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The crystal structures of ethylenediammonium chloride and tetramethylenediammonium chloride. By TAMAICHI ASHIDA and SAKUTARO HIROKAWA, *Department of Chemistry, Defense Academy, Yokosuka, Japan*

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Recently a *gauche* form of the tetramethylenediammonium (TDA) ion in a crystal was reported by the present authors (Hirokawa & Ashida, 1961 and 1962). Ethylenediamine (EDA) has been reported as being a *gauche* form (Nakahara, Saito & Kuroya, 1952; Scouloudi, 1953). On the other hand, the crystallographic data of EDA adipate (Hirokawa, Ohashi & Nitta, 1954) suggest that EDA is planar (*trans*). Then, a planar (*trans*) form of the TDA ion would be also possible in crystals, being similar to the configuration of the hexamethylenediammonium ion (Binnie & Robertson, 1949; Hirokawa *et al.*, 1954). Thus both EDA and TDA will be able to have either a *gauche* or a *trans* form in crystals. Ethylenediammonium chloride (EDA.HCl) and tetramethylenediammonium chloride (TDA.HCl) were chosen to be studied in order to elucidate this aspect of the problem.

Crystallographic data of EDA.HCl ($C_2H_4(NH_3)_2Cl_2$) and TDA.HCl ($C_4H_8(NH_3)_2Cl_2$) are:

EDA.HCl:

$$a = 9.95, b = 6.89, c = 4.42 \text{ \AA}; \beta = 90^\circ 40'$$

TDA.HCl:

$$a = 10.73, b = 8.35, c = 4.60 \text{ \AA}; \beta = 92^\circ 30'$$

and the space group is $P2_1/a$ for both crystals. (The data for EDA.HCl coincide with those given by Groth, 1910.) There are two organic ions in a unit cell of each crystal; hence the diammonium ions are centrosymmetrical. These crystallographic data suggest that the structures of both crystals are similar to each other but fairly different from that of hexamethylenediammonium chloride (Binnie & Robertson, 1949).

Intensity data for both ($hk0$) and ($h0l$) were used for the structure determination of both crystals. At this stage, the error indices for the four zones are from 0.066 to 0.082; in each case, contributions of hydrogen atoms to the F -values were not negligible, and they were included in the calculations of the structure factors.

The crystal structure of EDA.HCl projected on the (001) plane is shown in Fig. 1(a), and TDA.HCl on (010) in Fig. 1(b). The similarity of the structures of both crystals is interesting if the difference in size of these organic ions is considered. The modes of packing of the ions in the crystals are said to be identical. This situation is shown in Figs. 1(a) and 1(b). Four carbon atoms of the TDA ion have almost the same x and y coordinates (in \AA units) as those of the C's and N's of EDA.HCl.

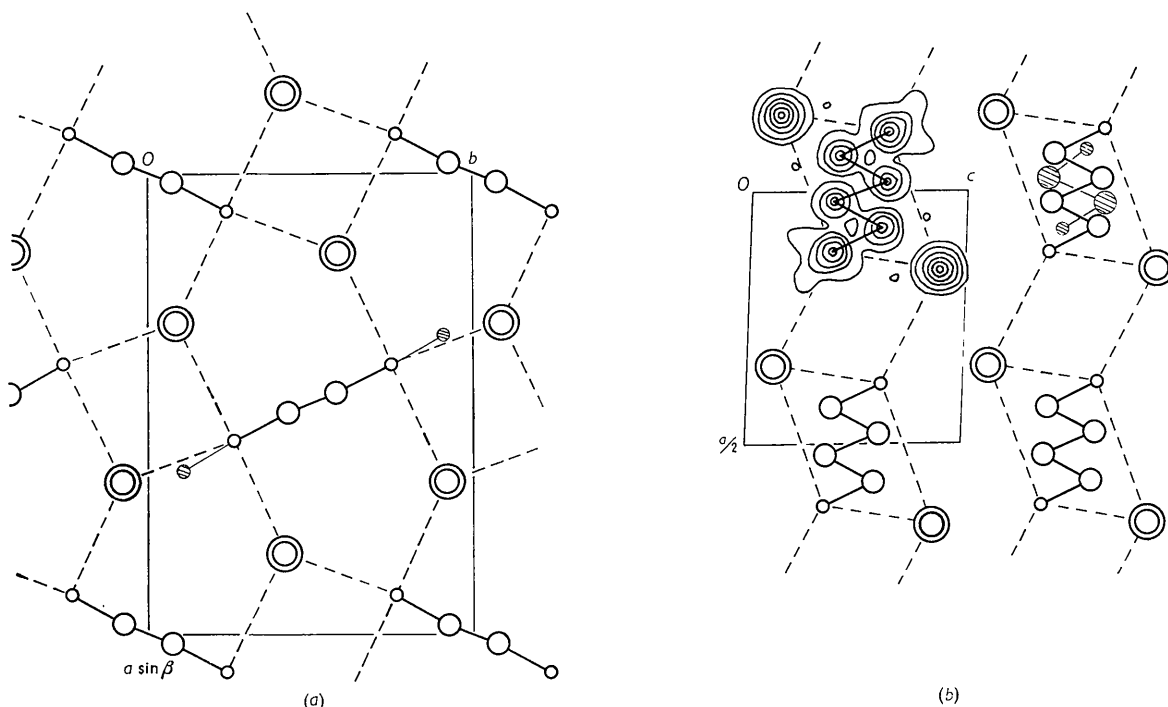


Fig. 1. (a) The crystal structure of EDA.HCl projected onto the (001) plane. (b) The structure of TDA.HCl on (010); in part of the electron-density function, contours are drawn at arbitrary equal intervals except at the Cl ions, where the interval is three times that for the lighter atoms. Large double, medium, and small circles represent Cl, C and N respectively. Broken lines represent hydrogen bonds. Shaded circles—see text.

Thus if two atoms shaded near the organic ion at the center of Fig. 1(a) are added and if the broken lines which show hydrogen bonds are drawn from these newly added atoms, the figure will show approximately the structure of TDA.HCl projected onto the (001) plane. And in Fig. 1(b), if the TDA ions are replaced by EDA ions in the manner shown by a shaded molecule at one site, that will correspond approximately to the structure of EDA.HCl projected onto the (010) plane. Each nitrogen atom in both crystals is linked to three Cl⁻ ions by hydrogen bonds, being separated from them by distances from 3.14 to 3.28 Å. And these hydrogen bonds make infinite two-dimensional networks parallel to the (001) planes as are shown in Figs. 1(a) and 1(b). These facts explain a perfect cleavage perpendicular to the c axes of both crystals.

Because both the EDA and TDA ions are centrosymmetrical, the skeleton of the EDA ion and the carbon chain of the TDA ion are geometrically planar (*trans*). The terminal N atoms of the TDA ion were found to be

in the plane of the carbon chain (the deviations of the N atoms from the plane are less than 0.001 Å). Thus both EDA and TDA so far determined can be either *gauche* or *trans* forms, depending on the structures of the crystals.

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Helical features in the X-ray pattern of poly-(γ -hydroxypropyl)-L-glutamine. By W. TRAUB, Department of X-ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel

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Yaron, Lupu, Berger & Sela (1962) have reported optical rotatory and viscosity measurements of solutions of poly-(γ -hydroxypropyl)-L-glutamine (Fig. 1) in a series of methanol-water mixtures. They concluded from these

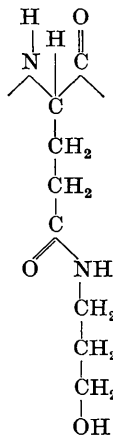


Fig. 1. Residue of poly-(γ -hydroxypropyl)-L-glutamine.

studies that the polymer exists in the α -helical conformation in methanol, and that, though the addition of water tends to destroy this structure, it is maintained to a substantial extent even in pure water. Evidence that this polymer has an α -helical structure in the solid state has now been obtained from X-ray diffraction.

Poly-(γ -hydroxypropyl)-L-glutamine of 50,000 molecular weight was kindly provided by Dr A. Yaron. X-ray powder photographs of some of this material recrystallized from methanol show a crystalline pattern of about a dozen fairly sharp lines. These include several

strong reflexions in the region 4 to 5 Å and an outstanding reflexion at 1.50 Å. Both of these features are commonly observed in X-ray patterns of α -helical structures.

Further strong evidence for an α -helical structure was obtained from photographs of an oriented fibre drawn from a concentrated solution of the polymer in methanol. The oriented diffraction pattern shows only two strong layer lines, one equatorial and the other with a layer-line spacing of about 5.4 Å, the value characteristic of the α -helical pattern (Crick & Kendrew, 1957). The moderately strong equatorial reflexions at 14.3 and 11.6 Å are consistent with the close packing of α -helices with the large side chains of poly-(γ -hydroxypropyl)-L-glutamine.

Powder photographs were also taken of a sample of the polymer recrystallized from water. They show a pattern which, though not identical with that obtained from the methanol preparation, includes all the stronger lines of the latter and in particular those in the 4 to 5 Å region and at 14.3, 11.6 and 1.50 Å. It therefore seems probable that this preparation too contains some material with an α -helical structure.

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