The Crystal Structure of Tetramethylenediammonium Chloride*

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There have been fewer published structural investigations of tetramethylenediamine (TDA) in the crystals than of the homologous compounds, ethylenediamine (EDA)[1-5] and hexamethylenediamine,[6-8] both of which are the nearest to TDA in the even-membered series of polymethylenediamines. Recently, the present authors reported a gauche-form of the TDA ion in the crystal of its adipate,[9,10]

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1) T. Ashida and S. Hirokawa, This Bulletin, **36**, 704 (1963).

2) A. Nakahara, Y. Saito and H. Kuroya, ibid., **25**, 331 (1952).

3) S. Ooi, Y. Komiyama and H. Kuroya, ibid., **33**, 354 (1960).

4) Y. Okaya and I. Nitta, *Acta Cryst.*, **5**, 564 (1952).

5) K. Sakurai, *J. Phys. Soc. Japan*, **16**, 1205 (1961).

6) W. P. Binnie and J. M. Robertson, *Acta Cryst.*, **2**, 180 (1949).

7) W. P. Binnie and J. M. Robertson, ibid., **3**, 424 (1950).

8) S. Hirokawa, T. Ohashi and I. Nitta, ibid., **7**, 87 (1954).

9) S. Hirokawa and T. Ashida, ibid., **14**, 1004 (1961).

10) S. Hirokawa and T. Ashida, *Memoirs of the Defense Academy*, Vol. II, No. 3, 95 (1962).

though they had expected a planar (trans-) configuration of the ion. Although no investigations so far published have shown the planar configuration of TDA in the crystals, a planar configuration as the cases of EDA[1] and hexamethylenediamine[6-8] may be expected for TDA. Thus, a trans-gauche stereoisomerism like that of EDA is possible for TDA. Tetramethylenediammonium chloride (TDA · Cl) was chosen to be studied in order to elucidate this aspect of the problem. The structural analysis of TDA·Cl may be interesting because the crystal structures of both ethylenediammonium chloride (EDA·Cl)[1] and hexamethylenediammonium chloride[6] have been reported. The present study will show a crystal structure analogous to that of EDA·Cl, and some comparisons between the present crystal and that of EDA·Cl will be made.

Experimental

Tetramethylenediammonium chloride, $H_3N(CH_2)_4NH_3 \cdot 2Cl$, was obtained as white precipitates from ethanol solutions of the components in a stoichiometric molar ratio. The crystals were grown from ethanol-water solutions. The three principal axes of the crystals were designated by referring to those of EDA·Cl.[1] Some of these crystals were obtained as needles elongated along the b-axis, and others, as plates, the main face being (1 0 0). A perfect cleavage perpendicular to the c-axis was found. The crystal belongs to the monoclinic system, and the unit cell dimensions were obtained from the Weissenberg photographs of (h 0 l) and (h k 0) by overlapping the powder patterns of aluminum as a standard; they are:

$$a=10.73\pm0.01\ \text{Å} \qquad b=8.35\pm0.01\ \text{Å}$$
$$c=4.60\pm0.01\ \text{Å} \qquad \beta=92.5\pm0.3°$$

The space group was found to be $P2_1/a$ from the systematic absences of the following spectra: (0 k 0) for $k=2n+1$, and (h 0 l) for $h=2n+1$. The density, 1.30 g.cm^{-3}, observed by the flotation method corresponds to two formula units in a unit cell; the calculated density is 1.30 g.cm^{-3}.

Weissenberg photographs were taken around the b- and c-axes using CuK_α radiation. The multiple-film technique was used, and the intensities of (h 0 l), (h k 0) and a part of the (h k 1) reflections were estimated visually, comparing them with a standard scale. Corrections for polarization and Lorentz factors were made. The linear absorption coefficient of the crystal for CuK_α is rather large ($\mu=64.0\ \text{cm}^{-1}$). However, the shapes of the crystals used in the experiments were irregular, and no absorption corrections were made.

Structure Determination

Since the crystal belongs to the $P2_1/a$ space group and since the number of formula units in the unit cell is two, the TDA ion has to occupy a center of symmetry of the unit cell. The position of the chloride ion was determined from the projections of the Patterson function along the b- and c-axes. The projections of the electron-density functions along the two principal axes were synthesized by using the structure factors whose phases were assigned by the coordinates of the chloride ion. The maps thus obtained showed the positions of the carbon and nitrogen atoms. The coordinates of the atoms were then refined by successive (F_o-F_c) syntheses. In the course of these refinements, it was found that the contributions of the hydrogen atoms to the structure factors were not negligible; the number of electrons which belong to the hydrogen atoms amount to 16% of the total number of electrons in the crystal. Then, the coordinates of all the hydrogen atoms were calculated geometrically, using the coordinates of the heavier atoms, and these calculations were confirmed on the $(\rho_o-\rho_c)$ maps. These hydrogen atoms were used in the further refinements of the structures, and the R factors of the two zones decreased by about 0.02. In these procedures, it was found that if the hydrogen atoms lying near the heavier atoms were disregarded, the coordinates of the heavier atoms cannot be improved by (F_o-F_c) syntheses. In fact, significant shifts in the positions of the atoms, especially carbon and nitrogen, were observed when the hydrogen atoms were included in the calculations. The

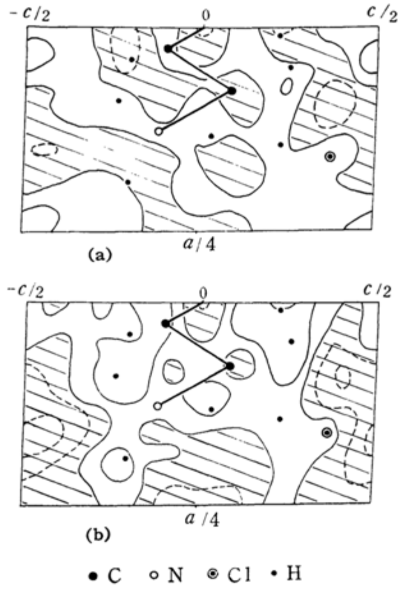

Fig. 1. Final $(\rho_o-\rho_c)$ projected on (0 1 0). (a): ρ_c includes all the atoms; (b): ρ_c does not include any hydrogen atoms. Contours at intervals of 0.4 e. Å^{-2}, broken lines represent negative contours, and negative areas are shaded.

final ($\rho_o - \rho_c$) maps of (*h* 0 *l*) are shown in Fig. 1, where significant changes due to the inclusion or exclusion of the hydrogen atoms are observed, not only at the positions of the hydrogen atoms but almost everywhere.

The final atomic coordinates and the temperature factors of the heavier atoms are listed in Table I. Each absolute value of the temperature factors listed in Table I may not have a rigid meaning, however, because no absorption corrections for the intensities were made. The comparisons between the observed and calculated structure factors are shown in Table II. The final *R* factors are 0.058 and 0.075 respectively for (*h* 0 *l*) and (*h k* 0), excluding a few reflections which showed marked

TABLE I. FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS (Å^2)

	x	*y*	*z*	*B**	*B***
C(1)	0.076	0.204	0.079	1.60	1.70
C(2)	0.025	0.063	0.903	2.45	1.70
N	0.126	0.331	0.885	2.35	1.70
Cl$^-$	0.158	0.600	0.375	1.85	1.70

* Temperature factors obtained for (*h* 0 *l*).

** Temperature factors obtained for (*h k* 0).

TABLE II. OBSERVED AND CALCULATED STRUCTURE FACTORS

In each column, the left hand column is the *h* index, the middle column the observed structure factor, and the right hand column, the calculated structure factor. All structure factors have been multiplied by ten.

(*h* 0 *l*)		
h 0 0		
2	116	124
4	402	−434
6	293	307
8	0	11
10	184	−186
12	107	114
h 0 1		
0	138	147
2	144	140
4	278	315
6	204	−199
8	107	−97
10	275	269
12	17	−1
−2*	370	642
−4	107	−82
−6	276	−277
−8	191	184
−10	26	−31
−12	196	−191
h 0 2		
0	57	54
2*	376	488
4	286	−281
6	153	−152
8	290	281
10	16	23
12	39	−33
−2	378	−412
−4	289	264
−6	115	104
−8	318	−319
−10	25	−26
−12	54	53
h 0 3		
0	135	133
2	257	−254
4	11	1
6	166	157
8	112	−110
10	57	54
−2	46	56
−4	224	−214
−6	121	118
−8	19	22
−10	257	−259
−12	8	−1
h 0 4		
0	318	−327
2	21	22
4	129	135
6	186	−169
8	28	24
−2	59	69
−4	191	196
−6	190	−173
−8	61	−52
−10	65	61
h 0 5		
0	0	14
2	36	−25
4	160	−151
6	68	72
−2	173	−167
−4	44	47
−6	118	124
(*h k* 0)		
h 0 0		
2	110	124
4	371	−420
6	313	315
8	0	24
10	179	−190
12	124	109
h 1 0		
1	107	−100
2	125	−126
3*	410	643
4	313	−331
5	0	8
6	0	−16
7	238	−219
8	165	163
9	163	154
10	80	−82
11	0	27
12	55	−48
13	126	−100
h 2 0		
0	20	7
1	302	−367
2	37	−29
3	75	−57
4	72	73
5	210	189
6	174	174
7	259	−246
8	0	9
9	79	−66
10	52	−56
11	182	191
12	31	26
13	84	−87
h 3 0		
1	196	190
2	377	414
3	224	−187
4	257	−249
5	0	21
6	130	−116
7	176	180
8	175	158
9	0	−4
10	148	−162
11	50	−59
12	133	−130
13	0	−13
h 4 0		
0	305	−324
1	248	−238
2	150	146
3	62	−60
4	227	223
5	204	214
6	249	−232
7	126	−112
8	0	−25
9	171	−182
10	150	130
11	0	1
12	79	−65
h 5 0		
1	186	184
2	59	48
3	291	−276
4	62	−45
5	0	30
6	103	−106
7	92	94
8	37	−38
9	193	−206
10	0	4
11	0	26
12	0	−28
h 6 0		
0	178	−175
1	96	102
2	42	52
3	56	−62
4	0	24
5	223	−210
6	213	−196
7	37	45
8	51	51
9	60	54
10	101	104
11	79	−71
h 7 0		
1	83	−72
2	293	−292
3	119	−107
4	119	118
5	37	33
6	82	81
7	48	49
8	163	−164
9	42	−42
10	31	29
h 8 0		
0	52	−52
1	190	207
2	69	−86
3	89	88
4	0	−34
5	165	−172
6	31	50
7	67	60
8	0	−19
9	42	51
h 9 0		
1	52	−65
2	46	−54
3	62	70
4	108	103
5	88	−96
6	0	34
7	78	−87
h, 10, 0		
0	141	135
1	0	−22
2	62	−62
3	27	−20
4	104	−104
(*h k* 1)**		
h 1 1		
0	322	330
3	105	−103
4	161	−168
5	0	−18
6	261	253
7	267	282
h 2 1		
0	217	−217
h 3 1		
0	372	404
h 4 1		
0	236	196
−1	0	25
−2	229	−188
−3	136	−137
−4	50	55
h 5 1		
0	0	−14

* These reflections were not used for the refinements because of their marked extinction effects.

** These reflections were not used for the refinements, and do not include contributions of the hydrogen atoms.

extinction effects (these are shown with asterisks in Table II).

Discussion of the Results

Some of the important interatomic distances and bond angles in this crystal are shown in Table III and in Fig. 2. Because the TDA ion occupies a center of symmetry, the four carbon atoms are completely coplanar. The terminal N atoms are also in the plane and join with the carbon atoms to make a coplanar zigzag chain; the displacement of the N atom from the plane of the four carbon atoms is found to be less than 0.001 Å. Thus, in the crystals, the TDA ion was found to have either a trans- or gauche-configuration, depending on the structures of the crystals.

TABLE III. IMPORTANT INTERATOMIC DISTANCES (Å) AND ANGLES (deg.)

C(2)-C(2′)	1.50	C(2′)C(2)C(1)	110.0
C(2)-C(1)	1.52	C(2)C(1)N	110.0
C(1)-N	1.50		
		C(1)NCl(1)	96.2
N-Cl(1)	3.19	C(1)NCl(2)	89.3
N-Cl(2)	3.28	C(1)NCl(3)	94.7
N-Cl(3)	3.28	Cl(1)NCl(2)	101.7
		Cl(1)NCl(3)	127.0
N-Cl(4)	3.28	Cl(2)NCl(3)	129.1
		C(1)NCl(4)	164.4

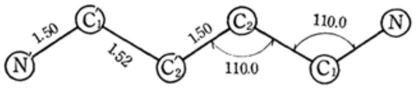

Fig. 2. Dimensions of TDA ion.

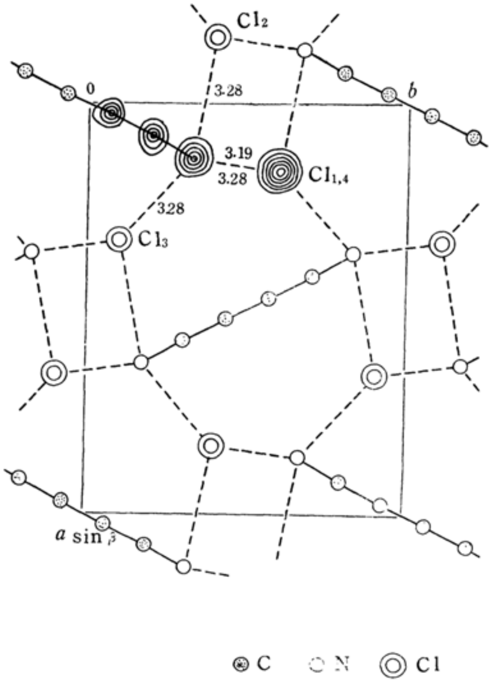

Fig. 3. The structure of TDA·Cl projected on (0 0 1). Broken lines represent hydrogen bonds. In a part of the electron-density function, contours are drawn at an arbitrary equal interval, except at Cl^-, where an interval is three times of that for lighter atoms.

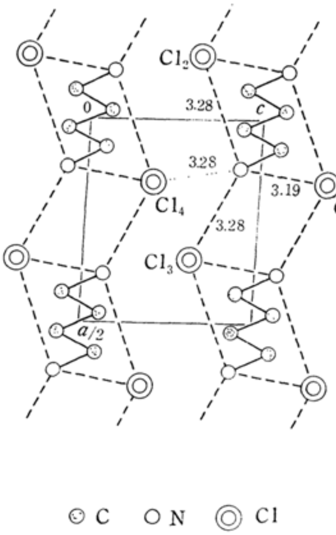

Fig. 4. The structure of TDA·Cl projected on (0 1 0). Broken lines represent hydrogen bonds. A dotted line shows another short contact between N and Cl^-.

The crystal structure projected on the (001) and the (0 1 0) planes is shown in Figs. 3 and 4. The nitrogen atom has four nearest neighbors among the chloride ions (Cl(1), Cl(2), Cl(3) and Cl(4) in Figs. 3 and 4), the N-Cl distances being 3.19, 3.28, 3.28 and 3.28 Å respectively. Such N-Cl lengths are comparable to the values of 3.10∼3.30 Å found in EDA·Cl,[1] hexamethylenediammonium chloride[6] and several other crystals.[11,12] These four short contacts correspond to the N-H···Cl hydrogen bond distance. However, three of these four contacts, excluding the ' bifurcated ' type, may be hydrogen bonds. The C(1)-N-Cl(4) angle (164.4°) is so large that N-Cl(4) may be excluded. The $(\rho_o-\rho_c)$ maps seem to support this view. In the $(\rho_o-\rho_c)$ projected on the (0 0 1) plane, Cl(1) and Cl(4) occupy the same position, and hydrogen atoms were found around the nitrogen atom pointing to Cl(1) or Cl(4), Cl(2) and Cl(3) respectively. On

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[11] G. C. Pimentel and A. L. McClellan, " The Hydrogen Bond," W. H. Freeman and Co., San Francisco (1960), p. 290.

[12] W. Fuller, *J. Phys. Chem.*, **63**, 1705 (1959).

the other hand, in the $(\rho_o-\rho_c)$ maps shown in Fig. 1, no hydrogen atom can be found between N and Cl(4), although in the three other short contacts hydrogen atoms are found to be present. Thus, Cl(1), Cl(2) and Cl(3) are considered as being hydrogen-bonded from the nitrogen atom. Another short contact between N and Cl(4) may be ionic in character; similar short contacts which are not hydrogen bonds have been reported in triazolo-pyrimidine hydrochloride, 3.29 and 3.31 Å.[13] Thus, in this crystal, the three N–H···Cl hydrogen bonds link the organic ions and the chloride ions and make two-dimensional, infinite networks parallel to the (0 0 1) plane. The forces which combine these layers along the c-axis may be van der Waals forces, together with electrostatic forces, if any. These facts explain the perfect cleavage parallel to the (0 0 1) plane.

A Comparison between TDA·Cl and EDA·Cl. —It may be worthwhile to make some comparisons between the structure of this crystal and that of EDA·Cl.[1] The similarity between these two crystals may be interesting if we consider the differences in the dimensions of the organic ions in the two crystals. There are considerable differences between the crystal structure of TDA·Cl and that of hexamethylenediammonium chloide, though the dimensions of the two organic ions differ from each other in just the same way as has been described above.

TABLE IV. CRYSTALLOGRAPHIC DATA OF EDA · Cl AND TDA · Cl

	EDA·Cl	TDA·Cl
a	9.95 Å	10.73 Å
b	6.89 Å	8.35 Å
c	4.42 Å	4.60 Å
β	90.7°	92.5°
Space group	$P2_1/a$	
Z	2	
Symmetry*	Center	
Cleavage**	(0 0 1)	
Needle axis	c	b
Predominant face	(0 0 1)	(1 0 0)

* Symmetry of the organic ion

** Cleavage parallel to

The crystallographic data of both EDA·Cl and TDA·Cl crystals are listed in Table IV. The a- and b-axes of TDA·Cl are a little longer than those of EDA·Cl because of the necessity to accommodate a larger organic ion. Only the crystal habits are different from each other.

The modes of packing of the ions in the crystals or of the hydrogen bonds are said to be, in effect, the same. This was one of the reasons why the possibility of a hydrogen bond between the nitrogen atom and Cl(4) was rejected in the present crystal. These situations may be understood if we compare Figs. 3 and 4 of this paper with Figs. 2 and 3 of the paper on EDA·Cl.[1] In Fig. 3 of this paper, if N is taken out and C(1) is changed to N, the figure thus obtained corresponds roughly to the structure of EDA·Cl projected on the (0 0 1) plane shown in Fig. 2 of Ref. 1. The coordinates of the atoms in both crystals (by Å unit) are listed in Table V for the sake of comparison. The inversions of the signs of the *z*-coordinates of the organic ions are inevitable in order to obtain the same packing. By considering these coordinates of the atoms, the differences in the unit cell dimensions of the two crystals may be elucidated. The equations of the planes of the zigzag chains of the organic ions are:

$$0.901X-0.434Y+0.030Z=0$$

and

$$0.895X-0.448Y-0.020Z=0$$

for TDA·Cl and EDA·Cl respectively, where $X=ax\sin\beta$, $Y=by$, and $Z=cz+ax\cos\beta$. Thus, the orientations of the organic ions to the principal axes are also not very far from each other.

TABLE V. ATOMIC COORDINATES (Å) OF EDA·Cl AND TDA·Cl

		X	*Y*	*Z*
C	EDA	0.259	0.496	0.518
C(2)	TDA	0.270	0.529	−0.458
N	EDA	0.826	1.661	−0.217
C(1)	TDA	0.815	1.705	0.327
N	TDA	1.351	2.762	−0.588
Cl	EDA	1.711	3.996	1.774
Cl	TDA	1.694	5.010	1.651

Summary

The crystal structure of tetramethylenediammonium chloride has been determined by the two-dimensional Fourier method. The crystal belongs to the monoclinic system, with $a=10.73$ Å, $b=8.35$ Å, $c=4.60$ Å and $\beta=92.5°$, and the space group is $P2_1/a$. The tetramethylenediammonium ion has been found to possess a center of symmetry of the unit cell, and the carbon and the nitrogen atoms in the ion, make a coplanar (trans-) zigzag chain. Thus, the tetramethylenediammonium ion has been found to have either a trans- or a gauche-configuration, depending on the structures of the crystals. There are four short approaches

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[13] P. G. Owston and J. M. Rowe, *Acta Cryst.*, **15**, 231 (1962).

between nitrogen and chloride ions with lengths of 3.19∼3.28Å ; three of them have been concluded to be hydrogen bonds. These hydrogen bonds make two-dimensional networks of the ions perpendicular to the c-axis. The structure of this crystal is similar to that of ethylenediammonium chloride, and some comparisons between them have been given.

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