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The crystal structures of some polymethylenediammonium adipates. II. Tetramethylenediammonium adipate.

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This investigation was undertaken to determine the molecular configuration of tetramethylenediamine, of which stereochemical data published seem to be rather few. Furthermore, this investigation may be interesting because the substance belongs to a series of polymethylenediammonium adipates studied by Hirokawa *et al.* (1954).

Crystallographic data of tetramethylenediammonium adipate $C_4H_8(NH_3)_2C_4H_8(CO_2)_2$ (4–6 nylon salt) are:

$$a = 15{\cdot}36,\ b = 5{\cdot}97,\ c = 14{\cdot}93\ \text{Å},\ \beta = 110{\cdot}5^\circ,\ Z = 4$$

and the space group is $A2/a$, in some revisions as compared with those already given (Hirokawa *et al.*, 1954).

Using the three-dimensional technique, the crystal structure was determined, and at this stage, the error index is 16·8% by including the contributions of hydrogen atoms; further refinements are now being carried on. A composite drawing of the electron-density function with sections perpendicular to the b-axis is shown in Fig. 1, where some of the hydrogens are clearly shown.

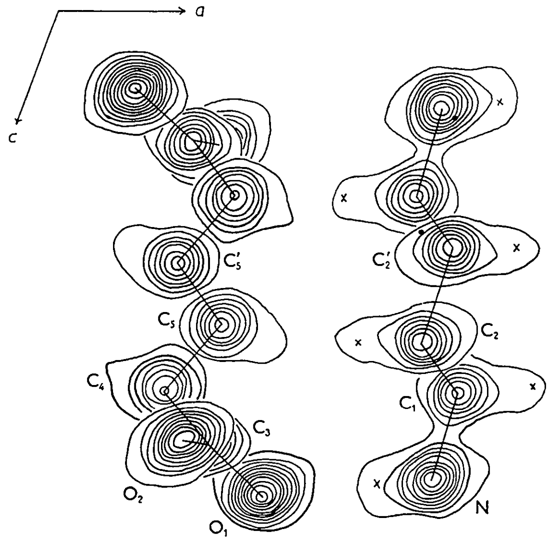

Fig. 1. A composite drawing of the electron-density function with sections perpendicular to the b-axis. The hydrogen atoms lying on the sections used in the calculation are also shown by crosses. Contours are drawn at arbitrary equal intervals.

The adipate ion possesses a center of symmetry like adipate ions in several other crystals; however, an imminent difference is found between the present result and those of other compounds. In the present case, the angle between the plane of the carboxyl group and that of the carbon zigzag chain is about 66°, which is larger than the values found in other compounds; for example, 6° in adipic acid (Morrison & Robertson, 1949), and 19° in hexamethylenediammonium adipate or 6–6 nylon salt (Hirokawa *et al.*, 1954). The situation may be due to different ways of the arrangements of the ions in the structures. The values of the bond lengths and angles in the adipate ion are quite reasonable.

The tetramethylenediammonium ion has a 2-fold axis at the middle point of the ion. The bond lengths and angles are also reasonable in this ion. The ion consists of two planar skeletal groups, each containing one half of the ion and the adjacent carbon atom (C_2'–C_2–C_1–N). The two planes thus formed make an angle of 72°; the tetramethylenediammonium ion is therefore found to possess a *gauche* form. This is characteristic if it is compared to the molecular configuration of the hexamethylenediammonium ion in the case of 6–6 nylon salt, where the ion possesses a *trans* form.

Each nitrogen makes three N–H · · · O hydrogen bonds to three different adipate ions. The situation is rather similar to the case of 6–6 nylon salt.

A detailed discussion will be published elsewhere.

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The thermal expansion of silicon.

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The results of the I.U.Cr. precision lattice parameter project, in which the lattice parameters of a series of substances were determined at ambient temperatures, have been published (Parrish, 1960). It may be of interest to note that using two 19 cm. high temperature powder cameras we have determined the lattice parameter of the silicon standard supplied for the project between 20 and 720 °C.

The camera used for the bulk of the work was a Unicam S150 (Goldschmidt type) slightly modified in so far as the 0·020″ platinum/platinum 13% rhodium thermocouple supplied was replaced by a 0·010″ ring type thermocouple and the leads brought to the cold junction in an unbroken length. This has a two-fold effect, it reduces the temperature drop across the furnaces and avoids thermal e.m.f. errors at any intermediate point in the thermocouple leads. This thermocouple was locked in such a position that the tip of the specimen actually lies inside the ring; the thermal characteristics of the camera were then determined using silver as the standard so that the specimen temperature was known to within 2 °C.

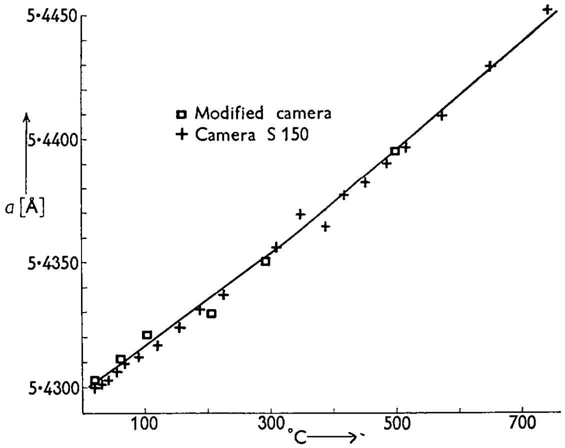

Fig. 1. The thermal expansion of silicon.

The second camera, a somewhat older type, was modified in a similar manner to that recommended by Berry, Henry & Raynor (1951).

The lattice parameter at 25 °C., corrected for refraction, was 5·43035 Å in reasonable agreement with the average parameter (5·43054 ± 0·00017 Å) obtained by the project. The coefficient of thermal expansion was found to vary from $3{\cdot}13 \times 10^{-6}$ at 25 °C. to $4{\cdot}45 \times 10^{-6}$ at 700 °C. as compared with the value of $4{\cdot}2 \times 10^{-6}$ between 10 and 50 °C. (Straumanis & Aka, 1952) assumed in the project for correction to the standard temperature of 25 °C. and the value of $2{\cdot}42 \times 10^{-6}$ between 20 and 50 °C. obtained by Erfling (1942) from macroscopic measurements.

The lattice parameter data were fitted by the method of least-mean-squares to the line.

$$a_t = 5{\cdot}429788 \pm 0{\cdot}000139 + (1{\cdot}6747 \pm 0{\cdot}1057) \times 10^{-5}t + (5{\cdot}315 \pm 1{\cdot}533) \times 10^{-9}t^2,$$

where t is in °C.

The results are shown plotted in Fig. 1.

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Crystallographic data for the α and β Isomers of 4-hydroxy-2:2:6-trimethylpiperidine.

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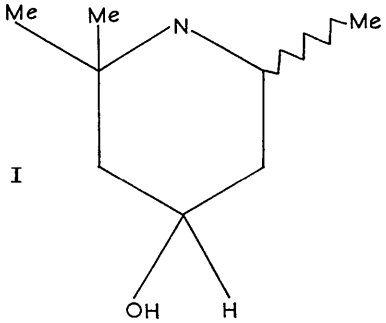
The isomers of 4-hydroxy-2:2:6-trimethylpiperidine have the formula $C_8H_{17}ON$ and the constitution I, but no definite assignment of configuration has yet been made. Both isomers were supplied as (±) mixtures.



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α-isomer (M.Pt. 137–8 °C.)

Good crystals were obtained with some difficulty from benzene. They were colourless, transparent, monoclinic laths, elongated along [100] with (010) prominent, and (001) and (011) also present.

A full survey of the reciprocal lattice was carried out using a stationary-film single-crystal camera and Cu $K\alpha$ radiation. This gave the results listed in the table below. The density was measured by flotation.

β-isomer (M.Pt. 160–1 °C.)

This was available only as colourless, transparent, platey fragments, the principal face being (001). The crystallographic data for this isomer were found in the same way and are also given in the table.

	α-isomer	β-isomer
a	$7{\cdot}6_6$ Å	$7{\cdot}7_3$ Å
b	$9{\cdot}4_5$	10·1
c	12·3	11·3
β	107°	110°
D_o	1·10 g.cm.$^{-3}$	1·15 g.cm.$^{-3}$
D_c	1·11	1·15
Z	4	4
Space group	$P2_1/c$	$P2_1/c$

The space group was determined uniquely from the systematic absences.

Detailed studies of these isomers are planned, with the object of determining both the configuration and conformation of each.

I am indebted to Dr F. Perks for suggesting this problem and supplying the specimens, and to Dr D. Rogers for guidance and encouragement.