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**High Pressure, Low Temperature Structural Studies
of Orientationally Ordered C₆₀**

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Abstract

The low-temperature orientationally ordered structure of C_{60} consists of rapid reorientation between two structurally distinct configurations. At ambient pressure, the lower energy orientation, described by pentagons facing $\langle 110 \rangle$ bonding directions, has a larger volume than the second orientation, described by hexagons facing $\langle 110 \rangle$. In this paper, it is shown that application of a modest pressure of around 2kbar is sufficient to make the "hexagon orientation" the more energetically favourable indicating that the structural ground-state of C_{60} is highly pressure-dependent. Entropic considerations suggest that the "hexagon orientation" at ambient pressure may best be described by a multiple local-minimum potential.

1. Introduction

The crystal structure of C_{60} has been extensively studied at ambient pressure as a function of temperature. The existence of a first order phase transition at around 260K was first confirmed by differential scanning calorimetry (Heiney *et al.*, 1991). The transition involves a reduction of space group symmetry from $Fm\bar{3}m$ to $Pa\bar{3}$. In the high temperature phase, the C_{60} molecules reorient quasi-isotropically resulting in a scattering density that is close to a spherical shell. Departures from isotropy are no more than 16% (Chow *et al.*, 1992; David *et al.*, 1993). In the low temperature phase, each molecule reorients between two energetically-similar but crystallographically-distinct orientations (David *et al.*, 1992a). These orientations are best described in terms of the inter-molecular bonding configurations. In the more energetically favourable ambient pressure configuration, the bonding motif may be described by pentagons facing C=C double bonds in a neighbouring molecule. In the less favourable orientation hexagons face the C=C bonds. The energy difference has been calculated to be around 122K (David *et al.*, 1992; Bürgi *et al.*, 1992; David *et al.*, 1993). These two orientations may be reached by hopping *ca.* 42° about $\langle \bar{1}10 \rangle$ directions over an activation energy of some 2600K. The magnitude of this activation energy has significant implications for the reorientational correlation times which follow an Arrhenius behaviour. At around the order-disorder transition at 260K, the reorientational correlation times are of the order of 10^{-9} s; at 86K, however, the reorientation is so slow ($>10^3$ s) that an orientational glass transition occurs (David *et al.*, 1992; Matsuo *et al.*, 1992; Gugenberger *et al.*, 1992). From the analysis of the lattice constant behaviour at the glass transition, it is evident that the lower energy "pentagon" orientation rather unusually has the larger volume. This is most likely a consequence of the fact that a facing hexagon, because of its larger area, may more easily accommodate a closer approach of neighbouring C=C bonds than a facing pentagon (Gugenberger *et al.*, 1992). Careful lattice parameter measurements (David *et al.*, 1993) have been modelled in a manner analogous to specific heat measurements using a combined Debye and Einstein model. From this model fit, the effective lattice

constant difference, Δa , between a hypothetical "pentagon-only" orientation and "hexagon-only" orientation structure is estimated to be $0.0439(10)\text{\AA}$ at ambient pressure. This corresponds to a rather large fractional volume change of $0.94(2)\%$ which implies that the relative stabilities of "pentagon" and "hexagon" orientations should be highly pressure-dependent. This observation provided the motivation for the present work. Indeed, a straightforward calculation of the free energy difference, $\Delta G^{HP}(p) = \Delta G_{(p=0)}^{HP} + p\Delta V^{HP}$, indicates that the two orientations will be of equal energy at a pressure given by the equation, $p_{("H"="P")} = -\Delta G_{(p=0)}^{HP} / \Delta V^{HP}$. Given that $\Delta G_{(p=0)}^{HP}$ is $\sim 122\text{K}$ and ΔV^{HP} is $-6.43(15)\text{\AA}^3$ for a single C_{60} molecule (David *et al.*, 1993) then it may be estimated that only 2.6kbar is required to make the "pentagon" and "hexagon" sites equivalent. At all pressures about 2.6kbar therefore the more preferred stable orientation of C_{60} should be the "hexagon" orientation. This has significant implications for understanding the high pressure transformations in C_{60} .

Previous work has already shown that modest pressures have a profound effect on the structure of solid C_{60} . The order-disorder transition in C_{60} has been studied as a function of pressure using the techniques of DTA and ^{13}C NMR (Samara *et al.*, 1991; 1993) and X-ray diffraction (Fisher *et al.*, 1991; Duclos *et al.*, 1991). These studies established that the ordered simple-cubic phase is stabilised with pressure. Using helium as the pressure-transmitting medium, Samara *et al.* (1993) report $dT/dp = 10.4(2)\text{Kkbar}^{-1}$. This result is not surprising and is consistent with a substantial reduction in the molecular separation since the C_{60} - C_{60} interactions are relatively weak and reminiscent of interlayer interactions in graphite. No compression of the C_{60} molecule has been detected. It is clear that increased pressure will hinder the reorientational motion of the C_{60} molecules thus frustrating the disordering process and raising the order-disorder phase-transition temperature. The initiation of orientational ordering with pressure is observed in many well-characterised molecular

solids such as methane, CH_4 , (Constantino & Daniels, 1975) molecular hydrogen, H_2 , (Sivera, 1980) and adamantane, $\text{C}_{10}\text{H}_{16}$ (David & Ibberson, 1993).

2. Experimental

Time-of-flight powder diffraction data were recorded at high pressure using the high resolution powder diffractometer, HRPD, at ISIS (Ibberson *et al.*, 1992). Approximately 1cm³ of pure C₆₀ was contained in an aluminium gas-pressure cell in a standard 'orange' cryostat. The cell utilises a Bridgeman seal and has a maximum operating pressure of 4.0kbar. Hydrostatic pressure is achieved by means of a gas intensifier system. On a pulsed neutron source, diffraction data are optimally recorded when using constrained sample environment equipment, such as a pressure cell, at a scattering angle of 90°. In this case, collimation can be used to define a scattering lozenge entirely within the sample volume. However, in the present experiments, high resolution backscattering data were required and so contamination by Bragg scattering from the cell was inevitable. The incident beam size was reduced to that of the sample cross-section; no collimation was used around the cell. The regions in which aluminium Bragg peaks occur were subsequently excluded during the profile refinement. Because of the high resolution nature of the diffraction patterns, the total excluded regions represented only 25% of the diffraction pattern.

Following the work of Samara *et al.* (1993), who report modifications to the structural behaviour of C₆₀ as a function of pressurising gas, argon was selected as the pressure transmitting medium. The van-der-Waals radius of argon is sufficiently large, 2.86Å so as not be accommodated in the tetrahedral and octahedral interstices of the C₆₀ structure. The use of argon, however, introduces additional technical problems. Around 90K at the ambient pressure orientational glass transition, argon becomes solid at very modest pressures. Problems were experienced in achieving a reliable sample pressure in the solid region of the argon phase diagram. Indeed, data were ultimately only obtained within the liquid regime of the argon phase diagram. The first datasets were recorded at 150K as a function of pressure. Measurements were subsequently collected at 2.8kbar and then at 2.0kbar as a function of temperature between 150K and 200K. Following a change in temperature, a manual adjustment was made to

maintain constant pressure (± 25 bar) in the cell. Data were recorded over a time-of-flight window of 30-130ms corresponding to a d -spacing range of *ca.* 0.6-2.6Å. The experiment collection times were of the order of 3 hours (*ca.* 120μAh).

3. The 150K structure as a function of pressure

Despite the modest hydrostatic pressures of the present measurements, significant structural changes are evident. At 150K, the lattice parameter reduces to 13.96074(12)Å at 2.8kbar compared with 14.06639(10)Å under ambient pressure conditions. The equation of state of C₆₀ at 150K data was determined using the Murnaghan equation (1944). The bulk modulus, K, is calculated as 127.4(8)kbar which compares with two previous measurements of (a) K=181(18)kbar and K₀'=5.7 (Duclos *et al.*, 1991) from a fit of ambient temperature data at pressures up to 200kbar and (b) K=140(20)kbar reported by Fischer *et al.* (1991) who measured at room temperature up to a pressure of 120kbar. Because of the restricted pressure range of the present data, deviations from a straight-line behaviour were not statistically significant and therefore, refinement of the derivative, K₀' of the bulk modulus, could not be justified. The expression of bulk modulus as a linear function of pressure over this limited pressure range is quite reasonable and agrees with the variations observed over the more extensive range of data collected by Duclos and co-workers (1991).

A full Rietveld analysis of the 150K data as a function of pressure was performed using the CCSL refinement package (David *et al.*, 1992b). Following the two orientation model described previously, the relative proportions of "pentagon" and "hexagon" orientations were refined as a function of pressure. The results for the fraction of "pentagon" orientations are presented in Figure 1a and clearly show that the expected increased stabilisation of the smaller volume "hexagon" orientation occurs as a function of pressure. The free energy difference (in K), $\Delta G^{HP} = -\ln[(1/n_p) - 1]$, is given as a function of pressure in Figure 1b.

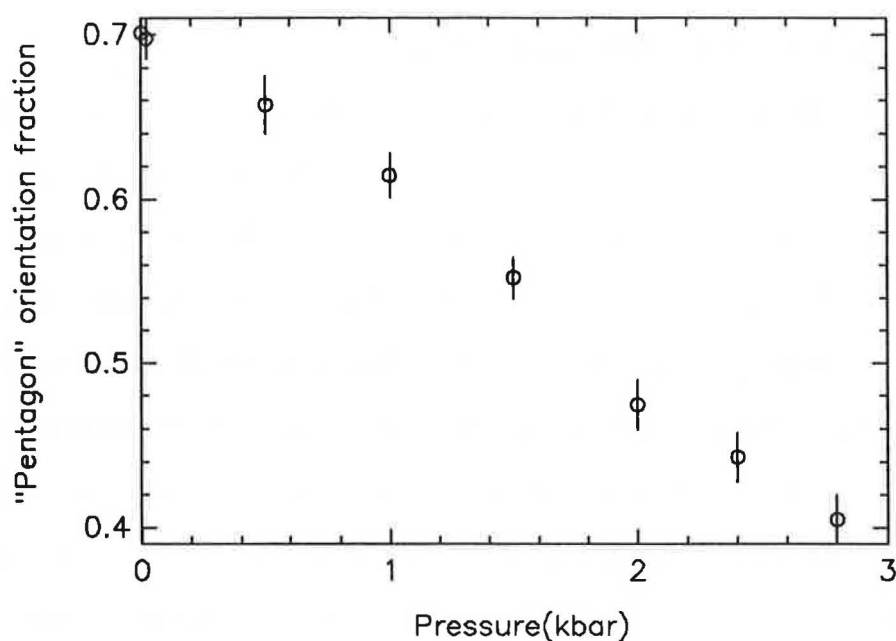


Figure 1a - Fractional occupation of the major "pentagon-facing" orientation as a function of pressure at 150K.

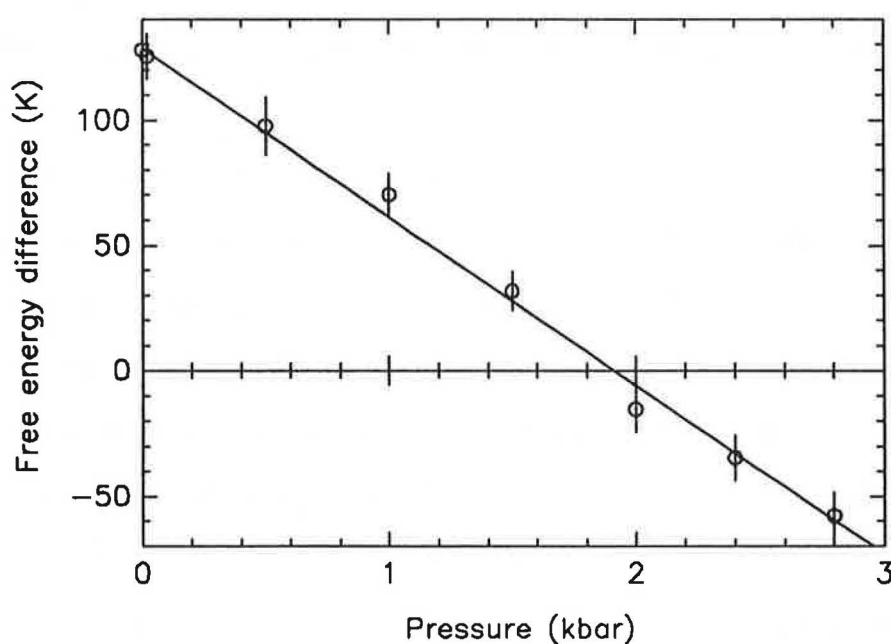


Figure 1b - The derived free energy difference, ΔG , expressed in degrees kelvin between the two orientations as a function of pressure at 150K. This was obtained from the equation, $\Delta G = -kT \ln((1/p_p) - 1)$. The straight line is a least-squares fit giving $\Delta G = 128.4(2.0) - 67.1(1.6)p$.

The free energy pressure variation, $\Delta G^{HP} = \Delta F^{HP} + p\Delta V^{HP}$, is, as expected, a straight line to within experimental errors. The fitted parameters (in K) give

$$\Delta G^{HP} = 128.4(2.0) - 67.1(1.6)p$$

The slope of the fit may be equated to the volume difference between a single C_{60} molecule in the "hexagon" and "pentagon" orientations. The fractional volume change is 0.0135(3) which is equivalent to a lattice constant difference of 0.0630(15)Å. This is some 50% larger than the value of 0.0439(10)Å obtained from extrapolation of the lattice constant as a function of temperature at ambient pressure. Although, these values differ by around 10σ , it must be noted (i) that they have been obtained from orthogonal variations in p-T space (ii) that the lower value is a model extrapolation based upon the assumption that the lattice constant, a , is a linear sum, $a = n_p a_p + n_H a_H$ and (iii) that there may be a small degree of argon incorporation within the C_{60} structure in the high pressure experiments. The discrepancy does not appear to be caused by a differential compressibility between "pentagon" and "hexagon" orientations (i.e. $\Delta a_p(p) \neq \Delta a_H(p)$). Within experimental errors the compressibilities appear to be identical from the absence of a p-T cross term in the evaluation of the lattice constant as a combined function of temperature and pressure. The following equation was found to fit the lattice parameter data to sufficient precision in the temperature range 150K to 200K and a pressure range 0-2.8kbar:

$$a = 14.0619(30) - 1.39(30) \times 10^{-4} T + 1.12(10) \times 10^{-6} T^2 \\ - 0.0442(6)p + 2.36(20) \times 10^{-3} p^2 + 3(3) \times 10^{-5} pT$$

(The precision of the cell constants derived at elevated pressures were typically an order of magnitude less precise than previous ambient pressure results (David *et al.*, 1993).) It is therefore reasonable to conclude that the simple two-orientation model is an adequate description of the behaviour of the solid as a function of pressure and temperature in the ordered simple cubic phase. The analysis of the temperature variations of the relative populations of "pentagon" and "hexagon" orientations at

ambient pressure and at 2.0kbar and 2.8kbar, however, indicate that the assumption of a single potential minimum associated with each of these orientations may be an oversimplification.

4. The ambient pressure, variable temperature behaviour of ordered C_{60}

Early measurements of the relative proportions of the "pentagon" and "hexagon" orientations as a function of temperature (Bürge *et al.*, 1992; David *et al.*, 1992a) indicated an essentially constant free-energy difference in the temperature range between 110K and 200K. At lower temperatures, the glass transition precludes the notion of thermal equilibrium; above 200K, there is clear premonitory behaviour of the 260K order-disorder transition that requires a more sophisticated model. More comprehensive recent measurements (David *et al.*, 1993) have indicated that in the 110K to 200K temperature range, the free-energy difference only approaches a constant value above 160K (Figure 2).

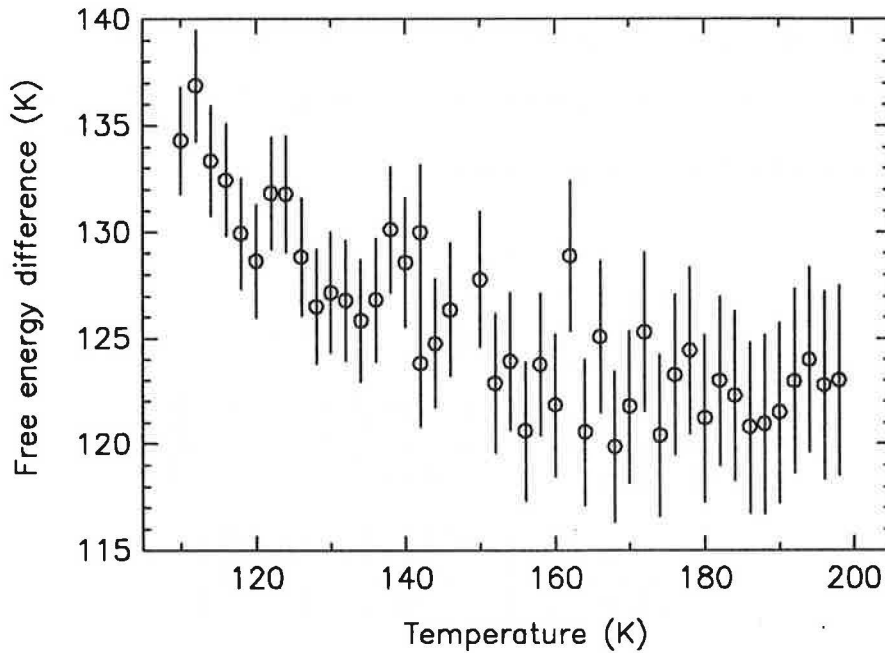


Figure 2 - The derived free energy difference, ΔG , expressed in degrees kelvin between major and minor orientations as a function of temperatures at ambient pressure. Note that ΔG is independent of temperature only in the region 160K-200K.

There would thus appear to be a variable entropy contribution as a function of temperature that is most straightforwardly explained as an effectively-variable multiple

degeneracy of the "hexagon" orientation. This is appropriately modelled as a multiple potential well with a low activation energy between the various local minima. There is additional experimental evidence from specific heat measurements (Matsuo *et al.*, 1992). The anomalous excess specific heat above the orientational glass transition may be modelled to a variable degeneracy Schottky anomaly (T Matsuo, personal communication) and leads to a relative degeneracy, g_H/g_P , of 3.4 ± 0.9 . We have therefore developed the following simple model to explain the unusual free energy difference as a function of temperature.

Consider a two energy-level system; the lower level is singly degenerate while the upper level, an energy ΔU higher, consists of a multiple-well potential with an energy barrier of ΔB separating these potential minima. The energies are quantised with a small energy separation, ζ , such that $\Delta U = M\zeta$ and $\Delta B = N\zeta$. Expressing $1/kT$ as β , leads to a partition function for such a system of the form:

$$\begin{aligned}
 Z &= \underbrace{\sum_{n=0}^{\infty} e^{-n\beta\zeta}}_{\text{"pentagon"}} + \underbrace{\left\{ \sum_{n=M}^{M+N-1} g e^{-n\beta\zeta} + \sum_{n=M+N}^{\infty} e^{-n\beta\zeta} \right\}}_{\text{"hexagon"}} \\
 &= \frac{1}{(1 - e^{-\beta\zeta})} + \left\{ \frac{[g e^{-\beta\Delta U} (1 - e^{-\beta\Delta B})] + [e^{-\beta(\Delta U + \Delta B)}]}{(1 - e^{-\beta\zeta})} \right\} \\
 &= \frac{1}{(1 - e^{-\beta\zeta})} + \left\{ \frac{e^{-\beta\Delta U} [g - (g-1)e^{-\beta\Delta B}]}{(1 - e^{-\beta\zeta})} \right\}
 \end{aligned}$$

From this equation, it is clear that the ratio of the "hexagon" to "pentagon" orientation fraction, n_H/n_P , may be expressed as

$$\frac{n_H}{n_P} = e^{-\beta\Delta U} [g - (g-1)e^{-\beta\Delta B}] = e^{-\beta\Delta G}$$

and thus the free energy difference, ΔG^{HP} , between "hexagon" and "pentagon" orientations may be expressed in degrees Kelvin as

$$\Delta G^{HP} = \Delta U - T \ln \left[g - (g-1)e^{-\Delta B/kT} \right]$$

In refining the free energy term, there was found to be a high correlation between the relative degeneracy, $g = g_H/g_P$, and the potential hump, ΔB . The specific heat measurements, however, suggest that the relative degeneracy is no less than three and is unlikely to be greater than six. Fixing the degeneracy, g , equal to three results in a plausible energy hump, ΔB , of 51(3)K and an energy difference, ΔU , of 194(K). For $g=6$, the values are 205(4)K and 22.4(1.5)K respectively. There is perhaps a particular appeal in choosing a "hexagon" degeneracy of three. The bonding motif associated with the "pentagon" orientation is highly symmetrical (Figure 3a). The interaction may be easily understood as a compromise between van-der-Waals bonding and an effective electrostatic repulsion of the electron-rich double bonds. In contrast to this the ideal "hexagon" orientation is significantly less symmetrical (Figure 3b). More intuitively appealing orientations may be achieved by a small rotation away from this ideal configuration (Figure 3c) that break the equivalence of the "hexagon" orientation

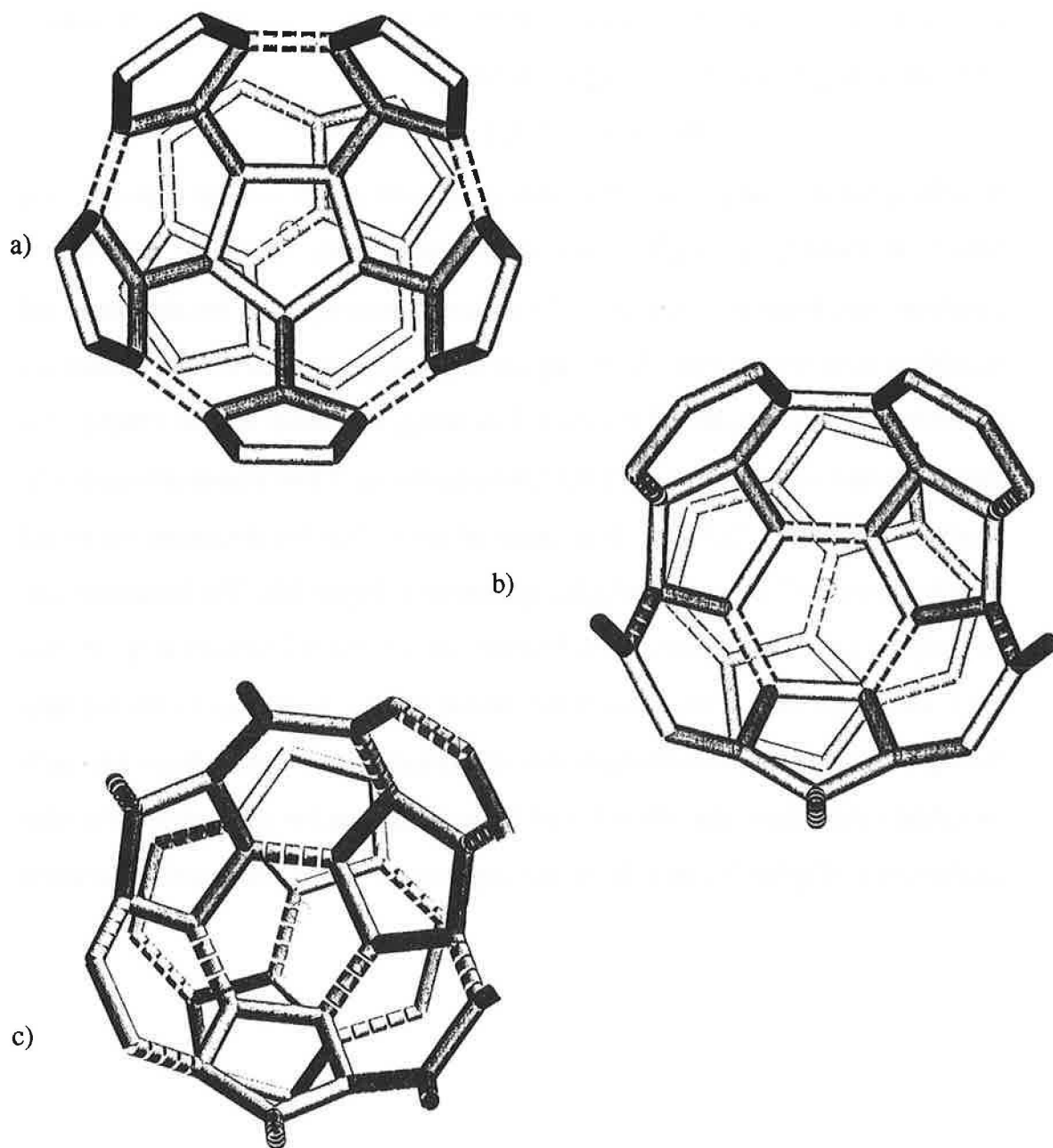


Figure 3 - The atom-atom configuration between neighbouring molecules projected along $[1\ 1\ 0]$. (a) The more energetically favourable, major orientation, involves the facing of a pentagon of "single" C-C bonds towards one "double" C=C bond in the next molecule. (b) The less energetically favourable, minor orientation, involves the facing of a hexagon of mixed "single" and "double" bond character. (c) A small 5° rotation away from the ideal minor orientation results in a more symmetrical "hexagon-facing" orientation, more reminiscent of the "pentagon" orientation.

bonding motif along [110], [101] and [011]. Given the $\bar{3}$ site symmetry of the C_{60} molecule implies that the degeneracy, g , of equivalent "hexagon" orientations must be $3n$. In principle it is possible to follow the degeneracy ratio, $g = g_H/g_P$, as function of pressure from extracting an entropic term in the free energy variation as a function of temperature at elevated pressures. It is difficult in the present work to obtain a meaningful measure of the degeneracy variation as a function of pressure. There is, however, rather surprisingly a weak indication that g is highly pressure dependent and that at above 2kbar is less than unity implying that multiple degeneracy is associated with the "pentagon" orientation rather than the "hexagon" orientation.

6. Conclusions

In this paper, the structure of C_{60} has been studied at simultaneous high pressure and low temperature. The main conclusion of the present work is that the most stable orientation state at ambient pressure, involving a pentagon face opposite the $C=C$ double bond of the adjacent molecule, is destabilised in preference to the orientation involving a hexagon facing an adjacent $C=C$ bond. This result is clearly expected from a straightforward analysis of the ambient pressure behaviour as a function of temperature which indicates that the "pentagon" orientation, although more favourable in energy than the hexagon orientation, has a larger associated volume. The application of pressure thus stabilises the "hexagon" orientation. In the temperature range investigated at elevated pressures, no evidence was found for the orientational glass transition. On the one hand, applied pressure might reasonably be expected to increase the activation energy of hopping thus raising the orientational glass transition temperature, T_g . On the other hand, at only a few kbar, the "hexagon" orientation will completely dominate thus making T_g difficult to observe. Within the "pentagon"/"hexagon" orientation model, the observed pressure dependence indicates that T_g will effectively disappear above 10kbar. More precise, higher pressure data are required to ascertain this. Consideration of the ambient pressure behaviour of the relative occupancies of "pentagon" and "hexagon" orientations indicates that the derived free energy difference between the two distinct orientations varies in a non-linear manner as a function of temperature. A simple local multi-minimum potential for the hexagon orientation was invoked to describe this result. These measurements indicate that ordered C_{60} has a rich structural variation even at modest pressures (<3kbar) at low temperatures. Further studies of the high pressure structure and dynamics of C_{60} up to 100kbar should be equally rewarding.

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