Short Communications

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Refinement of the crystal structure of $N(CH_3)_4I_5$.

By J. Broekema, E. E. Havinga and E.H. Wiebenga,
Laboratorium voor anorganische en fysische chemie der Rijksuniversiteit, Groningen, The Netherlands

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An X-ray study of $N(CH_3)_4I_5$ by Hach & Rundle (1951) showed this compound to be monoclinic, space group $C2/c$. In this space group the 20 iodine atoms in the unit cell occupy one special, fourfold, position and two general, eightfold, positions. The iodine atoms form planar V-shaped I_5^- ions, approximately parallel to (001). Since for a comparison of the bond lengths in $N(CH_3)_4I_5$ with those in other polyhalogen compounds an improvement of the accuracy of this structure determination was desirable, a refinement of the structure was attempted.

$N(CH_3)_4I_5$ was prepared by the method of Buckles, Yuk & Popov (1952) and was obtained as greyish-green plates with a metallic shade. The intensities of 106 independent reflexions $hk0$ were measured on ordinary and integrated anti-equi-inclination Weissenberg photographs. These photographs had been taken of a very thin crystal (0·02 mm.) with Mo radiation. Since the c axis is approximately perpendicular to the plane of the crystal, the absorption was rather small; it was estimated to range from about 12 to 25% for the different reflexions and was not taken into account. As the bond lengths depend mainly on the x and y coordinates, the intensities of the reflexions $0kl$ and $h0l$ were not re-measured; the corresponding structure factors were taken from the paper by Hach & Rundle.

The coordinates of the iodine atoms were refined by successive Fourier syntheses of the three projections, and corrections for series-termination errors were made by the backshift method. In the later stages of the refinement (F_o-F_c) syntheses were used. From these syntheses it followed that different temperature factors $\exp(-B\sin^2\theta/\lambda^2)$ had to be assigned to scattering factor of the three independent iodine atoms; the thermal motion of the iodine atom in the fourfold position appeared to be anisotropic. No conclusive indications about the positions of the light atoms were obtained. The final parameters are listed in Table 1; $B_{\parallel}$ and $B_{\perp}$ refer to the thermal motions approximately in and perpendicular to the plane of the I_5^- ion respectively.

Table 1. *Final parameters*

	x	y	z	B (Å^2)
I_1	0	0·1775	$\frac{1}{4}$	$\parallel 3{\cdot}6,\ \perp 6{\cdot}1$
I_2	0·1612	0·0202	0·1976	3·6
I_3	0·1932	0·3733	0·3177	5·1

During the refinement the disagreement index R decreased from 0·21 to 0·13. The standard deviation in the final coordinates was estimated by Cruickshank's formula (1949); making an allowance for the error in the cell dimensions, we calculated a value of 0·015 Å for the standard deviation in the bond lengths.

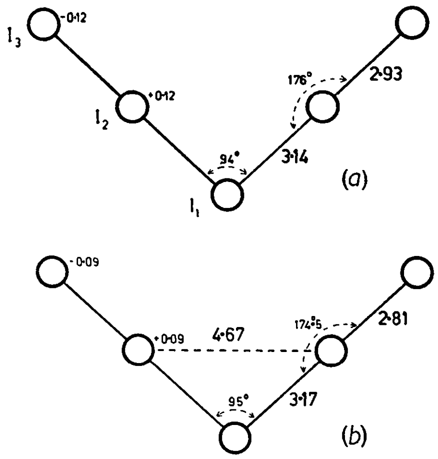

Fig. 1. (*a*) Bond lengths from the structure determination by Hach & Rundle. (*b*) Bond lengths from the refined structure.

A comparison of the bond lengths given in Fig. 1 shows that the distance I_2–I_3, in particular, has changed considerably. The shortest distance between iodine atoms of different ions changed from 3·55 to 3·63 Å.

A list of observed and calculated structure factors and other details of this work are given by Havinga (1957).

In agreement with the accepted space group, no piezo-electric effect* was observed; the crystals did show a pyro-electric effect, however, which indicates a transition point at low temperature.

References

Buckles, R. E., Yuk, J. P. & Popov, A. I. (1952). *J. Amer. Chem. Soc.* **74**, 4379.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Hach, R. J. & Rundle, R. E. (1951). *J. Amer. Chem. Soc.* **73**, 4321.

Havinga, E. E. (1957). Thesis, Groningen.

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