, 3.370 (4) Å, but the C≡N--Cl angle is "bent", 87.7 (3)°, with the C–Cl vector being nearly perpendicular to the C≡N bond: The normal C≡N bond length suggests that there is no disorder of the Cl and CN groups. The poor quality of the crystal in this case must be due to a large mosaic spread.

(c) Solid-State Phase Transformation of 4-Chlorobenzonitrile. As previously noted, freshly sublimed and ground microcrystals of ClBzCN have the centrosymmetric structure referred to as form I and produce no SHG signal. We noted, however, that, on standing overnight, a small SHG signal was observed; this signal continued to growth with time, leveling off at values in the range 30–150× quartz (1.05 μm). An X-ray powder diffraction study was then carried out to follow the phase change, and a representative set of patterns as a function of time is shown in Figure 5. Also shown in the figure are the calculated patterns for the centrosymmetric form I and the noncentrosymmetric form II. Although the crystal structures reported above were done on crystals cooled to −100°, a second determination was carried out in all cases (except for IBzCN) at room temperature. While the structures at room temperature were of lower quality, it is the room-temperature results, i.e., unit cell parameters and atomic coordinates, that were used to generate the calculated patterns of forms I and II. Clearly, it is the conversion of form I to form II that is responsible for the growth of the SHG signal.

Large crystals of form I do not undergo this transformation when they are kept sealed in a glass tube for several weeks. The transformation seems to require some form of initiation; in the present case, grinding appears to provide the necessary impetus possibly through the introduction of shear forces along the molecular ribbons. Not only does it reduce the particle size and increase the surface area, but it may well introduce defects into the particles. The peaks in the powder pattern of the freshly ground material are notably broad, a clear indication that the crystallite size is much smaller than the particle size. Defect regions in the form I crystallites where chains of molecules are reversed and therefore parallel (the regions of disordering of the Cl and CN groups) may well serve as nuclei for the growth of form II crystals. A second X-ray powder study in which the sample was only lightly ground (i.e., no broadening of the peaks) showed much slower conversion to form II; after several weeks, the transformation was still incomplete.

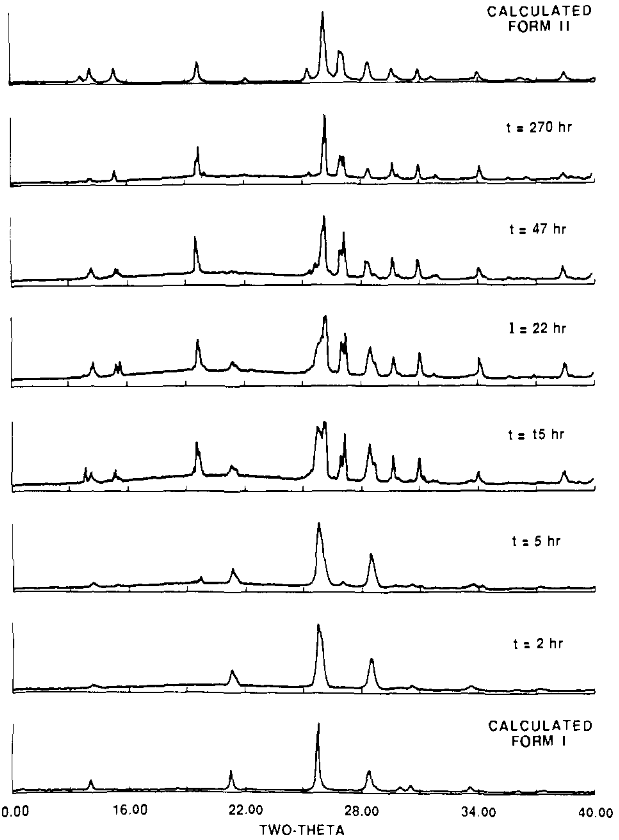

Figure 5. X-ray powder diffraction patterns of 4-chlorobenzonitrile as it undergoes a phase transformation from form I to form II. Calculated patterns for the two forms were derived from single-crystal studies.

(d) The Role of C≡N--X Interactions. Intermolecular interactions between cyano and halogen groups appear to be of two types, a shorter, more linear interaction in the range 3.00–3.40 Å and a longer contact, greater than 3.40 Å. The shorter contacts seem to play a decisive role in organizing molecules into one-dimensional arrays. In the case of the 4-halogen-substituted benzonitriles, these arrays assume the form of linear or zigzag ribbons. The ability to identify such motifs facilitates efforts at structure prediction and design, i.e., crystal engineering, because a structure is systematically built up from the primary structure (molecule) via the secondary structure (motif) to the tertiary structure (complete crystal).

This kind of a conceptualized dissection has been attempted for other categories of compounds such as quinones, amides, carboxylic acids, chloro aromatics, nitroanilines, and phenols.[38] However, the example of the 4-halogen benzonitriles shows that the unambiguous identification of a secondary motif does not necessarily imply that the tertiary structure is satisfactorily defined. The crystal structures of ClBzCN, BrBzCN, and IBzCN may be visualized in terms of linear ribbons of molecules linked by CN--X interactions. These ribbons are themselves stacked in a parallel or antiparallel fashion to yield two-dimensional molecular slabs. The tertiary structure is generated by a lateral alignment of these slabs, which can also occur in either a parallel or antiparallel fashion. So weak are the lateral interactions between molecules that, in practice, it is entropically favorable for the slabs to be disordered. The degree of coupling between lateral molecules is greatest for IBzCN, which is completely ordered, slightly reduced for BrBzCN in which there is some degree of misregistry between slabs, and the least in ClBzCN where the degree of disorder is so pronounced that there are distinct regions which can nucleate the formation of a noncentrosymmetric polymorph. This difference in behavior between Cl, Br, and I is probably the result of differences in atomic size and polarizability, the largest and most polarizable, I, being the most able to specifically recognize lateral neighbors, and the smallest and least polarizable,

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(38) Desiraju, G. R. *Crystal Engineering. The Design of Organic Solids*; Elsevier: Amsterdam, 1989.

Table III. Bond Distances and Angles for the 4-Halobenzonitriles Arranged According to Chemical Equivalence

			ClBzCN		
			form I		
	IBzCN	BrBzCN	good crystal	anomalous crystal	form II
C(1)–X	2.093 (3)	1.899 (5)	1.745 (2)	1.756 (2)	1.739 (4)
C(1)–C(2)	1.391 (3)	1.384 (5)	1.387 (5)	1.370 (7)	1.378 (5)
C(1)–C(6)			1.380 (6)	1.399 (7)	1.384 (6)
C(2)–C(3)	1.387 (4)	1.384 (6)	1.384 (5)	1.407 (11)	1.386 (6)
C(5)–C(6)			1.382 (6)	1.354 (11)	1.374 (6)
C(3)–C(4)	1.394 (3)	1.393 (5)	1.397 (5)	1.385 (8)	1.396 (6)
C(4)–C(5)				1.404 (8)	1.397 (6)
C(4)–C(7)	1.438 (5)	1.458 (10)	1.454 (3)	1.470 (4)	1.445 (6)
C(7)–N	1.142 (6)	1.085 (9)	1.110 (3)	1.064 (4)	1.131 (5)
X--N	3.127 (4)	3.249 (5)	3.350 (2)	3.361 (3)	3.370 (4)
X–C(1)–C(2)	119.7 (2)	119.4 (3)	118.8 (3)	118.6 (4)	119.5 (3)
X–C(1)–C(6)			119.3 (3)	119.5 (4)	118.8 (3)
C(2)–C(1)–C(6)			121.7 (2)	121.9 (2)	121.7 (4)
C(2)–C(1)–C(2)′	120.6 (3)	121.1 (5)			
C(1)–C(2)–C(3)	119.6 (2)	119.6 (4)	119.4 (2)	118.8 (3)	119.1 (4)
C(1)–C(6)–C(5)			118.8 (2)	119.3 (4)	119.6 (4)
C(2)–C(3)–C(4)	120.1 (2)	119.5 (4)	119.1 (2)	119.3 (4)	119.9 (4)
C(4)–C(5)–C(6)			120.2 (2)	120.2 (3)	119.8 (4)
C(3)–C(4)–C(5)			120.6 (2)	120.5 (2)	120.0 (4)
C(3)–C(4)–C(3)′	119.9 (3)	120.6 (5)			
C(3)–C(4)–C(7)	120.0 (2)	119.7 (3)	119.5 (3)	119.8 (5)	119.8 (4)
C(5)–C(4)–C(7)			119.8 (3)	119.7 (5)	120.2 (4)
C(4)–C(7)–N(1)	180	178.0 (9)	179.3 (6)	180 (1)	178.6 (5)
C(7)–N(1)--X	180	168.8 (3)	169.7 (3)	165.7 (4)	87.7 (3)

Cl, being the least able to discriminate between parallel and antiparallel alignments of lateral neighbors.

Finally, we would like to strike a cautionary note in that, even in this age of routine small-molecule X-ray crystallography, the structures of some simple organic compounds may not be so simple after all! The vast majority of structural results with common space groups and low *R* indices are routinely consigned to the depositories of supplementary material. At a casual glance, even the results obtained for ClBzCn ($P2_1/c$; $R = 0.043$) and BrBzCN (*Am*; $R = 0.028$) do not hint at the unexpected perspectives that these crystal structures have afforded.

Experimental Section

Structure Determinations via Single-Crystal, X-ray Diffraction. All of the structural studies were carried out on a Syntex P3 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) and with a low-temperature device that kept each of crystals reported here cooled to −100 °C. Intensity data were collected via ω scans out to $2\theta = 55°$ with scans speeds that generally ranged from 2.0° to 9.8° min^{-1}. Check reflections were monitored every 197 reflections; corrections for intensity variations were applied, as were Lorentz and polarization corrections. An analytical absorption correction was applied in the case of IBzCN. An empirical absorption correction, based on ψ-scan data, was applied to the BrBzCN data. All the structures were refined by full-matrix, least-squares techniques. Weights were generally assigned based on counting statistics plus a small "ignorance" factor. The non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms with isotropic thermal parameters. The crystallographic information is listed in Table I. The resulting atomic coordinates and the (refined or equivalent) isotropic thermal parameters are given in Table II. Table III lists the important bond distances and angles. ORTEP drawings of the molecules are shown in Figure 3 and packing diagrams in Figure 4.

Room-temperature data sets were also collected for ClBzCN (forms I and II) and BrBzCN. These refinements were clearly inferior to the refinements of the low-temperature data and have, therefore, been submitted only as supplementary material. However, the room-temperature cell parameters, atomic coordinates, and thermal parameters were used to calculate powder diffraction patterns in order that these could be compared with the actual powder patterns of these materials.

X-ray Powder Diffraction. All patterns were run on a Philips APD diffractometer equipped with Cu Kα radiation. The samples were run at room temperature and thus had to be covered with Mylar tape in order to prevent them from subliming away; the tape produced a small amorphous hump centered at a 2θ value of approximately 20°. Because of the potential of these compounds to form polymorphs, it was considered expedient to run patterns on each recrystallization batch to make sure that the crystal selected for the single-crystal studies was representative of the bulk material. Figure 5 shows the change in the pattern of a freshly sublimed and ground sample of ClBzCN (form I) as a function of time.

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Supplementary Material Available: Complete structural reports for the five crystal structures reported in this paper, each report containing detailed crystallographic information including the unit cell parameters, atomic coordinates, thermal parameters, and structure amplitudes, and calculated powder diffraction patterns for the room-temperature studies (45 pages); tables of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.