Single-crystal structures and electron density distributions of ethane, ethylene and acetylene

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CHAPTER 2

COOLING EQUIPMENT AND PREPARATION OF SINGLE CRYSTALS *

The crystals are grown *in situ* on the Nonius CAD-4 diffractometer. The open N_2 cooling system applied, is an improved version of the Nonius system and the system described by van Bolhuis (1971). The Dewar tube K (Fig. 2.1) is of high vacuum quality and as short as possible. The outlet at the end of K must be as close as possible above the crystal. The liquid nitrogen level in the evaporation vessel is kept stable and just below the isoprene layer V. Destabilisation due to gas formation during the transport of liquid nitrogen into the evaporation vessel is prevented, (a) by placing the end of IV which is given a conical shape, in the centre and just above the narrow outlet of the funnel, and (b) by use of a liquid-gas separator VII at the end of this funnel. In tube K a very long thoroughly winded wire is used both as a throttle for stabilisation of the N_2 flow, and as a

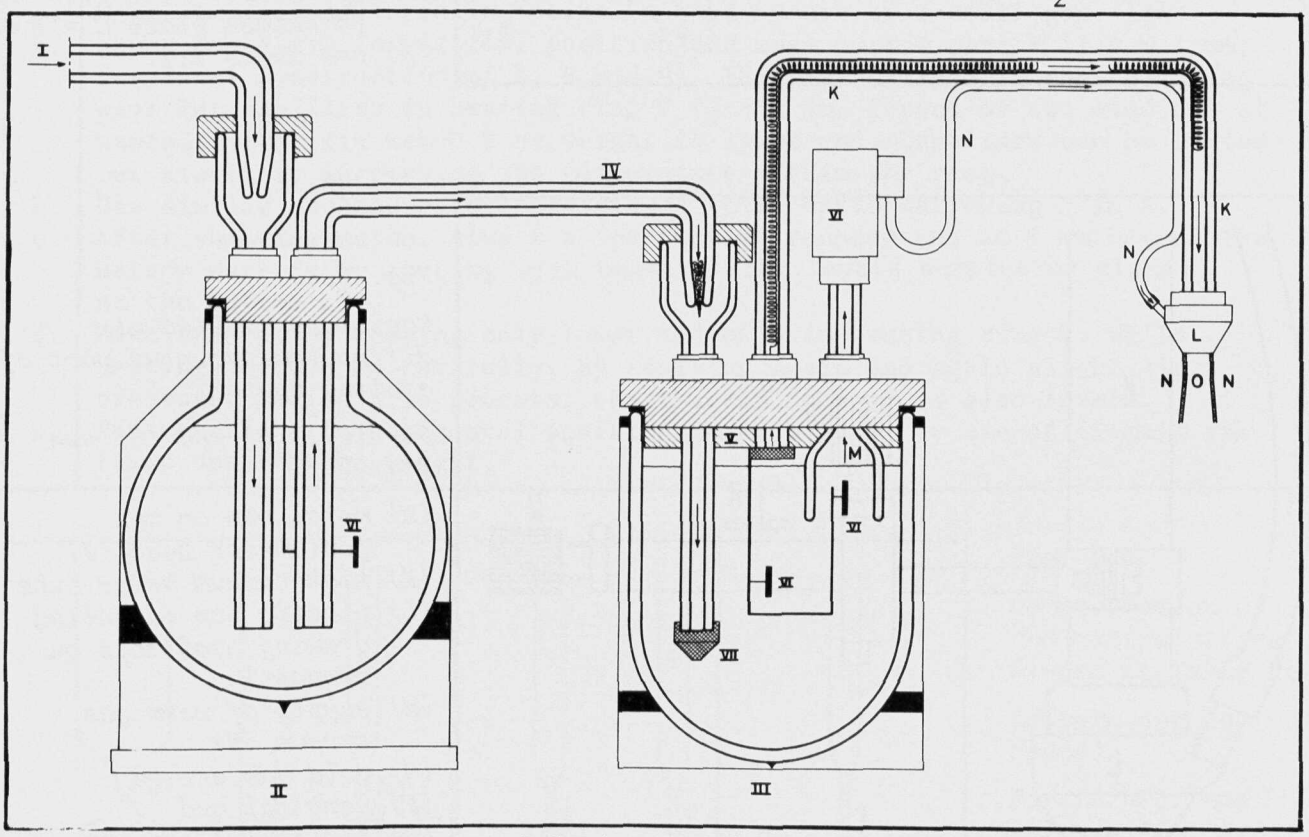

Fig. 2.1. Cooling equipment used during our diffraction experiments (see also Fig. 2.4).

(I) from 50 l container; (II) 10 l container; (III) evaporation vessel; (IV) supply of liquid N_2; (V) isoprene layer; (VI) heaters; (VII) liquid-gas separator; (K) high-vacuum Dewar tube; (L) plastic box; (M) supply of warm gas stream (N); (O) cold gas stream

* This chapter is a (slightly) extended version of the paper: "Sperical crystals crystals grown *in situ* for low temperature X-ray work on volatile compounds", by van Nes & van Bolhuis (1978). *J.Appl.Cryst.* *11*, 206-207.

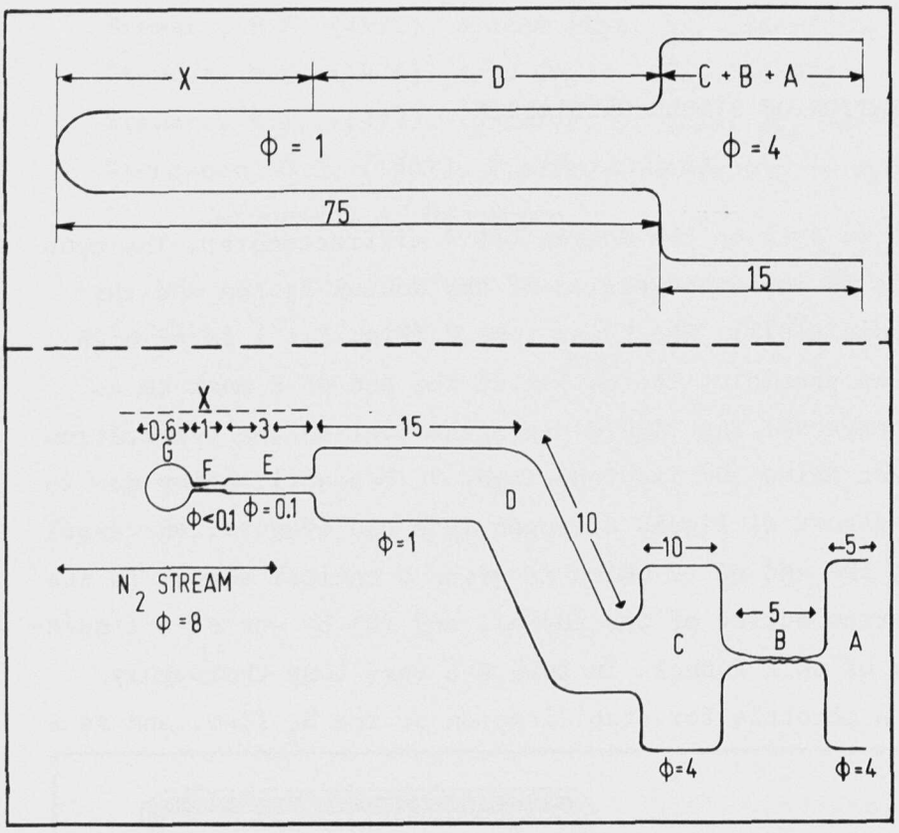

Fig. 2.2.

Above: Commercially available capillary.
Below: Capillary tube for present work before filling with a gas.

(Figures not to scale, dimensions given in mm).

(A) to gas cylinder
(B) sealing point
(C) gas reservoir
(D) bend necessary for mounting (Fig. 2.4)
(E) and (F) narrow part to avoid turbulence of N_2 stream
(F) small opening to obtain well defined spherical crystal, ϕ(inner,F) = 0.01-0.02 mm
(G) sphere with ϕ ≃ 0.60 mm; thickness glass G ≃ 5μm
(X) see Table 2.1.

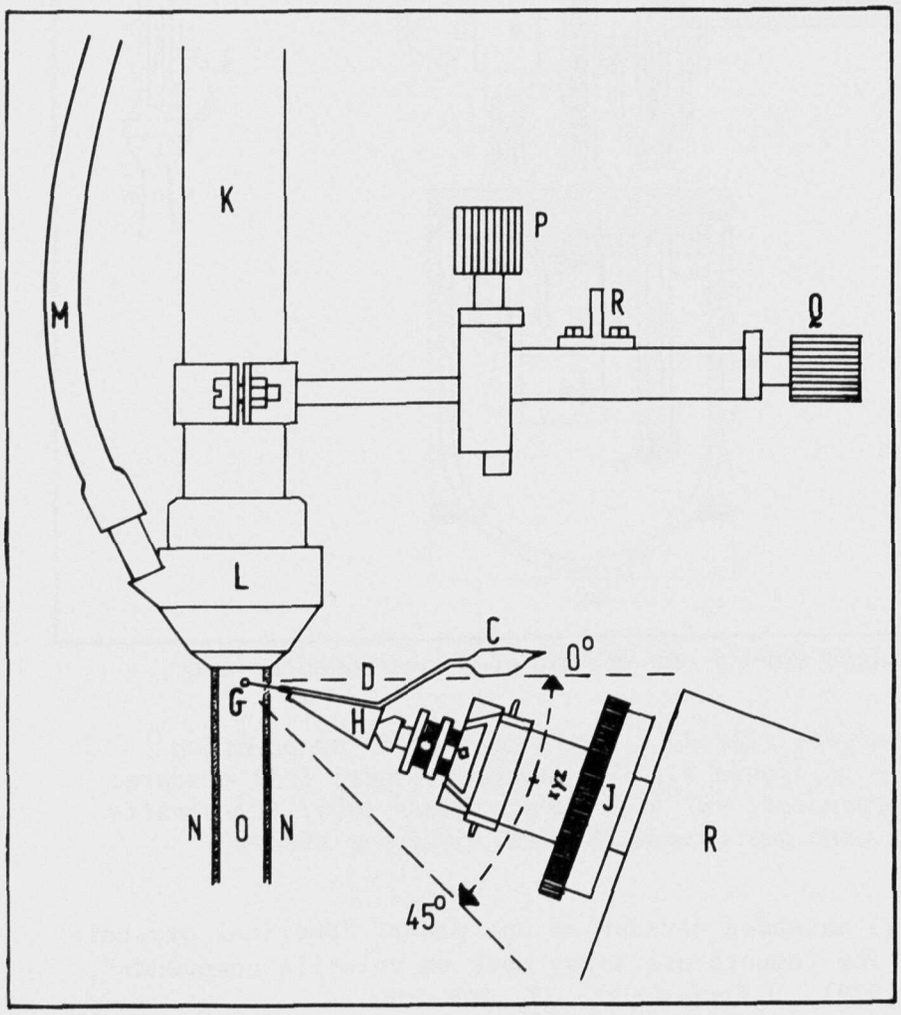

Fig. 2.4.

Capillary mounted at diffractometer plus part of cooling system.

For (C), (D) and (G) see Fig. 2.2.

(H) metal pin on xyz goniometer head (J)
(K) high-vacuum Dewar tube
(L) plastic box (detailed drawing available on request)
(M) supply of warm gas stream (N)
(O) cold gas stream
(P) vertical and
(Q) horizontal adjustment screws
(R) part of diffractometer

heater filament for measurements at higher temperatures. The Chromel-Alumel thermocouple is fixed inside K at L.

During the intensity measurements of C_2H_6 and C_2H_4, a temperature of 85 K, stable within 0.1 K, was used with a liquid N_2 consumption of about 1.5 l/h. For C_2H_2 the temperature during the measurement was 141 K, with a stability of 0.1 K and the same liquid nitrogen consumption as before.

Fig. 2.2 (above) shows the commercially available Helmut Hanff X-ray capillaries (Paul Räbinger, Simplex Apparate, Berlin) which are used as a starting point to prepare the capillaries necessary for the crystal growth . The capillary tube in which the crystals are grown, is shown in the lower part of the figure. Before preparing these capillaries, the commercial capillaries have to be cleaned thoroughly (strong acid, distilled water). The outer end (head) is used for the

Table 2.1. Manipulations necessary to obtain capillaries of the required shape (see also Fig. 2.2 and Fig. 2.3).

a.	Make (provisional) sealing point in head by use of a small gas flame.
b.	Mount capillary in vertical position and make narrow part X ($\phi \simeq 0.1$ mm; for later construction of E, F and G). This is realized in the following way: Put capillary in heating ring V (ϕ = 4 mm) formed by two windings of kanthal wire; fix match U as weight to lower end. Capillary can be pulled out slowly by increasing the temperature within the ring.
b'.	Use similar procedure for obtaining a local extra narrowing F in X.
c.	After removing match, give X a (perfectly) rounded end at 1 mm beyond the narrow part F, by cutting with heating ring. Avoid surplus of glass at the bottom of G.
d.	Make sphere, by keeping only lower end of G in heating ring V. While heating, blow G up carefully, by applying again and again slight air pressure. During this process, the thickening in F is also formed.
e.	Put capillary in horizontal position. Make bend D, by use of a small gas flame and its own weight.

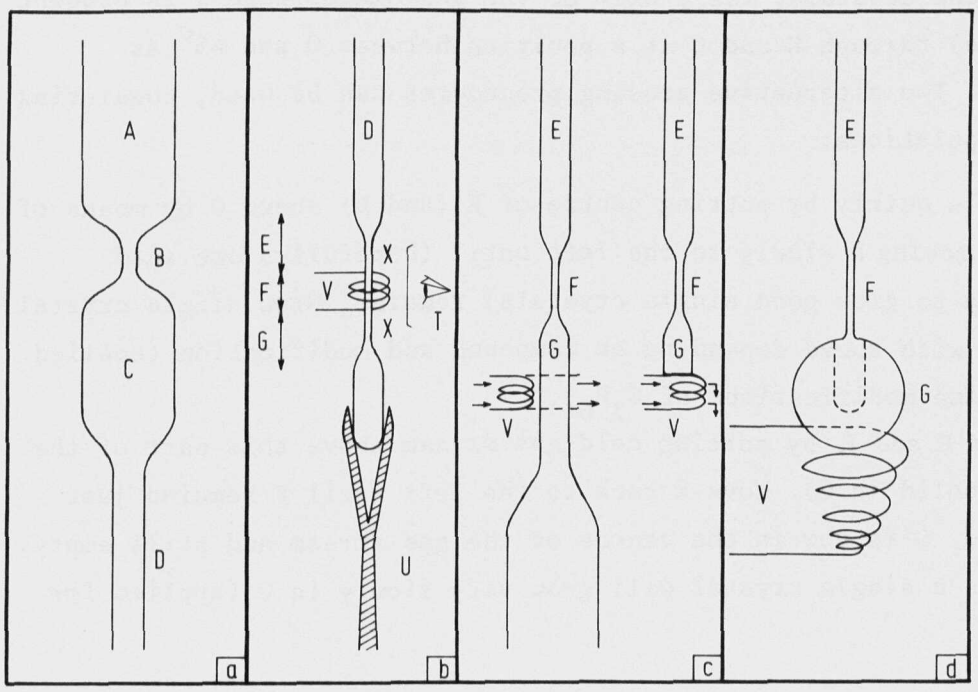

Fig. 2.3.

Demonstration of the manipulations listed in Table 2.1.

(Figure not to scale).

For (A)-(G) and (X) see Fig. 2.2. and text.

(T) microscope
(U) match
(V) heating wire

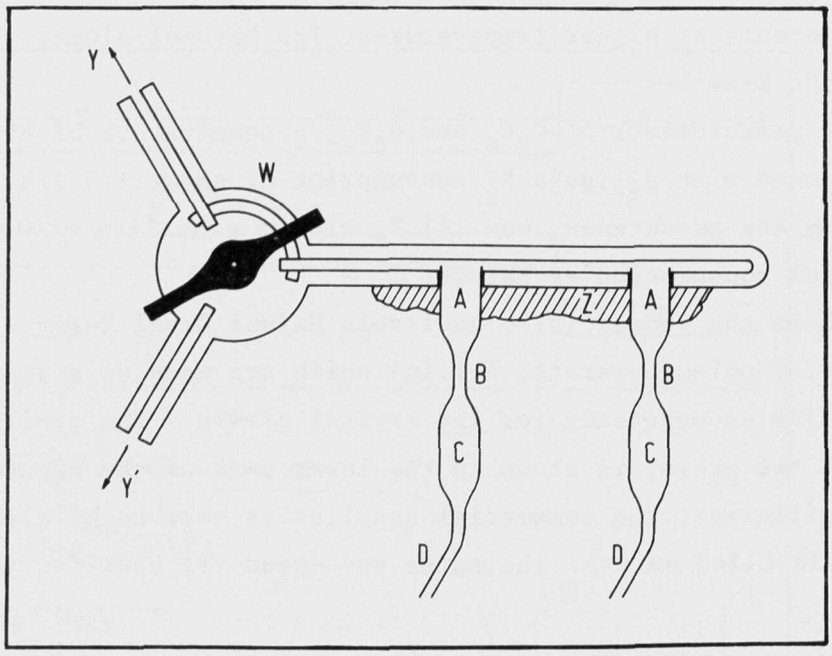

Fig. 2.5.
Filling of the capillaries.
(Figure not to scale).
For (A)-(D) see Fig. 2.2.
(W) three-way cock
(Y) to waterpump
(Y') to gas cleaning devices and gas cylinder
(Z) plasticine for attaching capillaries

construction of parts A+B+C. The manipulations necessary to obtain a capillary of the correct shape are summarized in Table 2.1 and demonstrated in Fig. 2.3. By carrying out the manipulations carefully, capillaries with an almost perfect spherical end G (within some μm's) can be made.

Fig. 2.4 shows the mounting of the capillary tube at the diffractometer. As is clearly shown, the bend at D is necessary to avoid clashes between the capillary and parts of the diffractometer.

To fill the capillary with gas, A is connected to a tube (Fig. 2.5) giving access (by means of a three-way cock W) either to a waterpump Y or to the cylinder with gaseous compound Y'. By using the two connections alternately, the capillary is washed repeatedly with gas before being filled. Finally the tube is sealed off at B by means of a small gas flame, and mounted at the diffractometer (Fig. 2.4).

Before growing the crystals, the ϕ axis of the goniometer head J is brought in the (vertical plane) through K and Q at a position between 0 and 45^{o} as indicated in Fig. 2.4. Two alternative growing procedures can be used, consisting of the following manipulations:

(a) Solidify the sample quikly by putting centre of K (and L) above G by means of Q. Melt sample by moving K slowly to the left until (hopefully) one seed crystal (necessary to grow good single crystals) remains. Grow single crystal by moving K back, with speed depending on compound and modification (applied for C_2H_4 and for two modifications of C_2H_6).

(b) Solidify sample in E and F, by putting cold gas stream above this part of the capillary (avoid solid in G). Move K back to the left until F remains just blocked with solid. G is now in the centre of the gas stream and still empty. Over several hours a single crystal will grow very slowly in G (applied for C_2H_2).

The temperature during the crystal growth must be chosen carefully. Crystals of smallest mosaic spread ($m < 0.2^{o}$) were obtained at temperatures just below their melting point. However, subsequent cooling of the crystal increased m; especially detectable if the temperature of the experiment differs largely from the melting point (C_2H_2). In our opinion, it seems best to grow crystals at the temperature of the diffraction experiment.

References

Bolhuis, F.van (1971). *J. Appl. Cryst.* 4, 263-264

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