$2C_{60}\cdot 3CS_2$: orientational ordering accompanies the reversible phase transition at 168 K

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At 168 K crystals of $2C_{60}\cdot 3CS_2$ undergo a reversible phase transition (from orthorhombic to monoclinic), which is accompanied by orientational ordering of both C_{60} molecules in the asymmetric unit.

Carbon disulfide and aromatic hydrocarbons are widely used as good solvents for C_{60} and for the higher fullerenes. Both carbon disulfide and benzene solutions of C_{60} form crystalline solvates when they are allowed to evaporate to dryness. The structure of $C_{60}\cdot 4C_6H_6$ has been reported[1–3] and shown to contain van der Waals interactions of the types: benzene–benzene, benzene–C_{60}, and C_{60}–C_{60}. In spite of numerous intermolecular interactions, the C_{60} molecule is disordered with two orientations of the molecules occupying a common site at 104 K. Solutions of C_{60} in carbon disulfide produce brown crystals of $2C_{60}\cdot 3CS_2$.[4–6] Crystallographic studies at room temperature have identified the space group as either orthorhombic,[5] *Pbnm*, a = 24.97(6), b = 25.52(3), c = 9.98(1) Å or as orthorhombic,[6] $Pn2_1a$, a = 25.588(2), b = 9.984(2), c = 24.997(2) Å. The latter study reported a complete structure determination and showed the gross packing of molecules. However the resulting R value was high (0.18), and each of the two independent C_{60} molecules was modeled with four different orientations of the C_{60} molecule at each of the two independent sites. Additionally, the carbon disulfide molecules were disordered with two orientations at each of the three sites, and the structure could only be refined using a set of bond constraints. In this report we examine the structure of $2C_{60}\cdot 3CS_2$ at low temperatures and show that a reversible phase transition occurs at 168 K.

The structure of $2C_{60}\cdot 3CS_2$, obtained by evaporation of a carbon disulfide solution, was determined at 90 K. At this temperature the crystals belong to the monoclinic space group $P2_1/n$, with a = 9.8722(12), b = 25.466(3), c = 24.671(3) Å, β = 90.047(3)°.† The crystal was treated as a pseudo-merohedral twin. Refinement proceeded satisfactorily with a model that included two fully ordered C_{60} molecules and three ordered carbon disulfide molecules in the asymmetric unit. The average values and average deviations for the low temperature form are: fullerene; C–C bond distance (5 : 6 ring junctions) = 1.382(11) Å; C–C (6 : 6 ring junctions) = 1.450(11) Å; carbon disulfide; C–S bond distance = 1.544(6) Å; S–C–S bond angle = 179.0(4)°. A stereoview of the monoclinic structure perpendicular to the shortest axis is given in Fig. 1. In this structure, the set of three CS_2 molecules approach one another end-on to form a triangle with non-bonded S··S contacts of 3.696, 3.697 and 3.808 Å (Fig. 2). The closest contact between any sulfur atom and C_{60} is 3.460 Å (between S6 and C59), and the next shortest (3.468 Å) involves S3 and C1. The twenty shortest contacts between sulfur atoms and fullerene carbon atoms have an average value of 3.602 Å. Interestingly, one of the sulfur atoms, S5, has no contacts in this group; its shortest contact to a fullerene carbon is 3.834 Å. The shortest contact between the central carbon of CS_2 and C_{60} is 3.278 Å.

In view of the similarities of the orthorhombic and monoclinic cell parameters, the structure at room temperature was reexamined, and we confirmed that at room temperature $2C_{60}\cdot 3CS_2$ has an orthorhombic cell with a = 24.988(9), b = 25.602(8), c = 9.984(3) Å. We also confirmed that the structure cannot be solved in the centrosymmetric space group, *Pbnm*. After two days of data collection a 25% reduction in the intensity of check reflections had occurred, presumably as a result of loss of CS_2.

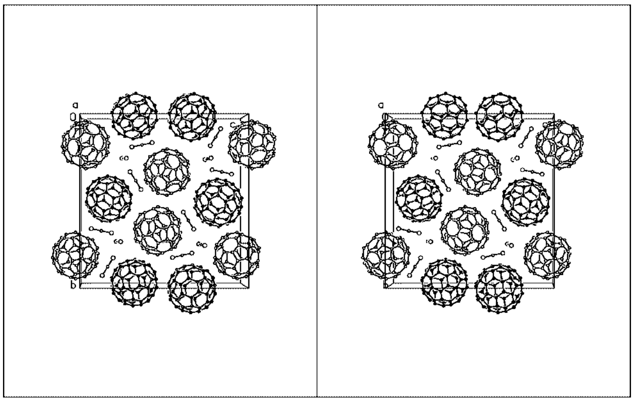

Fig. 1 A stereoview down the short (9.872 Å) axis of the monoclinic structure of $2C_{60}\cdot 3CS_2$. The two fullerene molecules are differentiated by using open circles for one and shaded circles for the other.

In order to understand the relationship between the two crystallographically distinct forms of $2C_{60}\cdot 3CS_2$, variable temperature crystallographic studies were conducted. The orthorhombic setting for the high temperature form will match the monoclinic B setting of the low temperature form if it is described in the space group $P2_1nb$, the *cab* setting of $Pna2_1$, (no. 33). In this space group the symmetry elements differ from $P2_1/n$ by the addition of a b glide, and by a 2_1 screw axis that lies along the a-axis instead of the b-axis. Although the presence of

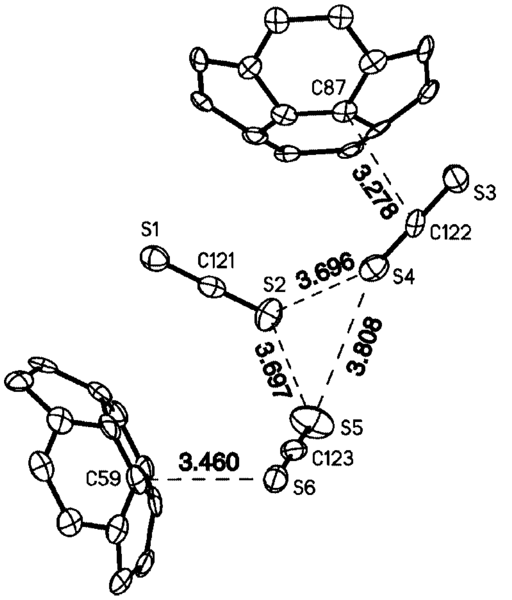

Fig. 2 A drawing showing selected intermolecular contacts associated with the CS_2 molecules in the monoclinic form.

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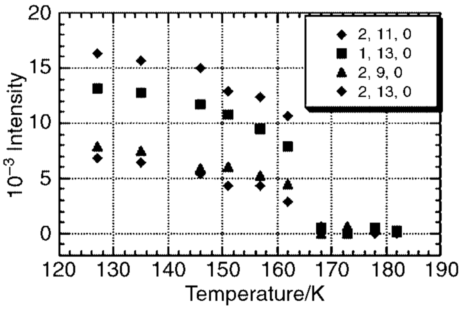

Fig. 3 A plot of the reflection intensity as a function of temperature for four selected *hk*0 reflections of $2C_{60}\cdot 3CS_2$.

the screw axis does not confer any extra conditions; the presence of the *b* glide in the orthorhombic form leads to the condition, *hk*0, $k = 2n$, which is distinct from that of the monoclinic form, for which *hk*0 has no conditions.

A set of ten strong reflections in the set of *hk*0, $k = 2n + 1$ were identified in the low temperature form. A small data set was collected on these reflections at selected temperatures between 127 and 183 K. Without exception, extinction was observed at 168(2) K. This can be seen in the plot of the intensities of four of these reflections as a function of temperature shown in Fig. 3. The temperature was raised and lowered three times through the above range, and no loss in intensity of the benchmark reflections was observed.

Since the high temperature, orthorhombic, and low temperature, monoclinic, structures are interconvertible without loss of crystallinity, it is not surprising that they contain similar arrays of molecules. Each form has two distinct C_{60} sites and three CS_2 sites. The pattern of packing of these constituents is exactly the same, and the orientation of the CS_2 molecules matches. The orthorhombic space group has an additional glide plane, but the principal difference is that in the high temperature form there are four different orientations of the C_{60} molecules and two different orientations of the CS_2 molecules at sites which themselves contain no crystallographic symmetry. However, as a consequence of the higher orthorhombic symmetry, there would be higher order in the high temperature form if the disorder did not occur. Thus, the phase transition results in an increased disorder upon warming and is entropically driven.

Some compression of the structure at low temperature would be expected due to the reduction in temperature, and this is clearly seen by a comparison of the average center-to-center distances. For the orthorhombic form (298 K), the average value is 10.051 Å, while for the monoclinic form (90 K), the average value is 9.961 Å. An accurate comparison of the individual bond distances and angles cannot be made due to the disorder at room temperature. Likewise, comparison of temperature-dependent changes in the contact distances between C_{60} and CS_2 is flawed by the same inaccuracies due to the disorder, but, based upon the packing, no remarkable differences are expected.

Despite the ordering observed in this crystallographic study, the fullerene molecules in $2C_{60}\cdot 3CS_2$ still undergo dynamic reorientation at low temperatures. Crystalline $2C_{60}\cdot 3CS_2$ has been studied previously by solid state ^{13}C NMR spectroscopy.[7] Over the temperature range 125 to 263 K, the spectrum consists of a single narrow line which exhibits a minimum in the spin–lattice relaxation time, T_1 at 170 K. Those results were interpreted to indicate that an orientational ordering transition occurs and that the fullerene molecules jump between equivalent orientations with a correlation time of $< 10^{-5}$ s. The nature of the interactions between C_{60} and CS_2 has been examined by quantum mechanical calculations.[8]

Reversible phase transitions in molecular crystals are relatively rare occurrences. More commonly, molecular crystals undergo cooling without phase change or fragment upon cooling owing to irreversible phase changes which generally make determination of the structure of the low temperature phase inaccessible. Reversible phase changes in molecular crystals are likely to involve an aspect of increased molecular order at low temperature owing to a reorganization process such as the molecular ordering seen for $2C_{60}\cdot 3CS_2$ or the side chain ordering and molecular reorientation observed in cholesterol.[9] Since orientational disorder is common in fullerenes, it is likely that other reversible phase changes will be seen in the large number of crystals in which a fullerene co-crystallizes with one or two other molecules. The present study emphasizes the value of examining fullerene structures at the lowest experimentally obtainable temperature.

Notes and references

† The crystal used was a dark brown lath of size 0.065 × 0.13 × 0.36 mm. Data for the structure determination was collected on a Bruker SMART 1000 equipped with a CRYO Industries low-temperature apparatus. Selection of the monoclinic space group, $P2_1/n$, followed directly from the observation of systematic absences. The unit cell was based upon a least-squares fit of 5907 reflections with $2.3 < \theta < 24.3°$. Solution of the structure was achieved with some difficulty from direct methods and subsequent refinement and difference maps. Refinement of the structure stopped with an $R1$ of 0.28, yet there was no indication in the difference maps of another, rotationally disordered, C_{60} molecule. At this stage a twin law was introduced because there were two strong indicators of pseudo-merohedral twinning.[10] One was a mean $|E^2 - 1| = 0.749$, a value near to that expected for a non-centrosymmetric structure rather than a centrosymmetric one, and the other was the β angle very near 90°. A twin law [1 0 0 0 −1 0 0 0 −1] and twin component of 0.5 were introduced, which led to a 20% reduction in the value of $R1$. Another 2% reduction in the $R1$ value was achieved by the introduction of anisotropic thermal parameters for all atoms, leading to an $R1$ of 0.0579 computed for 8239 observed data $[>2\sigma(I)]$ and 1162 parameters. The twin component converged to 0.5032(10) and was subsequently set to 0.5000. The largest difference map peak had a value of 0.42 e $Å^{-3}$.

Crystal data for $2C_{60}\cdot 3CS_2$, $M = 1669.59$, monoclinic, space group $P2_1/n$, $a = 9.8722(12)$, $b = 25.466(3)$, $c = 24.671(3)$ Å, $\beta = 90.047(3)°$, $U = 6202.5(7)$ $Å^3$, μ(Mo-Kα) = 0.297 mm^{-1}, $Z = 4$, $T = 90$ K, 60760 reflections collected, 14233 unique ($R_{int} = 0.115$), $wR(F^2)$ was 0.1224 (all data). CCDC 182/1546. See http://www.rsc.org/suppdata/cc/a9/a908147j/ for crystallographic files in .cif format.

A Siemens P4 diffractometer equipped with a rotating Cu anode and LT-2 low temperature apparatus was used for the study of the phase change. The temperature at the crystal and calibration of the readout were determined by a separate study of the phase transition (at 123 K) of potassium dihydrogen phosphate. The Bruker SMART diffractometer was funded in part by NSF grant CHE-9808259.

1 M. F. Meidine, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 1534.
2 A. L. Balch, J. W. Lee, B. C. Noll and M. M. Olmstead, *J. Chem. Soc., Chem. Commun.*, 1993, 56.
3 H. B. Bürgi, R. Restori, D. Schwarzenbach, A. L. Balch, J. W. Lee, B. C. Noll and M. M. Olmstead, *Chem. Mater.*, 1994, **6**, 1325.
4 K. Kikuchi, S. Suzuki, K. Saito, H. Shiromaru, I. Ikemoto, Y. Achiba, A. Zakhidov, A. Ugawa, K. Imaeda, H. Inokuchi and K. Yakushi, *Physica C*, 1991, **185–189**, 415.
5 B. Morosin, P. P. Newcomer, R. J. Baughman, E. L. Venturini, D. Loy and J. E. Schirber, *Physica C*, 1991, **184**, 21.
6 J. C. A. Boeyens, M. Ramm, D. Zobel and P. Luger, *S. Afr. Tydskr. Chem.*, 1997, **50**, 28.
7 Y. Maniwa, K. Mizoguchi, K. Kume, K. Kikuchi, I. Ikemoto, S. Suzuki and Y. Achiba, *Solid State Commun.*, 1991, **80**, 609.
8 A. Tamulis, J. Tamuliene and A. Graja, *Fullerene Sci. Tech.*, 1998, **6**, 1097.
9 L.-Y. Hsu and C. E. Nordman, *Science*, 1983, **220**, 604.
10 R. Herbst-Irmer and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1998, **54**, 443.

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