Crystal Structure of a Cyclotetraicosaphenylene

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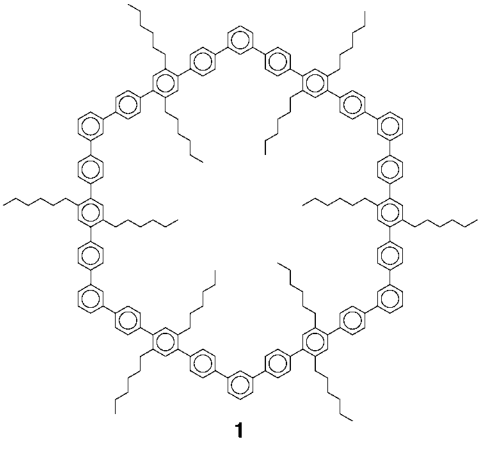
The biggest known quasi-rigid macrocycle is the cyclotetraicosaphenylene **1**. Determining the X-ray crystal structure was a challenge which took more than a year. The three-dimensional packing shows the molecules to be piled up like coins or more precisely like garden chairs, giving rise to potentially endless tubes with diameters of *ca.* 28 Å. In the crystal these channels are filled with liquid solvent which is amorphously frozen during data collection at 133 K. In principle, it should be possible to replace the solvent molecules in the channels by metal atoms forming quantum wires.

1. Introduction. – Cyclic oligophenylenes are ideal compounds to study aromaticity, guest-host interactions and aggregation, and have been the subject of research for many years [1]. Recently, these molecules have become even more interesting for supramolecular chemistry; due to their rigid shape, the cyclooligophenylenes can be used to build up molecular constructions in different architectures. Most interesting are macrocycles with inner diameters on a nanometer-scale [2–4]. They are able to enclose particularly large guest molecules and can lead to 'organic zeolites' [5]. The biggest quasi-rigid macrocycle known so far is the cyclotetraicosaphenylene **1**, which was synthesised by *Hensel* and *Schlüter* [6]. Although of great interest, a three-dimensional structure determination – preferably a single-crystal X-ray analysis – of **1** seemed to be virtually impossible. In particular, the highly flexible hexyl chains, which are essential for the solubility of **1** in organic solvents, made crystallisation difficult.



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2. Experimental. After many unsuccessful trials, rhombohedral crystals were obtained from $CHCl_3$. However, it was very difficult to handle them: when removed from the mother liquor, the crystals became opaque and ugly, losing their ability to diffract X-rays within seconds. This is an effect frequently observed in crystals containing volatile solvents like hexane or $CHCl_3$ in their lattices. The solvent molecules evaporate from the lattice at room temperature leaving empty spaces [7]. In many cases, this results in a breakdown of the crystal lattice and a significant and sometimes total loss of diffraction power. Cooling the crystals under the microscope to about $-50°$ using a technique developed by *Kottke* and *Stalke* in our laboratory [8], we succeeded in mounting a crystal of **1**. Diffraction data were collected at 133 K on a *Siemens* three-circle goniometer with graphite monochromated CuK_α radiation ($\lambda = 1.54178$ Å), rotating anode generator and multiwire proportional counter. The observed diffraction pattern, however, is only of limited quality: many reflections show an unusual high mosaicity or a strange spot profile, and, at very low resolution, the background is rather high, indicating that a relevant part of the scattering matter does not possess crystalline order. 15 φ- and 15 ω-scans were performed to obtain a high redundancy (44) in order to improve the data quality.

The data reduction was performed using SAINT [9], and the data were corrected semiempirically for absorption and other effects with SADABS [10] (max. and min. values of correction: 0.7178 and 0.8425). The phase problem was solved by conventional direct methods using SHELXS [11], and the model was refined against F^2 on all data by full-matrix least-squares with SHELXL [12]. All non-H-atoms were refined anisotropically. All H-atoms were included at geometrically calculated positions and refined using a riding model. The disordered regions were modelled with the help of similar distance restraints as well as rigid bond restraints for the anisotropic displacement parameters.

Further crystal data for **1**: $C_{216}H_{240} + 6\ CHCl_3$ $M_r = 2836.27 + 6 \cdot 119.38$, Crystal size: $0.10 \times 0.20 \times 0.20$ mm, rhombohedral, space group $R\bar{3}$, $a = b = 54.982(8)$ Å, $c = 8.549(2)$ Å, $V = 22381(6)$ Å^3, $Z = 3$, $\rho_{calc} = 0.791$ g $\cdot$ cm^{-3}, 291303 reflections were measured, 6618 of which were independent ($R_{int} = 0.1136$), and 5710 were considered observed $[I > 2\sigma(I)]$, absorption coefficient: $\mu = 1.775$ mm^{-1}, resolution range: $5.5 < \Theta < 56.9°$, data/restraints/parameters: 6618/609/492. The refinement converged to $R1 = \Sigma || F_o - | F_c || / \Sigma | F_o | = 0.1096$ $(F_o > 4\sigma(F_o))$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2} = 0.3197$ (all data). Highest positive and negative residual electron density: 0.748 and -0.418 e $\cdot$ A^{-3}. Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-130250. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and Discussion. – Compound **1** crystallises in the rhombohedral space group $R\bar{3}$ with a sixth of a molecule of **1** and one molecule of $CHCl_3$ in the asymmetric unit. The rest of the molecule (and five more molecules of $CHCl_3$) are generated by the $\bar{3}$-axis. The molecule (*Fig. 1*) consists of six units of four 1,4-linked benzene rings, bonded *via* 1,3 links to one another. Thus, a hexagon containing 24 benzene rings is formed. The edges of the hexagon consist of five benzene rings, the rings at the corners being shared by two edges. The whole macrocycle is not planar but, in accordance with the $\bar{3}$-geometry, possesses a cyclohexane-like chair conformation (*Fig. 2*). The middle ring of each edge carries two hexyl groups *trans* to one other. One of them is directed towards the centre of the macrocycle and the other one points out of it. These hexyl chains are highly disordered. As the difference between discrete disorder and diffuse movement is fluid, and since refinement of more than two sites for the disordered hexyl groups was not stable, the model was reduced to the two main components for each hexyl group. As shown in *Fig. 3*, the disorder causes about half of the hexyl groups to lie above the mean ring plane and the other half to lie beneath it. Thus, in the three-dimensional lattice a fork-like structure is formed, which seems to be favourable for the crystal packing. The site occupation factors refined to 0.50/0.50 for the hexyl chains pointing out of the macrocycle, and to 0.55/0.45 for the other hexyl groups. In contrast, the positions of the benzene-ring atoms are well defined and their anisotropic displacement parameters are relatively small.

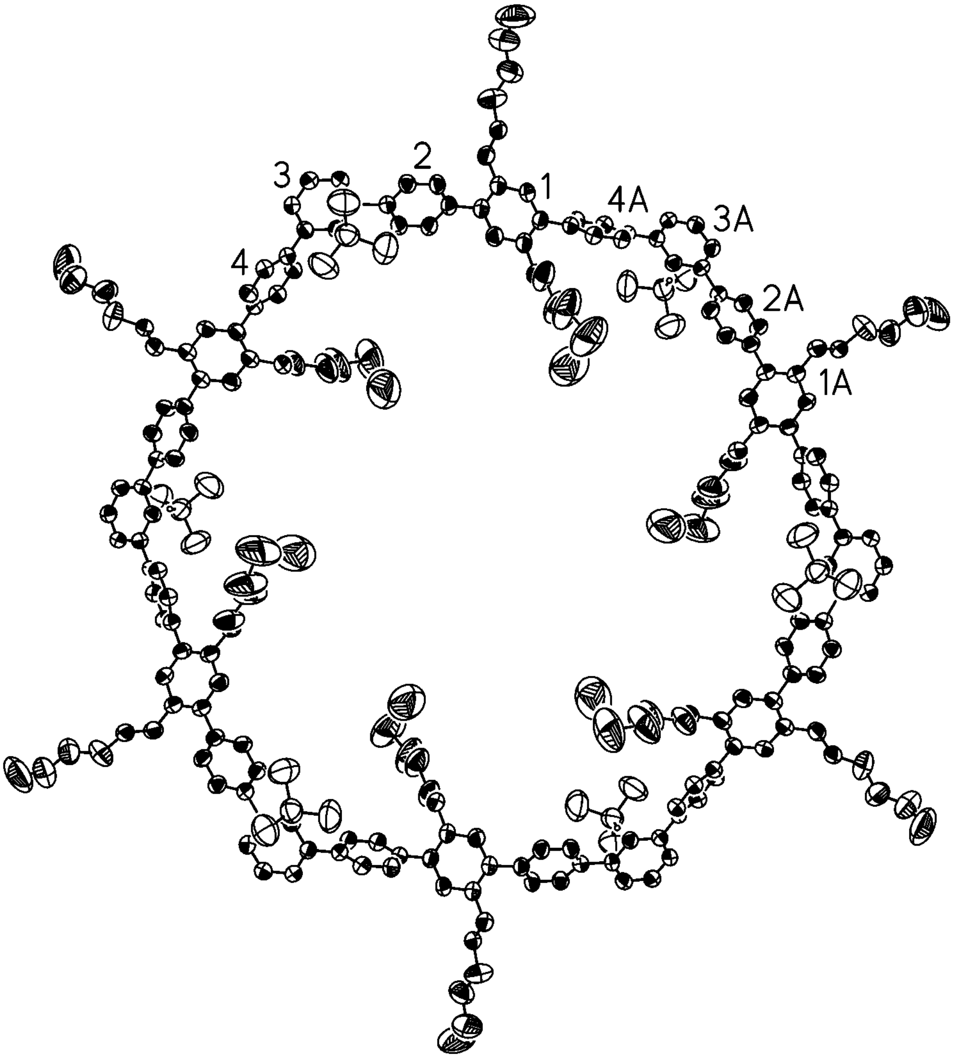

Fig. 1. *View along the crystallographic* c-*axis of the crystal structure of* **1**. H-Atoms and second sites of disordered parts are omitted for clarity. The thermal displacement ellipsoids are drawn at 50% level. Dihedral angles [°]: ring (1) – ring (2): 57.6(1), ring (2) – ring (3): 13.7 (3), ring (3) – ring (4): 39.1(2), ring (4) – ring (1A): 56.5(2).

In addition to the *Van der Waals* guest-host interactions known from ordinary inclusion compounds, the $CHCl_3$ molecules are coordinated to an aromatic ring of the host *via* weak CH$-\pi$ H-bonds (distances C$-\pi$: 3.38 Å, H$-\pi$: 2.38 Å; angle C$-$H$-\pi$: 174.3°, π is the ring centre; see *Fig. 3*). An interaction like this – but slightly weaker – has been reported earlier for the structure of a cyclooctaphenylene [13]. Other weak H-bonds of the similar type have been described for acetylene [14].

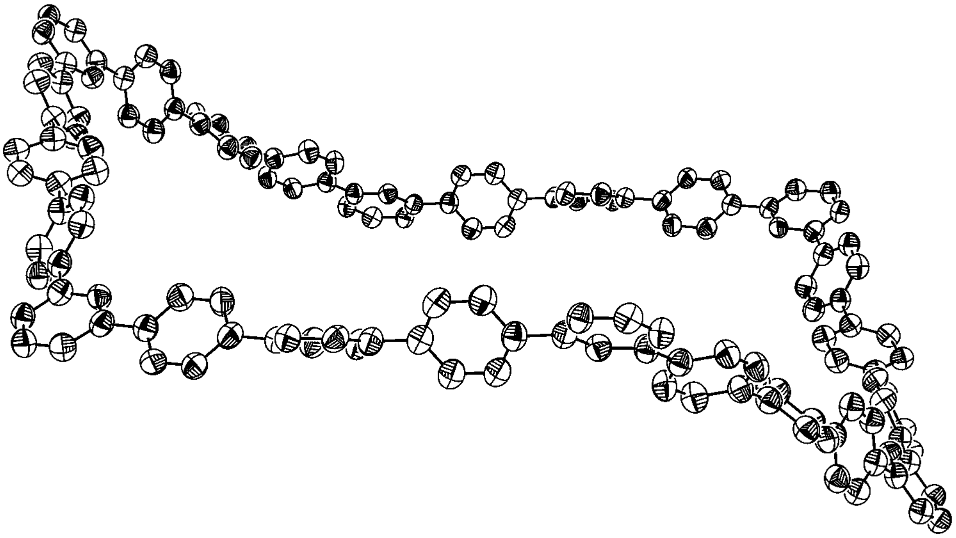

Fig. 2. *Side view of* **1**, *with $CHCl_3$ molecules and hexyl chains omitted for clarity.* The thermal displacement ellipsoids are drawn at the 50% level.

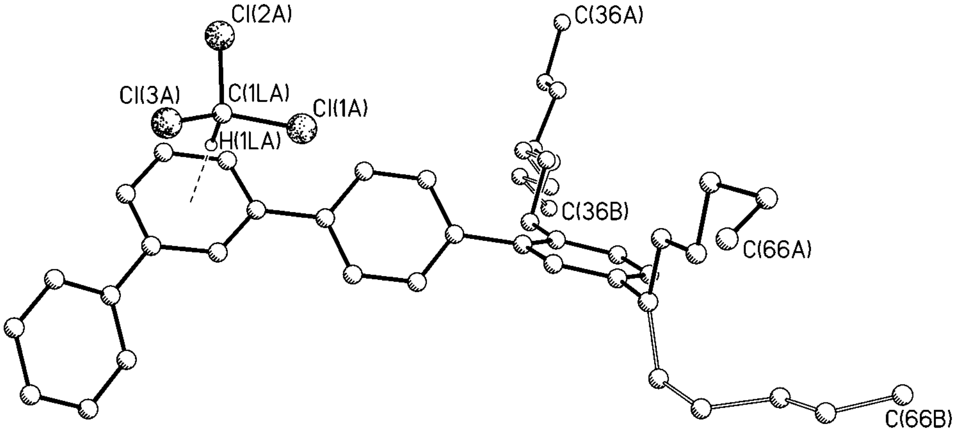

Fig. 3. *Plot of the asymmetric unit of* **1** *showing the CH$\cdots\pi$ H-bonds and the disorder of the hexyl chains.* The minor components of the disordered groups are drawn with light bonds.

Particularly interesting is the diameter of **1**. Given the chair conformation of the molecule, the inner diameter is somewhat smaller than estimated by *Hensel* and *Schlüter* [6]. As shown in *Fig. 4*, it measures 30.750(9) Å from corner to corner and 26.831(9) Å from edge to edge. When compared with the dimensions of the well-known C_{60}-Fullerene (diameter 7.02 Å), the hole in **1** would be large enough to accommodate seven C_{60}-molecules allowing for *Van der Waals* distances (3.2 Å in the crystal) between the 'buckyballs'.

In the three-dimensional packing the hexagons are stacked like coins, or more precisely like garden chairs. The disordered hexyl chains dovetail with the $CHCl_3$

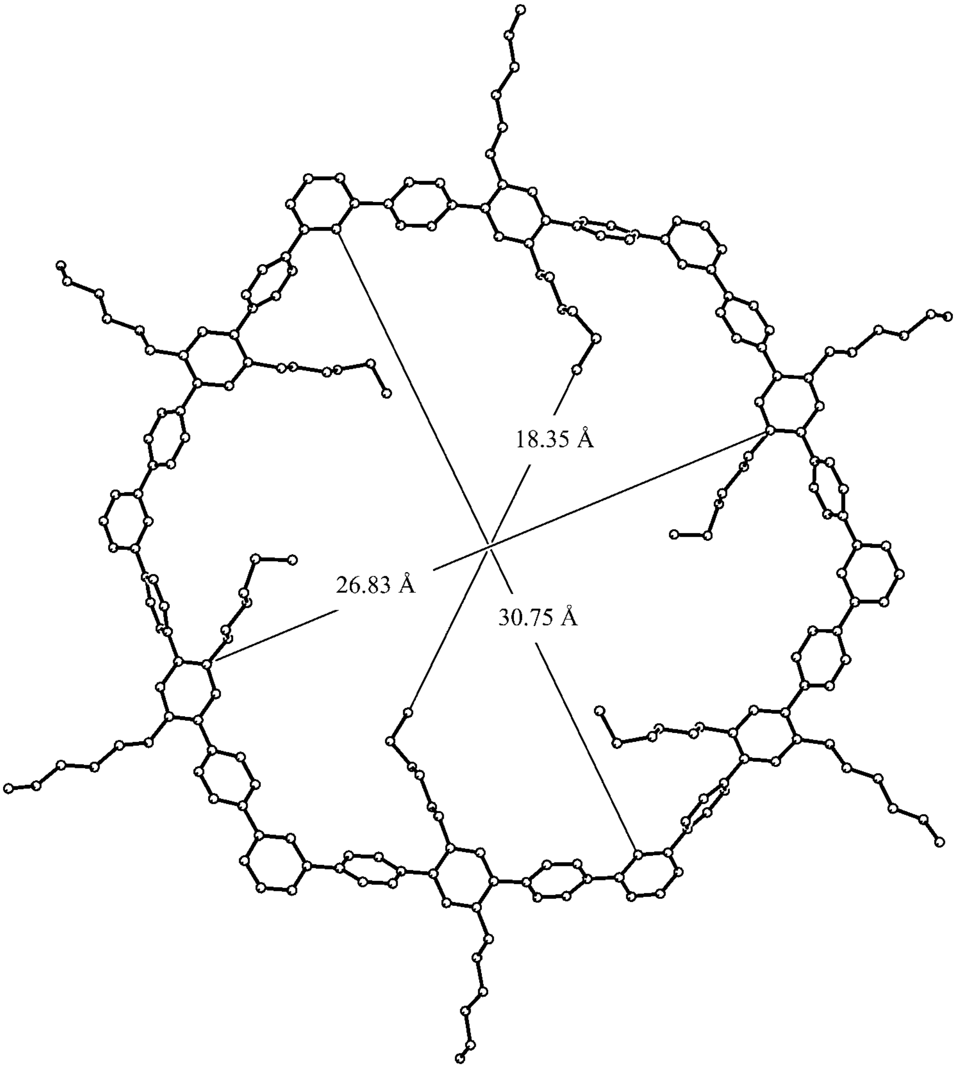

Fig. 4. *Inner diameter of* **1**. $CHCl_3$ Molecules and alternative sites of disordered parts are omitted for clarity.

molecules and with other hexyl groups. Although this part of the packing is very compact, the relatively large holes at the centre of the molecules lie directly over one-another, giving rise to potentially endless tubes through the whole crystal (*Fig. 5*). The interior of these channels appears to be completely empty since no solvent molecules can be located nor any relevant residual electron density could be found in the difference *Fourier* syntheses. Since the absence of any matter in cavities of this size is impossible, we assume that they are filled with liquid $CHCl_3$ like the pores of a sponge. During data collection at 133 K, the $CHCl_3$ is amorphously frozen. This explains the behaviour of the crystals under the microscope: when removed from the mother liquor

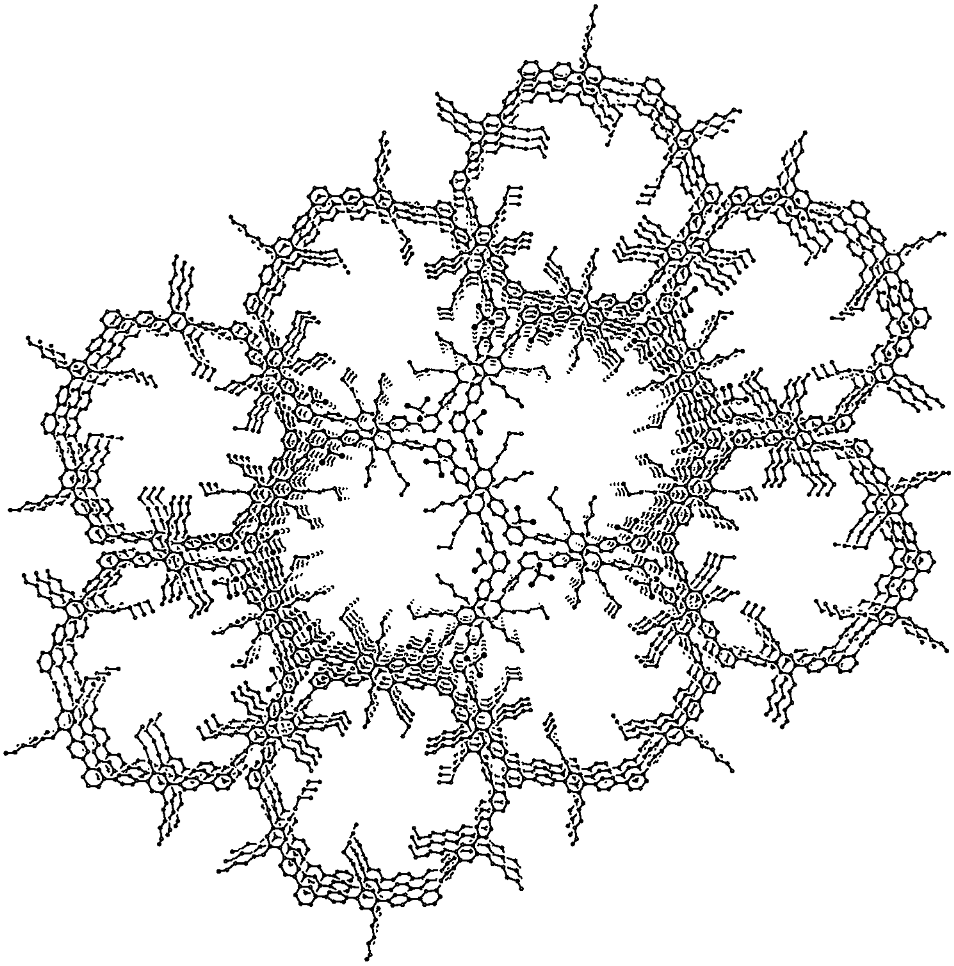

Fig. 5. *View along the crystallographic* c*-axis showing the crystal packing of* **1**. The figure does not show the alternative sites of the disordered side chains.

at room temperature, the crystals lose the $CHCl_3$ that was in the channels and the lattice breaks down. This hypothesis also helps to explain the appearance of the diffraction pattern: The unusual high background at very low resolution is a result of the diffuse scattering of the chaotically disordered $CHCl_3$ molecules; the high mosaicity of some reflections could be the result of small, randomly distributed damage in the crystal lattice caused by evaporation of some of the $CHCl_3$ molecules. Consequently, a bulk solvent correction has been performed; this improved the R-values of the refinement and the standard deviation of the bond lengths and angles significantly. Following *Babinet*'s principle SHELXL refines two parameters [15]: The first grows with the amount of diffuse solvent and usually possesses values around 1 when the mean electron density of the solvent and ordered parts of the structure is similar, as in most protein crystals. A large value of the second parameter indicates that only the low-angle data are influenced by the diffuse scattering of the bulk solvent; values of 2 to 5 are typical. In the case of the liquid $CHCl_3$ in **1**, the first parameter refined to 13, the second to 9, which indicates extremely large regions of disordered solvent of higher mean electron density than the rest of the structure, affecting exclusively the low-resolution data.

4. Conclusions. – The most interesting property of the solid-state structure of **1** is the formation of potentially endless tubes of large diameter. Possibly this compound could lead to new materials like 'organic zeolites' [5] or could extend the concept of guest-host chemistry by allowing the inclusion of very large guest molecules. Furthermore, it should be possible to replace the solvent molecules in the channels by metal atoms; analogous compounds containing bipyridine or terpyridine units integrated in the cyclophenylene have been shown to complex metal cations into the pipes [16]. In the next step, a reduction of these ions to the metal could lead to quantum wires. Such new materials would have numerous interesting applications with respect to semiconductor technology or experimental quantum chemistry.

Until recently, it would have been virtually impossible to determine the crystal structure of **1**. Eventually several factors were responsible for the success. First of all, the growth of suitable crystals is essential. Often underestimated is the tremendous benefit of data redundancy: although a higher redundancy tends to increase the merging R-value R_{int}, it also improves the quality and I/σ ratio of the averaged reflections [17]. To collect the best possible data up to high resolution, both area detectors and the use of cryo techniques [18][19] should be emphasised. In particular, the handling of the crystals at low temperature under the microscope [8] is in many cases an essential prerequisite for the determination of the structure of highly temperature-sensitive crystals. Cooling the crystals of **1** with a cold N_2 stream prevented them from losing too much $CHCl_3$ out of their channels. The same technique also makes it possible to mount crystals with melting points lower than room temperature or which are particularly sensitive to air and moisture, in which case the N_2 acts simultaneously as coolant and as inert gas [8][20].

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