J. Am. Chem. Soc. **1994**, *116*, 105-110

Azaaromatic Chlorides: A Prescription for Crystal Structures with Extensive Nitrogen–Chlorine Donor–Acceptor Interactions

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Received August 4, 1993[*]

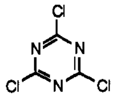
Abstract: The crystal structures of cyanuric chloride (**1**) 2,4,6,8-tetrachloropyrimido[5,4-*d*]pyrimidine (**2**), 9-methyl-2,6,8-trichloropurine (**3**), and 2,4,6,7-tetrachloropteridine (**4**) display extensive networks of intermolecular nitrogen–chlorine donor–acceptor interactions. Compounds **1–3** form layered structures in which two-dimensional N···Cl linked arrays are separated by approximately 3.3 Å, while crystals of compound **4** exhibit a herringbone structure interwoven with N···Cl contacts. The peripheral N=C—Cl subunits in these molecules appear to be particularly prone to form such interactions in the solid state. All of the nitrogen and chlorine atoms in compounds **1** and **2** participate in N···Cl interactions (thus each molecule of **1** forms six N···Cl contacts and each molecule of **2** forms eight), while the N···Cl arrays in **3** and **4** are less complete. Ab initio calculations suggest that each of these weak bonds may be worth as much as 1.2 kcal/mol.

Short nitrogen–halogen intermolecular contacts are frequently observed in the crystal structures of organic and inorganic compounds, and these close contacts undoubtedly reflect weakly attractive donor–acceptor interactions.[1] Furthermore, there is a marked preference for a nearly linear arrangement of atoms in the approach of nitrogen nucleophiles to halogen–carbon groups in the solid state, a directional preference which has been exploited to some degree for the design of crystalline organic solids.[2-5]

Not all nitrogen–halogen interactions are equally favorable, and one might ask which are the most strongly attractive. The interatomic distances for N···Cl, N···Br, and N···I contacts in crystals are typically on the order of 3.2 Å,[3] but there is considerable scatter in the data, and it is difficult to separate steric from electronic effects, especially in complex structures. However, there are a few simple structures (such as that of bromotetrazole,[6] which contains chains of 2.96-Å N···Br contacts) which suggest that shorter, possibly stronger, nitrogen–halogen interactions may result when the halogen is attached to a nitrogen-rich aromatic heterocycle. In this paper we report and analyze the crystal structures of several "azaaromatic chlorides" (aromatic compounds containing many N=C—Cl subunits), a remarkable class of compounds which display extensive networks of intermolecular nitrogen–chlorine donor–acceptor interactions in the solid state.[7]

Results

Structure of Cyanuric Chloride. Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine, **1**) contains only nitrogen and chlorine atoms on its periphery, and thus the opportunity for intermolecular N···Cl contacts should be nearly maximized in its crystals. Large crystals were obtained from carbon tetrachloride, and the structure was solved and refined in the space group $C2/c$. The molecule itself possesses crystallographic C_2 symmetry, and, as expected, its molecular geometry closely approximates D_{3h} symmetry. The triazine ring is nearly planar and equilateral, but it is not a regular hexagon (see Figure 1) since the C–N–C bond angles average only 112.7° but the N–C–N angles are expanded to 127.4°, a distortion very similar to that observed in the parent *s*-triazine.[8] Most interesting, however, are the intermolecular interactions. The structure consists of π-stacked layers of nearly planar molecular arrays (Figure 2) with an interlayer separation of 3.26 Å, in which all in-plane intermolecular interactions are short N···Cl contacts (3.100 and 3.113 Å) with linear or nearly linear N···Cl–C bond angles (180.0° and 172.9°). This crystal packing is dramatically different from that of other compounds with idealized D_{3h} symmetry and related functionality, such as 1,3,5-trichlorobenzene,[9] 1,3,5-tribromobenzene,[9] B-trichloroborazine,[10] and 2,4,6-trichloro-1,3,5-tricyanobenzene,[11] all of which pack in various herringbone patterns.



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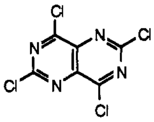

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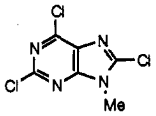

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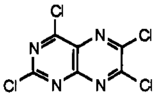

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The anomalous packing of cyanuric chloride is easily rationalized as the geometry which affords the maximum number of close, nearly linear N···Cl–C contacts, with the implication that nitrogen–chlorine donor–acceptor interactions are the controlling element in the formation of the crystal structure. In order to test this hypothesis, we decided to determine the crystal structures of several other molecules in which equal numbers of nitrogens and chlorines are distributed, more or less alternately, about their peripheries. Of the monocyclic possibilities, 3,5,6-trichloro-1,2,4-triazine[12] is a low-melting solid and 4,5,6-trichloro-1,2,3-triazine is unknown, so we turned our attention to three bicyclic azaaromatic chlorides (compounds **2–4**) with known syntheses.[13-15]

Structure of 2,4,6,8-Tetrachloropyrimido[5,4-*d*]pyrimidine. We speculated that 2,4,6,8-tetrachloropyrimido[5,4-*d*]pyrimidine[13]

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[*] Abstract published in *Advance ACS Abstracts*, December 15, 1993.

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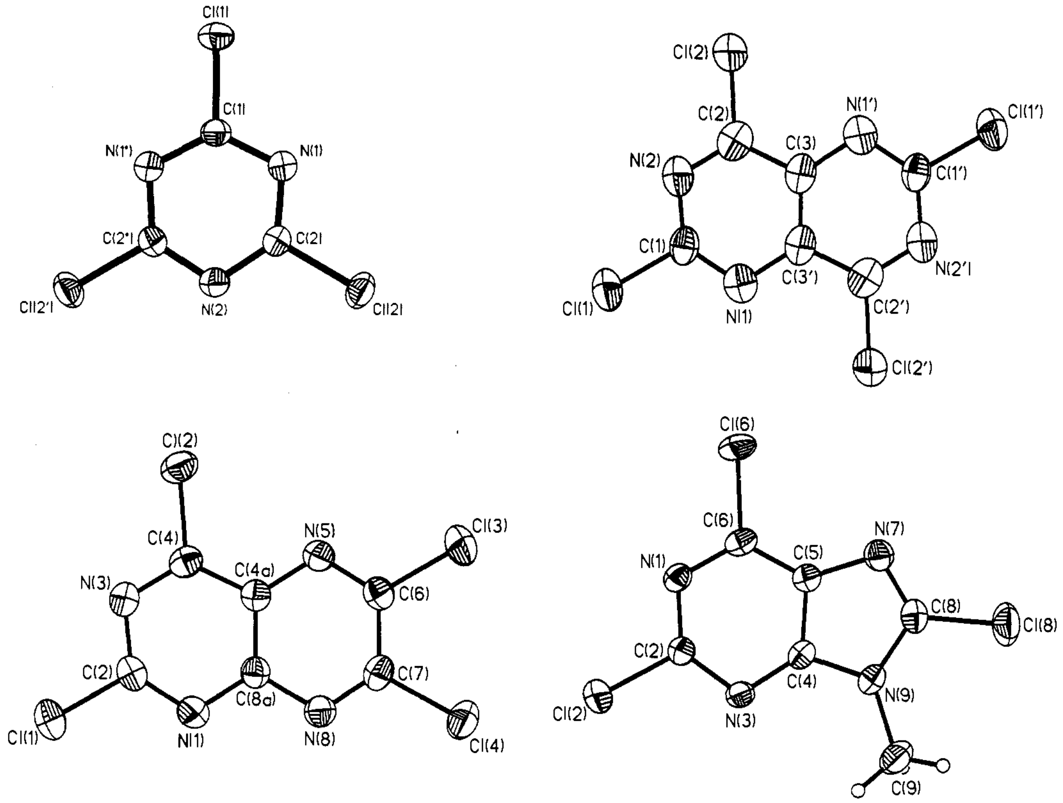

Figure 1. X-ray crystal structures and crystallographic numbering schemes for (clockwise from upper left) compounds **1**–**4**. Thermal ellipsoids are drawn at the 50% probability level.

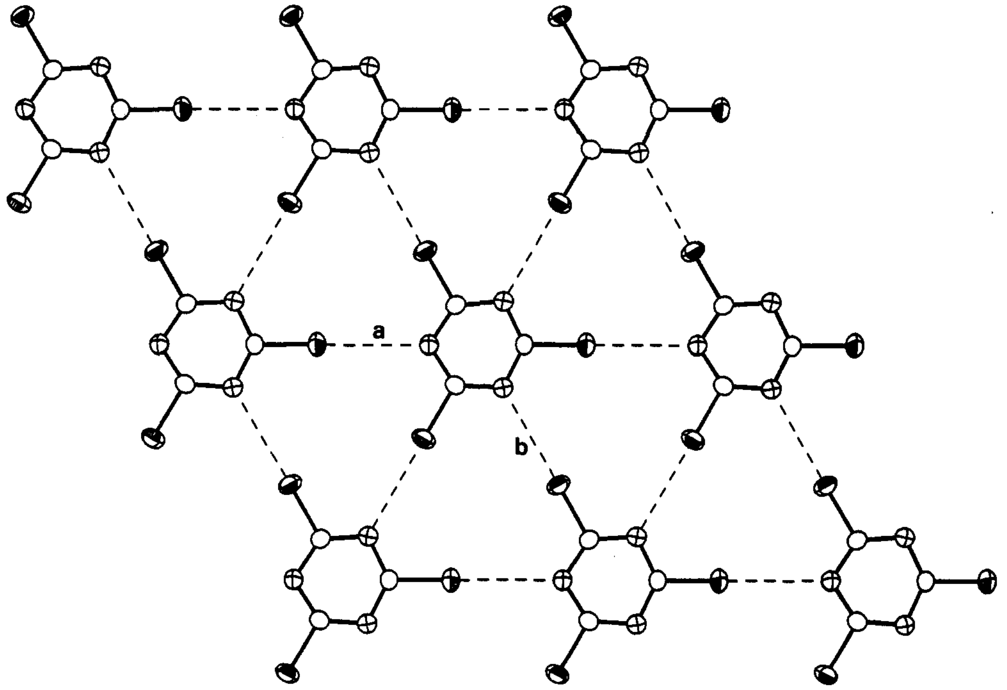

Figure 2. N···Cl interactions in the crystal structure of compound **1**. Carbon atoms are open ellipsoids, nitrogens are crossed ellipsoids, and chlorines are shaded crossed ellipsoids. For contact a, d_{NCl} = 3.100(3) Å, $\angle_{\mathrm{NClC}}$ = 180.0°; for b, d_{NCl} = 3.113(2) Å, $\angle_{\mathrm{NClC}}$ = 172.9(1)°.

(**2**) would crystallize in a layered structure manner analogous to that of cyanuric chloride, in which all in-plane interactions are N···Cl contacts; perhaps fortuitously, this actually proved to be the case. Crystals of compound **2** were obtained from chloroform solutions, and the structure was solved and refined in the space group $P2_1/c$. The molecule possesses crystallographic C_i symmetry, and the molecular geometry of **2** closely approximates C_{2h} symmetry. As in the case of **1**, the C–N–C bond angles in **2** are rather acute (average 115.4°), while the N–C–N bond angle is very wide (128.9°). The nearly planar arrays of **2** (Figure 3) have an average separation of 3.31 Å, very similar to the interlayer spacing in the structure of compound **1**. However, the two crystallographically independent intraplanar N···Cl contacts are significantly longer than for **1**: 3.207 and 3.332 Å. In the shorter of these (see Figure 2), the N···Cl–C angle approaches linearity (177.1°), but in the longer contacts, which bridge the *peri* positions of adjacent molecules, steric repulsion between the chlorine atoms (Cl···Cl distance, 3.580 Å) probably accounts not only for the

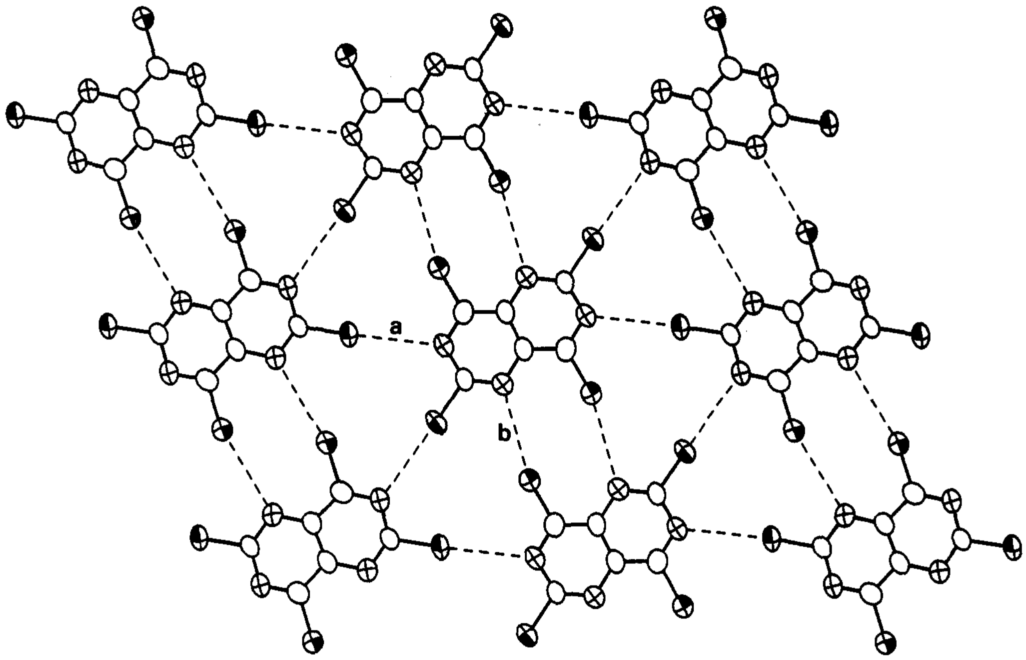

Figure 3. N···Cl interactions in the crystal structure of compound 2. For contact a, d_{NCl} = 3.207(5) Å, $\angle_{NClC}$ = 177.1(2)°; for b, d_{NCl} = 3.332(5) Å, $\angle_{NClC}$ = 162.8(2)°.

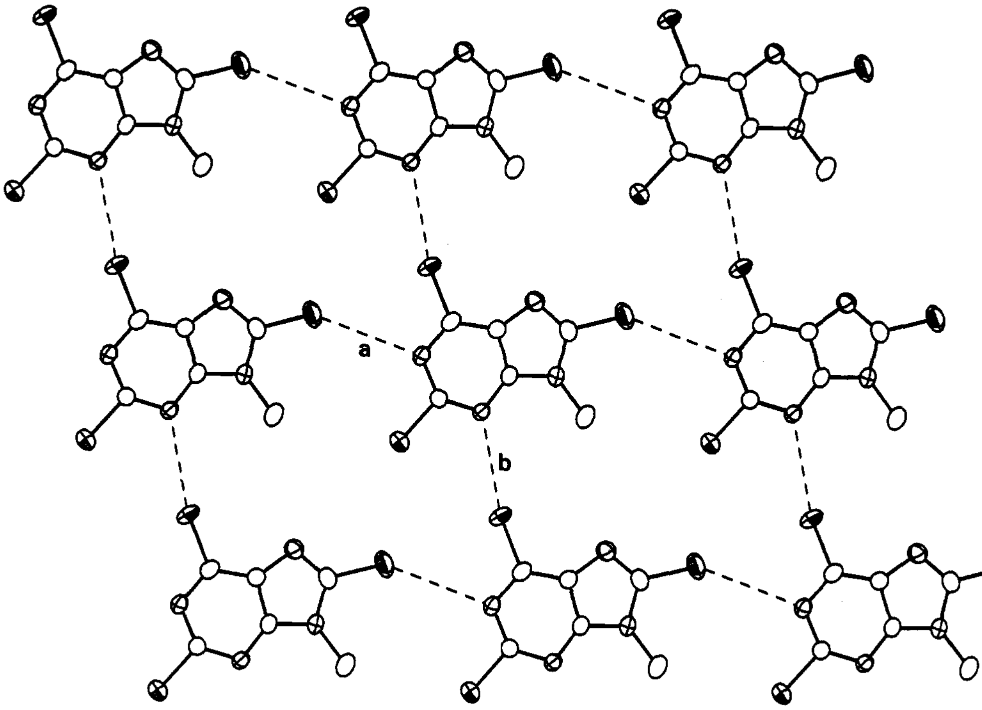

Figure 4. N···Cl interactions in the crystal structure of compound 3. For contact a, d_{NCl} = 3.416(3) Å, $\angle_{NClC}$ = 144.5(1)°; for b, d_{NCl} = 3.097(3) Å, $\angle_{NClC}$ = 168.5(1)°.

greater N···Cl distance, but also the more acute N···Cl–C angle of 162.8°. In this crystal structure, *every molecule participates in eight nitrogen–chlorine donor–acceptor interactions, the most of any molecule in any crystal structure of which we are aware.*

Structures of 9-Methyl-2,6,8-trichloropurine and 2,4,6,7-Tetrachloropteridine. Compounds **1** and **2** possess relatively high molecular symmetry, and in fact both lie on special positions in their crystal lattices. It is easy to see how such high-symmetry molecules might be arranged to form a planar array. However, it is much more difficult to predict how molecules of lower symmetry might pack in two dimensions, even though there is no reason to think that such packing should be any less favorable than in the higher symmetry cases.

The first of two low-symmetry azaaromatic chlorides to be examined was 9-methyl-2,6,8-trichloropurine[14] (**3**). Crystals of compound **3** were obtained from chloroform solutions, and the structure was solved and refined in the space group $P\bar{1}$, revealing yet another layered structure (average interlayer separation, 3.28 Å) with extensive intraplanar N···Cl interactions (Figure 4). However, in this case not all peripheral nitrogen and chlorine atoms are involved in donor–acceptor contacts. The N(3)···Cl(6)–C(6) interaction is short (3.097 Å) and approximately linear (168.5°), the N(1)···Cl(8)–C(8) is longer (3.416 Å) and quite bent (144.5°), but the third potential contact, between N(7) and Cl(2)–C(2) of adjacent molecules, is much too long to be even weakly attractive.

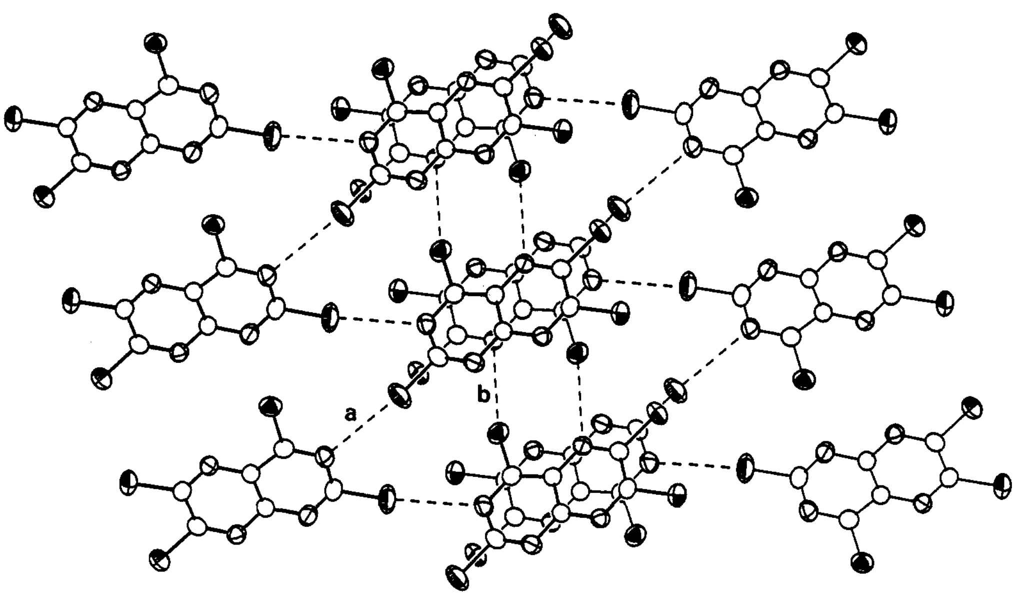

Figure 5. N···Cl interactions in the crystal structure of compound **4**. For contact a, d_{NCl} = 3.284(3) Å, $\angle_{\mathrm{NClC}}$ = 150.5(1)°; for b, d_{NCl} = 3.341(2) Å, $\angle_{\mathrm{NClC}}$ = 166.4(1)°.

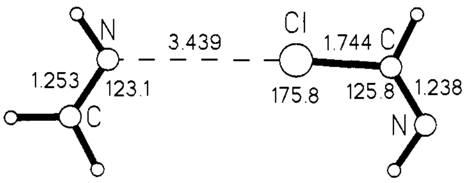

Figure 6. Optimized geometry (HF/6-31+G*) of the formimine–formimidoyl chloride N···Cl complex.

For the second low-symmetry azaaromatic we chose 2,4,6,7-tetrachloropteridine[15] (**4**). Crystals were obtained from methylene chloride, and the structure was solved and refined in the space group *P*2$_1$/*c*. We can imagine no way for this compound to pack in a two-dimensional array without incurring a penalty from nitrogen–nitrogen lone pair interactions (unless solvent molecules were to be incorporated into the crystal lattice), and in fact the crystals of compound **4** are not layered, but instead exhibit a herringbone structure, which is nevertheless interlaced with N···Cl interactions, as shown in Figure 5. The molecules are paired about centers of inversion with *peri*-bridging N···Cl links similar to those observed in the structure of **2**, and adjacent rows of molecules are connected by a zigzag series of N···Cl contacts. Still, only half of the nitrogen and chlorine atoms in this compound are involved in donor–acceptor interactions.

Computational Study. The crystal structures presented here support the notion that azaaromatic chlorides are particularly prone to form nitrogen–chlorine donor–acceptor interactions in the solid state. However, there is no way to measure the force of attraction for individual N···Cl interactions, so we turned to ab initio molecular orbital calculations for an estimate of the strength of these weak bonds. The simplest system which includes the essential features of the N···Cl contacts in the azaaromatic chlorides is the hypothetical complex of formimine and formidoyl chloride shown in Figure 6. All of the nitrogens and carbons are part of π-systems, and the N=C–Cl subunit is present. The geometry of this complex and the geometries of the individual molecules were fully optimized at the HF/6-31+G* level[16] under the constraint of C_s symmetry, so that the π-systems of the donor and acceptor remain coplanar,[17] as is the case in most of the crystal structures. The calculated N···Cl distance proved to be 3.439 Å, a bit long but within the range of our observations, and the N···Cl–C angle is nearly linear (175.8°). A comparison of the energy of the complex with those of the isolated molecules yields a very modest energy of association of –0.29 kcal/mol. However, when electron correlation is included in single point calculations at the MP2(FC)/6-31+G* level,[16] the energy of associations is a much more favorable –1.22 kcal/mol, significantly greater than a simple Van der Waals interactions, but still much less than a hydrogen bond.

Discussion

Interest in the crystal structure of **1** dates back to 1936, when K. Lonsdale reported that I. E. Knaggs, in an unpublished X-ray study, had determined that compound **1** crystallizes in a layered structure;[18] however, the full structure was never determined. More than 20 years later, Hoppe et al.[19] determined the unit cell parameters and space group of cyanuric chloride, and they positioned the molecule of **1** within the unit cell. The resulting crystallographic model is also a layered structure, and it does show an extensive network of close N···Cl contacts within the crystal. Although the structural model of Hoppe et al. was based on only a very limited 1.6-Å resolution film data set, it was accepted without criticism for 35 years and formed the basis for several brief discussions of N···Cl donor–acceptor interactions in crystals of compound **1**.[20–22]

In 1992, unaware of the work of Hoppe et al., we reported the first full determination of the structure of cyanuric chloride.[7] However, a comparison of our structure with that of Hoppe et al. shows that they are not the same. Hoppe's study and our own study report the same unit cell parameters and space group for cyanuric chloride, but after that the two determinations diverge. This is most easily seen by noting the positions of the chlorine atoms in the two structures (Figure 7). In our own determination the chlorines in adjacent layers appear nearly to eclipse one another when viewed down the *c* axis. In contrast, the chlorines in the Hoppe structure are staggered. We have evaluated the Hoppe

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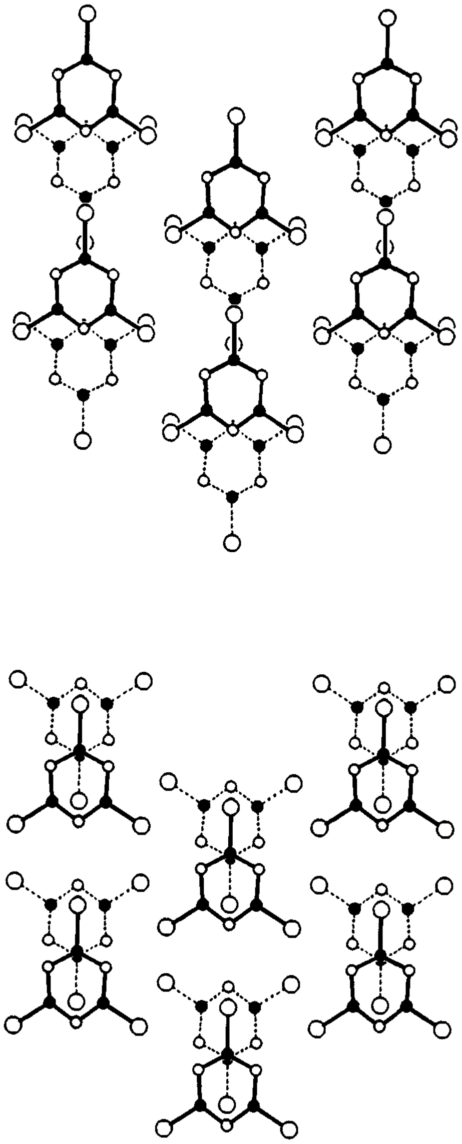

Figure 7. A comparison of the crystallographic model for cyanuric chloride reported in the present work (above) and that previously reported by Hoppe et al.[18] (below). Both views are along the *c* axis.

model against our data set, and all refinement tests indicate that the staggered Hoppe model is inconsistent with our intensity data. Conversely, those same tests suggest that the structure of Hoppe et al. is in error. While their final crystallographic model bears a superficial resemblence to ours, the molecules of **1** are mistranslated in the *b* direction such that the interplanar stacking, crystal packing, and crystal structure which they report are incorrect. Most recently, Maginn et al.[23] have redetermined the structure of **1**, and their results appear to be in complete agreement with our own.[24]

Layered, two-dimensional arrays of molecules were observed in three of the four crystal structures reported here. Maginn et al.[23] have noted and discussed a "fish-scale" effect in the structure of cyanuric chloride, whereby the mean planes of the individual molecules are tilted slightly with respect to the mean plane of the array, giving rise to the observed small out-of-plane nonlinearities in one of the N···Cl–C contacts. Similar effects are observed in the structures of compound **2**, where the *peri* N···Cl contacts are slightly disjointed (Figure 8), and compound **3**. In both cases, the dislocations appear to relieve steric interactions between chlorine atoms. In **2** the interacting *peri* chlorine atoms are separated by 3.580 Å, and in **3** there is a 3.531-Å interlayer nonbonded Cl···Cl contact between Cl(6) atoms.

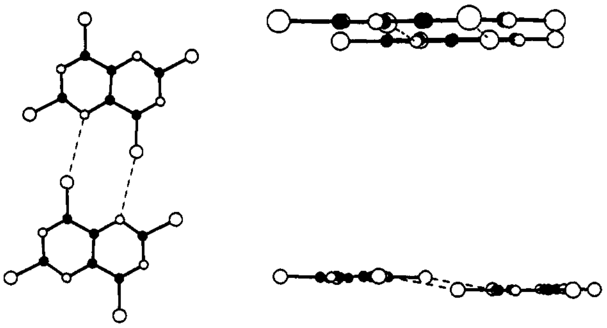

Figure 8. Three views of the *peri* interactions between pairs of molecules in the structure of compound **2**.

The azaaromatic chlorides are planar, highly chlorinated aromatic compounds, and as such one might expect them to obey the "chloro rule": chlorinated aromatics tend to form crystal modifications characterized by a short (~4.0 Å) crystallographic axis.[25,26] None of our compounds exhibit 4-Å axes; however, compounds **1–3** possess short axes of ~7.4 Å, roughly double the characteristic distance. In typical "chloro rule" systems, weakly attractive Cl···Cl interactions stabilize two-dimensional arrays, and these arrays in turn stack with an approximately 4-Å spacing in a manner dictated by other, interlayer Cl···Cl interactions.[26] In our structures, it is primarily N···Cl interactions which stabilize the two-dimensional arrays, but Cl···Cl interactions may play an important role in determining the orientation of adjacent layers. In cyanuric chloride, for example, the closest intralayer Cl···Cl contact is 3.94 Å, but there are interlayer Cl···Cl contacts of only 3.71 and 3.79 Å. There is no correspondingly short crystallographic axis because the adjacent layers of cyanuric chloride pack in an antiparallel fashion (see Figure 7), a feature which has been noted in other systems which vary from the usual "chloro rule".[26,27]

Are there closely related structures in the literature? A search of the Cambridge Structural Database[28] for azaaromatic halides revealed several structures containing one-dimensional chains of nitrogen–halogen donor–acceptor interactions (bromotetrazole,[6] pentachloropyridine,[29] and 1,3,4,5,6,8-hexachlorothieno[2,3-*c*:5,4-*c*′]dipyridine[30]) but in each of these compounds the numbers of peripheral nitrogens and chlorines are very unequal, so that there are fewer opportunities for the formation of a higher-dimensional array. Of all compounds in the database containing the N═C–halogen subunit in five- or six-membered rings, only two display two-dimensional arrays comparable to those reported here: the dichlorothiatriazine **5**[31] and the dibromotetraazapentalene **6**.[32] Interestingly, in the structure of the nonplanar compound **5**, the N···Cl linked layers are separated by largely aliphatic layers formed by the packing of the diisopropylamino groups, while in the structure of **6**, the N···Br linked arrays are not nearly planar, but highly corrugated.

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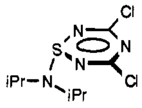

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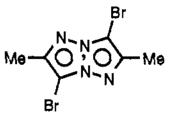

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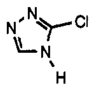

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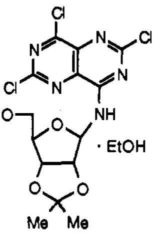

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A particularly intriguing structure is that of 3-chloro-1,2,4-triazole (**7**),[33] in which N···Cl interactions and hydrogen bonds combine to form a two-dimensional array of molecules. Such structures hold out the promise that "crystal engineers"[26] may be able to design crystals in which both types of interactions are used, potentially providing much greater control and flexibility in such ventures. Unfortunately, in most of the structures of azaaromatic halides possessing the necessary functionality for both kinds of interactions, hydrogen bonds are formed to the exclusion of nitrogen–halogen interactions. Of greatest relevance to the present work is the structure of the riboside **8**.[34] In this compound, one of the chlorines of compound **2** has been replaced by a partially protected amino sugar. While compound **2** participates in the maximum number of N···Cl interactions (eight) for a compound with four nitrogens and four chlorines, the crystal structure of **8**, which is an ethanol solvate, contains several hydrogen bonds, but no close N···Cl contacts. Presumably the formation of hydrogen bonds, which must be much stronger than N···Cl interactions, is of greater importance in determining the crystal packing.

In this regard, gas-phase experiments yield energies of association for simple hydrogen bonded dimers of 4–10 kcal/mol,[35] but there appears to be no experimental data which describe either the structure or energetics of nitrogen–halogen interactions in the gas phase.[36] Our computational estimate of 1.2 kcal/mol for the gas-phase interaction of azaaromatic chlorides seems reasonable, but in any case it is clear that at least four or five N···Cl interactions would be required to equal one hydrogen bond, and thus molecules which have the potential to form both types of interaction in the solid state will crystallize in a manner that gives precedence to the formation of hydrogen bonds.

In conclusion, aromatic compounds with several N=C–Cl subunits distributed about their peripheries tend to form crystals in which there are numerous nitrogen–chlorine donor–acceptor interactions. Three of the four structures determined in the present work, and two azaaromatic halides from the literature,[31,32] crystallize as layered structures in which many intralayer intermolecular contacts are short nitrogen–halogen interactions. Given the propensity for azaaromatic chlorides to form N···Cl interactions in the solid state, it will be interesting to determine if such forces can significantly influence molecular conformations or associations in solution.

Experimental Section

Cyanuric chloride (**1**) was purchased from Aldrich. 2,4,6,8-Tetrachloropyrimido[5,4-*d*]pyrimidine (**2**), 9-methyl-2,6,8-trichloropurine (**3**), and 2,4,6,7-tetrachloropteridine (**4**) were prepared by literature procedures.[13-15] The SPARTAN 2.0 software package (Wavefunction, Inc.) was used for all ab initio calculations.

X-ray Crystallographic Analysis of Compound 1. A crystal of **1** from CCl_4 measuring 0.12 mm × 0.40 mm × 0.42 mm was used for X-ray measurements. Crystal data: $C_3Cl_3N_3$; monoclinic, space group $C2/c$; $a = 12.925(2)$ Å, $b = 7.455(1)$ Å, and $c = 7.540(1)$ Å, $\beta = 120.057(9)°$, $V = 628.9(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.948$ g/cm^3. Intensity measurements were made with $4° \leq 2\theta \leq 50°$ by using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 230 K on a Nicolet R3m diffractometer. A total of 545 independent reflections were measured, of which 503 were considered to be observed [$|F_o| > 3\sigma(F_o)$]. The structure was solved by direct methods and refined with the SHELXTL PLUS software. Refinement of 44 parameters converged at $R = 0.026$, $R_w = 0.032$, with godness-of-fit = 2.52. Full details are given in the supplementary material.

X-ray Crystallographic Analysis of Compound 2. A yellow needle from chloroform measuring 0.05 × 0.10 × 0.50 mm was used for X-ray measurements. Crystal data: $C_6Cl_4N_4$; monoclinic, space group $P2_1/c$; $a = 7.407(2)$ Å, $b = 7.714(2)$ Å, $c = 7.942(2)$ Å, $\beta = 97.12(2)°$, $V = 450.31(14)$ Å^3, $Z = 2$, $D_{calcd} = 1.991$ g/cm^3. Intensity measurements were made with $4° \leq 2\theta \leq 50°$ by using graphite monochromated Mo Kα radiatin ($\lambda = 0.71073$ Å) at 235 K on a Siemens P4 diffractometer. A total of 791 unique reflections were measured, of which 567 were considered to be observed [$|F_o| > 3\sigma(F_o)$]. The structure was solved by direct methods using the SHELXTL PLUS software. Refinement of 64 parameters converged at $R = 0.051$, $R_w = 0.051$. Full details are given in the supplementary material.

X-ray Crystallographic Analysis of Compound 3. A colorless prism from chloroform measuring 0.12 × 0.15 × 0.22 mm was used for X-ray measurements. Crystal data: $C_6H_3Cl_3N_4$; triclinic, space group $P\bar{1}$; $a = 7.334(2)$ Å, $b = 7.568(2)$ Å, $c = 9.146(2)$ Å, $\alpha = 106.30(2)°$, $\beta = 90.20(2)°$, $\gamma = 115.65(2)°$, $V = 434.66(11)$ Å^3, $Z = 2$, $D_{calcd} = 1.814$ g/cm^3. Other experimental procedures were as for compound **2**: $4° \leq 2\theta \leq 50°$; Mo Kα radiation; 235 K; 1529 unique reflections; 1328 observed reflections; 118 parameters; $R = 0.033$; $R_w = 0.037$. Full details are given in the supplementary material.

X-ray Crystallographic Analysis of Compound 4. An orange plate from methylene chloride measuring 0.18 × 0.30 × 0.35 mm was used for X-ray measurements. Crystal data: $C_6Cl_4N_4$; monoclinic, space group $P2_1/c$; $a = 11.611(2)$ Å, $b = 5.923(1)$ Å, $c = 16.098(2)$ Å, $\beta = 122.67(1)°$, $V = 931.8(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.924$ g/cm^3. Other experimental procedures were as for compound **2**: $4° \leq 2\theta \leq 50°$; Mo Kα radiation; 235 K; 1644 unique reflections; 1381 observed reflections; 127 parameters; $R = 0.031$; $R_w = 0.034$. Full details are given in the supplementary material.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-9106903.

Supplementary Material Available: Atomic coordinates, anisotropic displacement coefficients, bond lengths and bond angles, and least-squares planes for **1–4** (49 pages); observed and calculated structure factors (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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