Simple pressure cell for single-crystal X-ray crystallography

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A simple pressure cell for single-crystal X-ray crystallography at pressures up to 1 kbar (10^5 kPa) has been developed. A special attachment for mounting the cell onto a goniometer and a new data collection procedure are described.

1. Introduction

High-pressure single-crystal X-ray analysis has became one of most rapidly growing developments of modern crystallography in recent years. Its fast growth is based mainly on the wide application of advanced diamond anvil cells (DAC), able to provide pressures on a sample up to 120 kbar (1 kbar = 10^5 kPa) and small enough to fit onto a standard goniometer. A light and compact DAC essentially consists of two conically shaped diamonds, their stainless-steel support and beryllium gasket (see, for example, Dunstan, 1999). However, as it is the case for almost any device, in spite of the excellent design the DAC also has some disadvantages. Amongst them, one can mention the presence of a vast blind region to X-rays in the shadow of the diamond anvil supports, the strong diamond diffraction peaks, the limited thickness of the sample, and the elaborate method of loading the cell and measuring the pressure at the crystal. The problems associated with the data collection and data processing for a crystal in a DAC using CCD area detectors were summarized recently by Dawson *et al.* (2004).

Not all investigations require such a high pressure and not all crystallography groups can afford such relatively sophisticated equipment as a DAC.

There have been several attempts to design more simple and inexpensive 'laboratory' pressure cells (Kundrot & Richards, 1986; Tilton, 1988). The more advanced of those cited (the Tilton cell) consists of a Be cup, which is placed over the crystal (fixed on top of a glass fibre by epoxy glue) and attached to a specially designed stainless-steel block by screws. This block is attached to a high-pressure valve. The whole unit is mounted on the φ-circle of a four-circle diffractometer, equipped with a single-point detector, using a standard goniometer head. The cell was designed to be used under pressure up to 400 bar. In spite of the advantages of simplicity, the absence of blind areas and relatively low cost, the Tilton cell is also not ideal for several reasons. The crystal is invisible during data collection, the cell is too heavy for a standard goniometer, which results in positioning errors, and, in spite of using beryllium of a special grade, powder reflections from Be are still present. The use of beryllium could also cause safety concerns.

In the present paper, we describe a new quartz pressure cell (QPC) for data collection at elevated pressure and an unusual data collection mode, which, we believe, may also be useful for other non-standard experiments using any bulky attachments.

2. Cell design

Several ways to improve the existing designs were possible. The planed improvements were not only to simplify the design of the pressure cell itself and make it more convenient to use, but also exploit the advantages of modern diffractometers, first of all the use of area detectors (CCDs in our case).

In order to allow the studied crystal to be visible, a quartz capillary was chosen as a 'working part' of the cell. A commercially available (Multi-Lab Ltd, Newburn, Newcastle-upon-Tyne, UK; http://www.multi-lab.co.uk) quartz capillary with an outer diameter (OD) of 3 mm and an inner diameter (ID) of 1 mm was used. Our tests show that these capillaries can withstand pressures of up to about 1 kbar. Obviously, a further decrease of the ID value will increase the possible pressure. The use of the quartz capillary, of course, results in the appearance of a halo in the frames; however (unlike the DAC and the Tilton cell), it does not produce additional reflections and indexing the crystal reflections is straightforward.

The capillary is sealed at one end; the other end is connected to a brass tube (5 mm OD, 1 mm ID) by a quartz–metal seal (TMS Vacuum Components, Hastings, UK; http://www.tmsvacuumcomponents.co.uk). This metal–quartz contact appeared to be the most vulnerable part of the whole device and improving this contact will increase the overall reliability of the QPC.

The crystal is attached to the inner wall of the capillary by a tiny drop of polyfluorinated oil and is clearly visible through the quartz (Fig. 1). Data collection on the three-circle area-detector machine involves few spatial movements and such a method of crystal fixing proved to be more than adequate. Even if the crystal moves during the pressurizing procedure (which never was the case), the transparency of the QPC allows it to be centred properly. Loading the QPC is very simple: the chosen crystal is placed into the capillary and then

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Figure 1
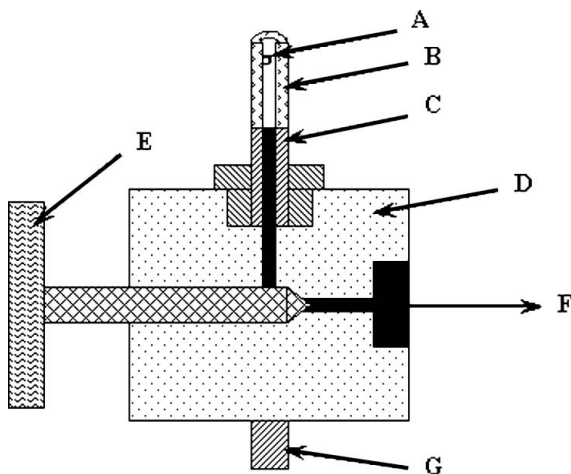View of a crystal inside the QPC.

Figure 2
Schematic of the QPC. A: Crystal. B: quartz capillary. C: brass part of quartz–metal seal. D: valve 30-12HF2. E: removable handle. F: standard 1/8″ connector to a pressure line. G: stud for attachment of the QPC to the goniometer head.

a drop of polyfluorinated oil is placed on the inner wall of the capillary with the help of a long needle/wire. The crystal usually sticks firmly to the oil drop after a gentle shake of the capillary.

In order to decrease the size and weight of the QPC, we decided to fix the capillary, with a crystal mounted inside, directly onto the body of the high-pressure valve, without any additional intermediate support blocks, such as in the Tilton cell. The chosen valve, the 30-12HF2 valve made by High Pressure Equipment Company (HiP) (High Pressure Equipment Company, Penn, USA; http://www.highpressure.com), is designed for pressures up to 2 kbar; however, similar valves of different weight and size could also be used. The body of the valve was modified in order to attach it to the goniometer head and the handle has been shortened and made removable to reduce the size of the valve. The end of the metal tube C in Fig. 2, connected to the capillary B, was threaded accordingly and the capillary was attached to the valve D using a standard gland-and-collar connection. The weight of the QPC is 290 g; the dimensions of the body of the valve D are $46 \times 38 \times 19$ mm; the total weight of the system (with a goniometer head and support unit, see below) is 710 g.
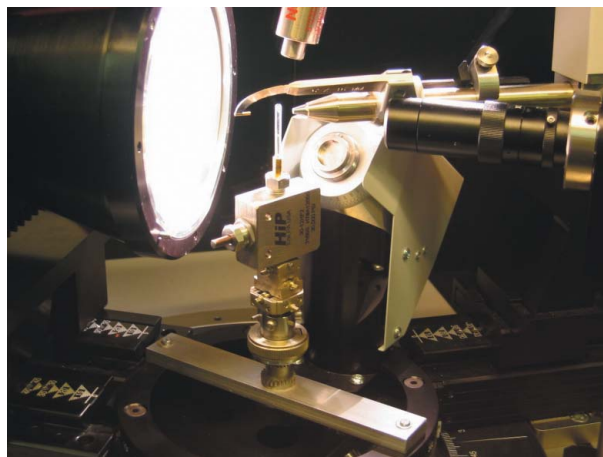

Figure 3
QPC on the goniometer of the Bruker Smart CCD 6000 diffractometer.

The pressurizing procedure is very simple: the valve with the capillary is attached to the high-pressure line and after applying the desired pressure, the valve is closed, detached and mounted on the diffractometer using a special attachment (see below). Nitrogen was used in our case; however, any other suitable gases can be used. Caution: some seals do not withstand the pressure applied and can explode, spreading the shattered quartz around, so wearing protective gear is essential.

Monitoring the pressure was performed using a standard pressure gauge attached to the pressure line. The accuracy of the gauge is 1% of the full scale reading, which in our case means about 30 bar. The present design of the QPC does not allow direct measurements of the pressure inside the cell during or after the data collection; however, further modifications of the cell in order to accommodate a pressure gauge are possible.

3. Mounting of the cell and data collection

As mentioned above, data collection on the three-circle area-detector diffractometer provides the possibility to collect data without any complicated spatial movements of the crystal. It gave us the idea to solve all the problems caused by the weight (as in case of the Tilton cell) and size of the cell in one step, by avoiding entirely the use of the φ block of the diffractometer. A special support unit was made to mount the goniometer head with the QPC directly onto the ω circle of the diffractometer (Fig. 3). It provides plenty of space to accommodate the QPC and its robust goniometer head, and to centre a crystal in the optical centre of the goniometer. The rotation of the QPC during the optical centring was performed manually, monitoring the process by a standard diffractometer video camera.

Obviously, an ω scan mode is the only available mode of data collection for the described configuration. The data were collected in two runs, each covering a $180°$ interval in ω. The only restriction on the range of ω rotation is imposed by the risk of collision between the unused φ block and the detector.

Table 1
Some parameters of the data collection and refinement of structure (1) at 400 bar.

Empirical formula	$C_{38}H_{32}N_2 \cdot C_6H_6$
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.387 (2)
b (Å)	10.224 (2)
c (Å)	10.421 (2)
α (°)	109.29 (3)
β (°)	114.97 (3)
γ (°)	90.50 (3)
Volume (Å^3)	842.8 (3)
Z	1
Reflections collected	2968
Independent reflections	2861
Completeness (%) to $\theta = 28.99°$	63.9
Goodness-of-fit on F^2	1.168
Weighting scheme a, b coefficients†	0.2, 0.0
Final $R1$ value $[I > 2\sigma(I)]$	0.0886
Final $wR2$ values (all data)	0.3232
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.364, −0.479

† Weighting scheme used: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [0.333 \times$ maximum of $(0$ or $F_o^2) + 0.666F_c^2]$.

Table 2
Parameters of the refinement of structure (2) at ambient conditions and under hydrostatic pressure of 200 bar (data from one run of 180° ω).

	1 bar	200 bar
Empirical formula	$C_{14}H_{16}$	$C_{14}H_{16}$
Formula weight	184.27	184.27
Temperature (K)	293 (2)	293 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	6.985 (1)	6.935 (2)
b (Å)	10.169 (2)	10.075 (2)
c (Å)	8.212 (2)	8.177 (2)
β (°)	102.31 (2)	102.59 (4)
Volume (Å^3)	569.9 (2)	557.6 (4)
Z	2	2
Density (calculated) (Mg m^{-3})	1.074	1.098
Reflections collected	2500	1425
Independent reflections	1525	807
Completeness (%) (maximum $\theta°$)	87.6 (30.48)	82.1 (24.99)
Data/restraints/parameters	1525/0/96	807/0/65
Weighting scheme a, b coefficients†	0.07, 0.0	0.1, 1.5
Goodness-of-fit on F^2	0.970	0.962
Final $R1$ value $[I > 2\sigma(I)]$	0.0515	0.0993
Final $wR2$ values (all data)	0.1285	0.2683
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.114, −0.182	0.310, −0.300

† Weighting scheme used: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [0.333 \times$ max of $(0$ or $F_o^2) + 0.666F_c^2]$.
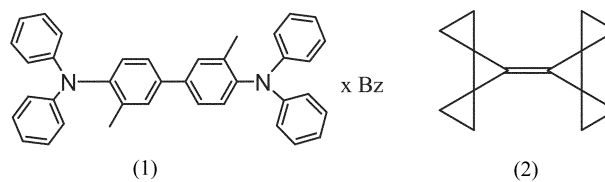
After the completion of the first run, the sample was rotated manually around the vertical axis by 180° and a second identical run was performed. The data from each run were indexed separately, corrected for absorption and other systematic errors by a standard *SADABS* (Sheldrick, 2003) procedure, and merged.

This is the simplest possible way of data collection, but even for triclinic crystals it provides enough data for a successful solution and refinement of the structure (see below). For crystals of higher symmetry, the coverage and redundancy of the data will be even higher. Moreover, the use of a goni-

ometer head with arcs will eliminate the blind areas close to the ω axis.

4. Examples

To date, just two experiments have been performed using the technique described. Both of them were performed at room temperature. The first example was the structure of N,N,N',N'-tetraphenyl-(3,3′-dimethyl)-(1,1′-biphenyl)-4,4′-diamine benzene solvate, (1) (Low *et al.*, 2005). The crystal was placed in the capillary as described above and pressurized to 400 (30) bar using nitrogen gas. The data collection mode was that described above. This crystal was chosen as an example of one of the worst possible scenarios: the crystal is triclinic. Nevertheless, even one run covered about 64% of possible reflections (Table 1) and it was possible to solve and refine the structure against these data. Of course, not all the compounds display significant structural changes under such relatively small pressure and in the case of crystal (1), the difference between the structure at ambient conditions and that under the pressure was negligible. There are several possible explanations of this fact. First of all, in the experiments with (1), two different crystals were used. Moreover, in contrast to structure (2), the structure (1) contains the disordered solvent, the behaviour of which during pressurizing is unpredictable. The partial loss of pressure at some point in the middle of the experiment also can not be excluded. However, the first experiment confirmed the feasibility of the approach.

(1)   (2)

As was mentioned above, the use of a high-pressure gas requires rigorous safety procedures and not every laboratory has a high-pressure gas generator on site. The pressure cell described is equally suitable for use with either gas or liquid. Moreover, hydrostatic pressure is much safer to work with and much easier to obtain. A crystal of 7,7′-bi-(dispiro[2.0.2.1]-heptylidene), (2), the structure of which at 210 K was reported previously by Zollner *et al.* (1991), was placed into the capillary and this time the cell was pressurized to 200 (4) bar with water, using a laboratory high-pressure generator (type 37-5.75-60 by HiP). A small amount of liquid did not produce any significant increase in intensity of the diffuse halo. As in the first case, it was possible to index the diffraction pattern, process the data, solve and refine the structure. For compound (2), the unit cell showed significant shrinking under pressure (Table 2). Comparison of the cell dimensions of the structure under ambient conditions and under pressure shows that the contraction of the cell is anisotropic. The maximum contraction is observed along the **b** direction, which is also the

predominant direction of $CH\cdots C(sp^2)$ weak hydrogen bonds, which shortened from 2.93 (2) to 2.86 (2) Å. A more detailed discussion of the changes in structure (2) will be published elsewhere.

The broadening of some peaks was observed after applying the pressure. This probably indicates that the crystal cracked during the pressurizing, which slightly affected the refinement.

5. Conclusions

A new simple quartz pressure cell for single-crystal X-ray crystallography has been designed and built. The cell keeps the sample visible during the experiment and does not have blind areas. A new attachment was designed to fix the cell on the diffractometer and a modified mode of data acquisition was developed, which can be employed for other experiments that might include the use of relatively bulky equipment. The cell is suitable for data collection at pressures up to 1 kbar, created by either gas- or liquid-applied pressure. A further increase of pressure can be achieved by improving the quality of the quartz/metal seal and by varying the quartz capillary parameters.

References

Dawson, A., Allan, D. R., Parsons, S. & Ruf, M. (2004). *J. Appl. Cryst.* **37**, 410–416.

Dunstan, D. J. (1999). *High Pressure Molecular Science*, edited by R. Winter & J. Jonas, pp. 87–101. Dordrecht: Kluwer Academic Publishers.

Kundrot, C. E. & Richards, F. M. (1986). *J. Appl. Cryst.* **19**, 208–213.

Low, P. J., Paterson, M. A. J., Yufit, D. S., Howard, J. A. K., Cherryman, J. C., Tackley, D. R., Brook, R. & Brown, B. (2005). In preparation.

Sheldrick, G. M. (2003). *SADABS*, Version 2.10, University of Göttingen, Germany.

Tilton, R. F. (1988). *J. Appl. Cryst.* **21**, 4–9.

Zollner, S., Buchholz, H., Boese, R., Gleiter, R. & de Meijere, A. (1991). *Angew. Chem. Int. Ed.* **30**, 1518–1520.