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# Evidence for Anisotropy in Chlorine/Nitrogen Interactions in the Cyanuric Chloride Crystal Structure

Stephen J. Maginn[a*], Richard G. Compton[b], Mark S. Harding[b], Colin M. Brennan[c], Robert Docherty[c]

a. Zeneca FCMO, PO Box 11, The Heath, Runcorn, Cheshire WA7 4QE
b. Physical Chemistry Laboratory, Oxford University, South Parks Rd., Oxford OX1 3QZ
c. Zeneca Specialties Research Centre, Blackley, Manchester M9 3DA

Abstract: The non-linearity of some of the chlorine/nitrogen intermolecular interactions upon which the known crystal structure of cyanuric chloride depends is evidence for the inadequacy of current isotropic models of interatomic potentials used for crystal packing predictions.

There is currently considerable interest in obtaining a better understanding of the forces directing the formation of organic crystal structures. In particular, crystal structure prediction methods rely heavily on the use of interatomic potentials, derived theoretically and empirically, to describe the intermolecular and packing interactions present in the lattice.

In the case of chlorine, however, relatively simple isotropic potentials such as the Buckingham exp-6 potential have proved inadequate to accurately predict the range of interactions and crystal structures observed. An attempt to derive a potential from the three polymorphs of p-dichlorobenzene showed that an anisotropic potential was necessary to fully describe the chlorine/chlorine interactions therein [1]; one such potential has been developed by systematic methods and refined using the crystal structure of molecular chlorine [2]. Close contacts are well-known between chlorine atoms and hydrogen, oxygen, sulphur and nitrogen atoms in crystal structures, and trends in their directionality have been noted [3].

In particular, interactions between chlorine (or bromine) and nitrogen atoms are said [3] to show a preference for linearity when short, but most of those observed are between the halogen atom and cyano-groups. Cyanuric chloride ($C_3N_3Cl_3$, formally 2,4,6-trichloro-1,3,5-triazine) is an example of a structure which is held together by close linear and non-linear chlorine/nitrogen interactions, where the nitrogen atoms are constituents of a triazine ring, so that it is possible to look at non-cyano interactions.

The full crystal structure determination of cyanuric chloride ($C_3N_3Cl_3$, formally 2,4,6-trichloro-1,3,5-triazine) was reported recently in this journal by authors Pascal Jr. and Ho [4], following on from earlier, less complete determinations [5,6]. It consists of layers of molecules held together in an almost hexagonal array by close chlorine/nitrogen intermolecular contacts. Our coincident study on the same compound revealed the same structure, albeit refined in a non-standard setting of the same space group (I2/a instead of C2/c). However, the most significant aspect of the structure is only referred to briefly by Pascal Jr. and Ho; they state that the intermolecular chlorine/nitrogen interactions that hold the layered structure together are "linear or nearly so". In fact, in our study, as in theirs, one of the two crystallographically independant interactions is exactly linear (180.0° in both studies) whereas the other differs very substantially from linearity (172.9° in Pascal Jr. and Ho, 173.1(5)° in this study). This produces a "fish-scale" effect, with the molecules' best planes tilted at an angle of 3.4° to the crystallographic (1 0 -1) plane (see Fig. 1).

*Crystallographic data:* $C_3N_3Cl_3$, Mr = 184.41, a = 7.595(5), b = 7.474(5), c = 11.253(8)Å, ß = 95.45(6), monoclinic, I2/a, Z = 4, V = 635.6Å$^3$, $D_x$ = 1.93gcm$^{-3}$, F(000) = 180.0, $\mu$ = 1.35mm$^{-1}$, Mo $K_\alpha$radiation, $\lambda$= 0.71069Å. Final crystallographic R = 0.0717 (wR = 0.0998), for 495 unique observed reflections for which $|F_o| > 4\sigma(|F_o|)$. Approximate crystal size 0.6 x 0.4 x 0.3mm, recrystallised from solution in petroleum ether 100-120° fraction. Data collected on a Rigaku AFC6S diffractometer, structure solved using direct methods in SHELXS [7], and refined using the TEXSAN software suite [8], by full-matrix least-squares analysis. Linear decay correction applied, as crystal was found to slowly degrade due to reaction with water vapour in the atmosphere. All atoms located and refined with anisotropic thermal vibration parameters - no constraints applied.

One would perhaps assume that a molecule such as cyanuric chloride would adopt a crystal structure with threefold or sixfold symmetry, as is the case with the analogous s-triazine ($C_3N_3H_3$) structure, which is rhombohedral at room temperature [10]. In fact, the structure is more closely related to that of cyanuric acid ($C_3N_3(OH)_3$), which consists of parallel chains of hydrogen bonded molecules, adjacent to each other in layers, yet with no hydrogen bonding interaction between the chains [11,12]. Also, the molecules of cyanuric chloride in adjacent layers do not lie in the correct relative orientation for the insertion of a 3-fold rotation axis perpendicular to the (1 0 -1) plane.

It is worth mentioning that the chlorine/nitrogen distances of around 3.10Å are significantly shorter than the sum of their van der Waals' radii, 3.30Å [13]. In other chloro-substituted triazine compounds, no such close interactions between the chlorines and triazine nitrogens exist, presumably because of the steric effects of other, bulkier substituents [9,14], although the structure of 5-chlorobenzfurazan-1-oxide is said to contain Cl---N contacts of 3.20Å [15].

Fig. 1: A perspective view of the cyanuric chloride lattice, as seen down the b-axis, showing "fish-scale" effect.

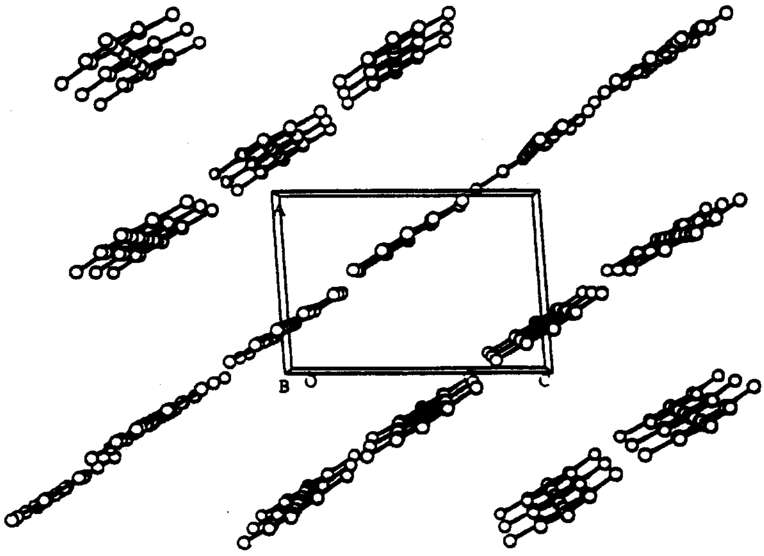

**Table 1.**

a. not included in the minimisation inside CERIUS. Taken from determined crystal structure.

| x = | C-Cl(x) (Å) | Cl(x)--N(x) (Å) | C-Cl(x)--N(x) (°) | source |
|---|---|---|---|---|
| 1 | 1.692(9) | 3.120(9) | 180 | x-ray (this work) |
| 2 | 1.708(8) | 3.15(1) | 173.1(5) | x-ray (this work) |
| 2' | 1.708(8) | 3.15(1) | 173.1(5) | x-ray (this work) |
| | | | | |
| 1 | 1.708 | 3.04 | 179.1 | MOPAC |
| 2 | 1.708 | 3.04 | 178.9 | MOPAC |
| 2' | 1.708 | 3.04 | 178.9 | MOPAC |
| | | | | |
| 1 | 1.692$^a$ | 3.12 | 178.6 | CERIUS |
| 2 | 1.708$^a$ | 3.12 | 177.2 | CERIUS |
| 2' | 1.708$^a$ | 3.13 | 176.9 | CERIUS |

It was decided to carry out some molecular optimisations and crystal packing calculations, to determine whether the observed structure could be reproduced with currently available interatomic potentials. In the first instance, a cyanuric chloride molecule was built using the standard fragments within SYBYL [16], and minimised in energy using MOPAC [17]. The MOPAC keyword "PRECISE" was used to tighten up tolerance levels during optimisation. The optimised molecule shows reasonable agreement with the observed structure. The C-Cl bond distance of 1.712Å compares with the mean C-Cl observed distance of 1.702Å. The optimised N-C-N angle of 125.8° is in good agreement with the mean observed angle of 126.23° (this determination; 127.4° in ref. 4). The optimised C-N bonds are slightly longer - 1.371Å as opposed to an average of 1.326Å in the determined molecule. The largest difference is the presence of perfect three-fold symmetry in the optimised molecule, which is 15.2 kcal/mol more stable than the observed molecule (calculated using MOPAC).

A layer containing nine molecules of the title compound was taken from the observed crystal structure and minimised using MOPAC. No symmetry constraints were applied; i.e. the system was considered to be triclinic, allowing the formerly constrained C(2)-Cl(1)...N(1) interaction to refine freely. In this case, considering only the central molecule in this array, the intramolecular bond lengths within the ring assume the values obtained from the single molecule optimisation. The C-Cl bond lengths are reduced to 1.708Å from 1.712Å in the isolated molecule case. Again, this is in good agreement with the mean C-Cl distance of 1.702Å in the determined structure. The C-Cl---N angles all tended towards linearity, converging at values of 179.1°, 178.9° and 178.9° for the angles through Cl(1) (the linear interaction in the determined structure), Cl(2) and Cl(2)' respectively. The non-bonded Cl---N contact distance was 3.04Å. The distinctive "fish-scale" arrangement was therefore removed, producing a much flatter, regular structure.

Full crystal packing calculations were carried out within CERIUS [18] using the open force-field parameters and charges from Goddard et al. [19]. The lattice energy calculated for the observed structure was -17.7 kcal/mol. This energy was then minimised with molecular translations and rotations allowed, but retaining triclinic symmetry. Convergence occurred at -18.9 kcal/mol, with intermolecular C-Cl---N angles of 178.6, 177.2° and 176.9° through Cl(1), Cl(2) and Cl(2)' respectively.

The intermolecular Cl---N contacts were 3.12Å. Thus, as in the MOPAC optimisation, the "fish-scale" effect is removed, although a small deviation from a perfect, flat, hexagonal layer structure is still apparent, perhaps due to the use of triclinic symmetry and the asymmetry present in the original molecular structure.

The molecular and crystal modelling work, all summed up in Table 1, therefore indicates that current sets of isotropic interatomic potentials are insufficient to successfully predict the observed crystal structure for cyanuric chloride. As it is thought that there would be significant anisotropy due to the axial nitrogen and equatorial chlorine lone electron pairs, and the $\pi$-electron density [20], this may be regarded as evidence for the importance of anisotropy in chlorine/heteroatom interaction potentials in influencing a crystal structure. It may be speculated whether application of anisotropic interatomic potentials for chlorine would successfully predict the observed structure. A charge density study on the system would also provide valuable information.

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