Role of Intermolecular Hydrogen-bonding in the Crystal Structure of α-Chloroacetic Acid

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Summary The crystal structure of α-chloroacetic acid has revealed that it exists as a hydrogen-bonded tetramer, which allows for the presence of two non-equivalent chlorine atoms.

As a part of a general e.s.r. study of the damage caused by radiation in crystals of carboxylic acids,[1] we have investigated the structures of halogenated acetic acids and have found evidence for the existence of anomalous hydrogen-bonding in the case of α-chloroacetic acid. Fluoroacetic acid[2] and the two forms of bromoacetic acid[3] have been shown to exist as centrosymmetric dimers formed by hydrogen-bonded carboxy group coupling. The i.r., Raman,[4] and n.q.r.[5] spectra of α-chloroacetic acid suggest a hydrogen-bonded network and two non-equivalent Cl atoms. Our X-ray work confirms this and shows that α-chloroacetic acid exists as a hydrogen-bonded tetramer.

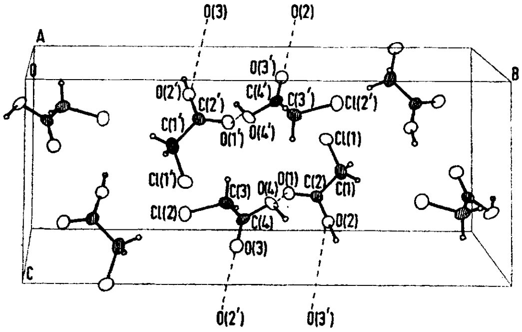

FIGURE. Crystal structure of α-chloroacetic acid with the hydrogen bonds of the tetramer (– – –). Atoms symmetry related to the asymmetric unit are indicated by primes.

Crystal data: $C_8H_{12}Cl_4O_8$, monoclinic, space group $P2_1/c$, $a = 5{\cdot}379(6)$, $b = 19{\cdot}148(9)$, $c = 7{\cdot}859(7)$ Å, $\beta = 109{\cdot}08(6)°$, $U = 762{\cdot}9$, $D_m = 1{\cdot}60$ g cm^{-3}, $Z = 8$, $D_c = 1{\cdot}58$ g cm^{-3}; for 810 reflections, $R = 0{\cdot}092$.

The unit cell contents, shown in the Figure, illustrate the tetrameric nature of the hydrogen-bonded network. The O(1) · · · O(4) distance of 2·70(1) Å is close to that expected with the presence of a hydrogen bond, and an equal length is also found for O(2) · · · O(3′). The centre of inversion which the tetramer possesses completes the array with O(3) · · · O(2′) and O(1′) · · · O(4′). Since the R factor is relatively high, the O · · · O distances are the most meaningful indicators of hydrogen-bonding.

The non-equivalence of the chlorine atoms is also seen in the Figure. Cl(2) appears to participate in a three-centre hydrogen bond with O(3) and O(2′). Cl(1) is on the 'outside' of the tetramer, and is not hydrogen-bonded. This difference is also manifested in the carbon–chlorine bond lengths. For C(3)–Cl(2), the distance is 1·789(6) Å, while the C(1)–Cl(1) separation is 1·725(6) Å. Thus the carbon–chlorine length is significantly longer for the chlorine atom involved in hydrogen-bonding.

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