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## LETTER TO THE EDITOR

### Layer disorder in $C_{60}$ -ether clathrates

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**Abstract.** We report structural studies on a new  $C_{60}$  clathrate formed with ether as a guest molecule. Single-crystal x-ray diffraction shows that the unit cell is based on the same square-planar layers of  $C_{60}$  molecules as found in the  $C_{60}$ -*n*-pentane clathrate. However, the stacking sequence of the layers is different, and reciprocal space maps reveal a significant stacking disorder. Model calculations suggest a simple rule for the sequence of layers.

The successful production of macroscopic quantities of  $C_{60}$  [1] opened a new field in chemistry. The new materials based on these cage-like carbon molecules show a wide variety of interesting structural and physical properties. Pure  $C_{60}$  undergoes an orientational ordering transition at 250 K [2] and electron diffraction reveals superstructure at lower temperatures [3]. The wide range of interesting physical properties is well illustrated by the existence of superconducting [4] and ferromagnetic [5] compounds.

While the crystallization of  $C_{60}$  by sublimation produces pure crystals with FCC structure, the precipitation from organic solvents often results in solvent containing crystals. These compounds are clathrates, a fact that little attention has been paid to in the search for other  $C_{60}$  compounds.

This tendency of  $C_{60}$  to form clathrate-type molecular compounds has been systematically utilized for the production of  $C_{60}$  clathrates containing small five-member linear molecules [6].

The preparation of the  $C_{60}$ -ether clathrate is described elsewhere [6]. Briefly, platelet-shaped single crystals up to the size of  $0.5 \times 1.0 \text{ mm}^2$  were precipitated from a saturated toluene solution of  $C_{60}$  under the effect of diethyl ether, introduced to the solution by isotherm distillation. The composition of the crystals has been determined by thermoanalytical methods [6]. The obtained ether to  $C_{60}$  ratio is 0.48. On the other hand, powder x-ray diffraction studies indicate the presence of a significant amount of FCC  $C_{60}$  in the batch, i.e. the actual ether content of the single crystals may be higher than the value given above.

X-ray single-crystal diffraction measurements were performed using a four-circle diffractometer based on Huber 424 and 511 goniometers. Copper  $K\alpha$  radiation was separated by a pyrolytic graphite monochromator. The crystal of  $200 \times 400 \times 30 \mu\text{m}^3$  size was placed on a thin glass fibre. After the initial blind search procedure, reflection centring and reciprocal space maps were measured with a  $0.2^\circ$  detector aperture.

The rocking widths of some of the peaks were several degrees and the indexing procedure failed with standard methods. For orientation matrix and unit cell determination we used a robust indexing method [7]. The strongest peaks were all well indexed by a monoclinic cell, a cell which can be transformed to an A-centred pseudo-tetragonal.

$$\begin{array}{lll} a_m = 10.05(1) \text{ \AA} & a_t = 10.05(1) \text{ \AA} & b_m = 10.05(1) \text{ \AA} \\ c_m = 23.48(2) \text{ \AA} & c_t = 45.85(4) \text{ \AA} & \beta = 77.6^\circ. \end{array}$$

Most of the weak (and broad) peaks can only be indexed by the tetragonal cell releasing the  $k + l = 2n$  centring condition. The total number of well centred reflections in the  $2\theta < 35^\circ$  range was only 60, quite few for such a large cell.

The cell dimensions suggest that the basis of the cell is the same square planar layer of  $C_{60}$  molecules as in the case of the  $C_{60}$ - $n$ -pentane structure [8, 9]. In that structure the ideal 'c' cell edge can be calculated on the basis of two different shifts which we will call  $\sqrt{2}$  and  $\sqrt{3}$  for short,  $\sqrt{2}$  stands for a shift of  $(1, 1, \sqrt{2})$  and  $\sqrt{3}$  for a shift of  $(1, 0, \sqrt{3})$  in  $R$  units, where  $R$  is the van der Waals radius of the  $C_{60}$  molecule  $\approx 5.03 \text{ \AA}$ . The A-centred orthorhombic structure can be described as the following sequence of slightly distorted square-planar layers:  $\sqrt{2}\sqrt{3}\sqrt{2}\sqrt{3}$ .

In the case of  $C_{60}$ -ether the monoclinic cell can be constructed as a  $\sqrt{2}\sqrt{2}\sqrt{3}$  sequence of layers while the tetragonal 'c' cell edge is approximately  $(4\sqrt{2} + 2\sqrt{3})R$  suggesting again an overall  $\sqrt{2} : \sqrt{3} = 2:1$  ratio. For all the reflections for which perfect centring was not possible or the  $l$  index was not an integer, the  $h$  and  $k$  indices were still perfect (independent of which cell was used for indexing). This means that any randomness in the structure causes reflection broadening in the  $l$  direction only.

To visualize this qualitative picture of the reciprocal space we measured the two-dimensional reciprocal space maps. Figure 1 shows selected reciprocal planes with tetragonal indices. The most obvious feature of these maps is the reflection broadening in the  $l$  direction while reflections in the  $h$  and  $k$  directions are perfectly sharp.

These experimental results suggest that while the  $C_{60}$  molecules constitute perfect square layers in the  $a$ - $b$  direction, the stacking of these layers in the 'c' direction perpendicular to the layers is not perfectly regular. To clarify the details of this structural picture we performed model calculations.

We have tried several models of disorder to calculate the intensity distribution in the reciprocal space. The following assumptions have been used: (i) the structure is constructed by perfect square layers of  $C_{60}$  molecules and all disorder was due to the relative shift of their origins; (ii) it was assumed that the  $C_{60}$  molecules are freely rotating, so the form factor of the infinitely thin charged shell can be used; (iii) the contribution of the ether molecules to the total scattering was neglected.

We wanted to identify the sort of randomness in the  $c$  direction perpendicular to the layers. This randomness could be either in the  $\sqrt{2}\sqrt{3}$  sequence itself or some sort of random variation of the shifts. We concluded that shift variation by itself cannot lead to the observed broadening of  $(h, k, l)$  reflections along the  $l$  direction. Sequence disorder is absolutely necessary and was enough to generate quite good correspondence between measured and calculated  $q$  maps.

Originally we did not fix the  $\sqrt{2} : \sqrt{3}$  ratio to 2:1 but allowed for slight variations. However, the calculations were rather sensitive to the composition; the quality of

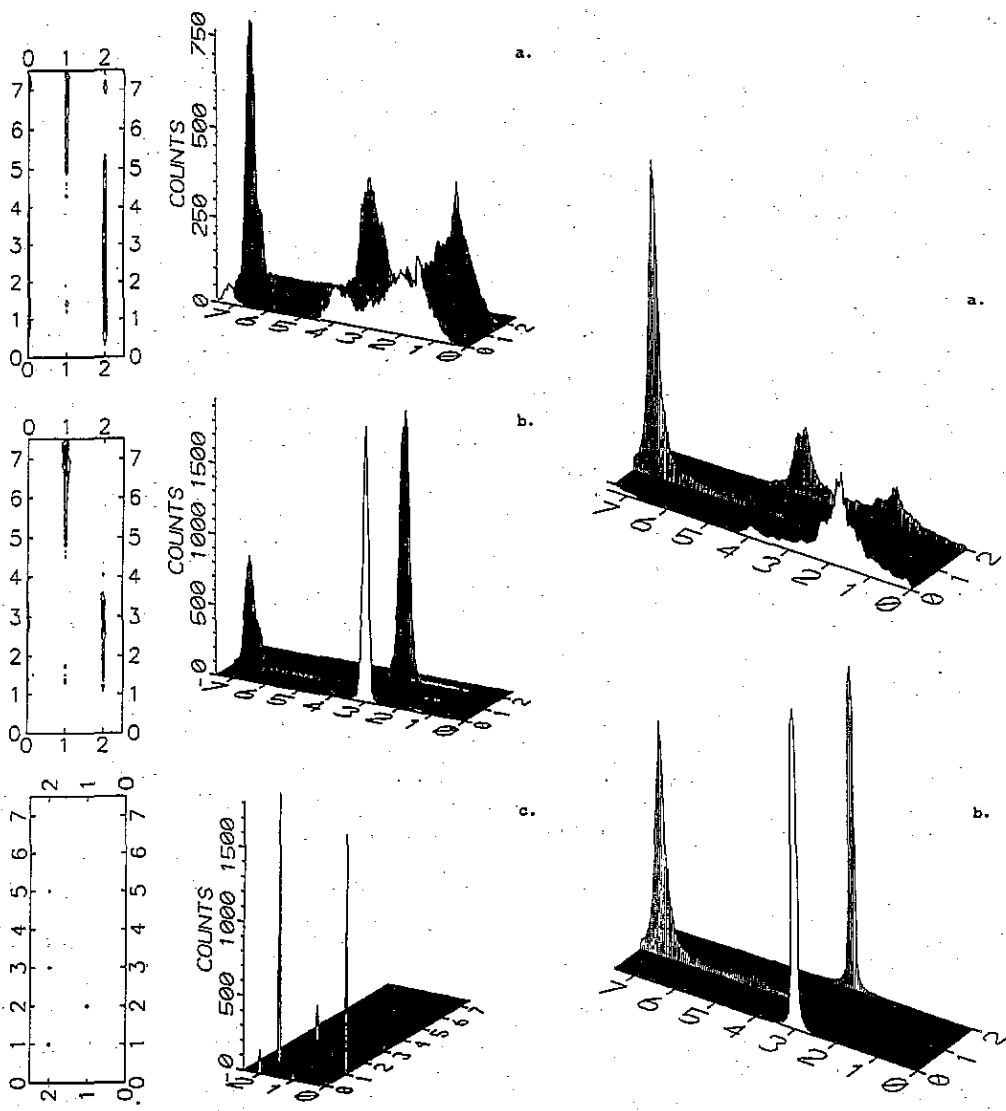


Figure 1.  $q$  maps measured in (a)  $(h, 1, l)$ , (b)  $(1, k, l)$ , (c)  $(h, k, 3)$  planes.

Figure 2. Calculated  $q$  maps of (a)  $(h, 1, l)$  and (b)  $(1, k, l)$  planes.

the correspondence between measured and calculated maps soon degraded with any deviation from the 2:1 ratio.

The quality of the correspondence was further improved by imposing one extra restriction, i.e. the possibility of two adjacent  $\sqrt{3}$  shifts was excluded. This is not a very strong limitation compared to the total randomness at a  $\sqrt{2} : \sqrt{3} = 2:1$  fixed ratio.

All calculations were effectively one dimensional: typically a crystal of 10 000 infinite perfect square layers was constructed, thus the calculation of  $q$  maps was needed only along  $[00l]$  directions. The calculated  $q$  maps can be seen in figure 2.

The structure described contains channels in which we think the ether molecules

are situated. The 'b' direction of the channels is the consequence of the  $\sqrt{3}$  shift. It is possible to have two different kinds of  $\sqrt{3}$  layer shift, which has not been mentioned up to this point. The second possible  $\sqrt{3}$  shift would be  $(0, 1, \sqrt{3})R$  and would mean the creation of a channel in the 'a' direction. However the equal pressure of both  $\sqrt{3}$  shifts would remove the difference between  $(h, 0, l)$  and  $(0, k, l)$  planes. Further evidence for the exclusion of the second  $\sqrt{3}$  layer shift is that  $(0, k, 0)$  reflections have different characteristics to all other reflections. The rocking widths off these reflections are quite sharp ( $0.2^\circ$ ) which can be related to the fact that the normal of the planes coincides with the direction of the channels.

In this paper we have reported layer disorder in a  $C_{60}$ -ether single crystal. The structure shows striking similarities to  $C_{60}$ -*n*-pentane. Both structures are based on square-planar arrays of  $C_{60}$  molecules which form channels containing guest molecules. However in the case of  $C_{60}$ -ether there is a significant stacking disorder which comes mainly from a random sequence of  $\sqrt{2}\sqrt{3}$  layer shifts. The condition that no  $\sqrt{3}$  shifts can be adjacent means that apart from the apparent disorder,  $C_{60}$ -ether and  $C_{60}$ -*n*-pentane are members of the same  $(C_{60})_{n+1}X_2$  homologous series described in [6].

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