

# Orientalional disorder as a function of temperature in the clathrate structure of hydroquinone and C<sub>60</sub>

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In the compound [C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>]<sub>3</sub>C<sub>60</sub>, hydroquinone (C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>) forms a three-dimensional hydrogen-bonded network enclosing roughly spherical cages with point symmetry  $\bar{3}m$  and a diameter of 13.2 Å at 100 K. Although C<sub>60</sub> fits tightly into these cages, it shows threefold orientational disorder, the molecular site symmetry being  $2/m$ . The disorder has been studied with single-crystal Mo  $K\alpha$  X-ray data at four temperatures, 100, 200, 293 and 373 K. In the refinement, C<sub>60</sub> was restrained to the icosahedral molecular symmetry  $m\bar{3}5$  and to rigid-body translational and librational displacements including third- and fourth-order cumulants to account for curvilinear atomic movements,  $R(|F|) = 3.2\text{--}4.7\%$ . At 100 K, bond lengths in C<sub>60</sub> refine to the expected values 1.450 (1) and 1.388 (1) Å. The ratio of these values increases with increasing temperature, but the radius of the molecule remains constant at 3.537 (2) Å. The r.m.s. libration amplitudes of C<sub>60</sub> are relatively small (5.5° at 373 K) and the probability function of orientations of C<sub>60</sub> inside the cage shows large values only at the refined positions, indicating that the energy barrier of reorientation is large. Refinement of an ordered twinned structure was unsuccessful; the orientations of neighboring C<sub>60</sub> appear to be uncorrelated.

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## 1. Introduction

Buckminsterfullerene and hydroquinone form a 1:3 complex [C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>]<sub>3</sub>C<sub>60</sub>, hereafter referred to by HQ<sub>3</sub>C<sub>60</sub>. Ermer (1991) found the crystal structure to be a clathrate, where the hydroquinone molecules form a hydrogen-bonded three-dimensional host network with cavities just large enough to tightly encapsulate the C<sub>60</sub> guest molecules; the van der Waals diameter of the cavity is 10 Å (the distance between opposite atom centers being 13 Å) and just about equal to the van der Waals diameter of C<sub>60</sub>. The site symmetry of the cavity is  $\bar{3}m$ , which is a subgroup of the icosahedral group  $m\bar{3}5$ . This permits, in principle, the accommodation of an orientationally ordered C<sub>60</sub> molecule. However, Ermer (1991) showed the C<sub>60</sub> molecules to be orientationally disordered, but at the time he could not determine the precise nature of this disorder.

A detailed description of the orientational disorder of C<sub>60</sub> is of interest since it provides information on the interaction between host and guest molecules. If the disorder is dynamic, it also permits the calculation of the average potential experienced by a molecule (David *et al.*, 1992; Bürgi *et al.*, 1992*a,b*, 1993). In the present work, the disorder of C<sub>60</sub> has been determined and refined at four temperatures, 100, 200, 293 (room temperature) and 373 K, using geometry restraints

**Table 1**

Crystal data.

Independent of temperature				
Formula $[C_6H_6O_2]_3C_{60}$	Enraf–Nonius CAD-4 diffractometer			
$M_r$ , 1050.996	$\omega$ scans			
Trigonal	No absorption correction			
$R\bar{3}m$	$h, k, l = -11, 0, -19 \rightarrow 22, 22, 19$			
$Z = 3$	$\theta_{\max} = 30^\circ$			
Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$	3 standard reflections, frequency: 120 min			
Cell parameters from 25 reflections	Refinement on $ F ^2$			
$\theta = 8.7\text{--}26.3^\circ$	Weights $u^{-2}( F ^2)$			
Crystal $0.41 \times 0.36 \times 0.33 \text{ mm}$	85 parameters			
Dark brown–red	68 angle restraints			
Thermal expansion ( $\times 10^5 \text{ deg}^{-1}$ ): $\alpha_{11} = 2.1 (3), \alpha_{33} = 5.0 (3)$	$(\Delta/\sigma)_{\max} = 0.01$ $\Delta\rho_{\min}, \Delta\rho_{\max} \pm 0.4 \text{ e \AA}^{-3}$ and less Extinction correction: Becker & Coppens (1974), $y_{\min}( F ) = 0.92$			
Depending on temperature				
	100 K	200 K	293 K	373 K
$a$ ( $\text{\AA}$ )	16.119 (2)	16.152 (2)	16.177 (2)	16.212 (2)
$c$ ( $\text{\AA}$ )	13.687 (2)	13.750 (2)	13.813 (2)	13.873 (2)
$V$ ( $\text{\AA}^3$ )	3079.5 (9)	3106.4 (9)	3130.5 (9)	3157.7 (9)
$D_x$ ( $\text{Mg m}^{-3}$ )	1.700	1.685	1.672	1.658
$\mu$ ( $\text{mm}^{-1}$ )	0.1075	0.1065	0.1057	0.1048
Measured reflections	3481	2676	3365	3607
Independent reflections	1106	1115	1124	1136
Observed reflections $I > 3\sigma(I)$	823	739	751	702
$R_{\text{int}}$	0.0147	0.0215	0.0110	0.0166
Variation of standards	None	None	None	–10%
$R( F  \text{ observed})$	0.0355	0.0322	0.0422	0.0471
$wR( F ^2)$	0.0574	0.0565	0.0599	0.0733
$S$ including restraints	3.807	2.871	5.274	6.133

and the TLS rigid-body formalism (Schomaker & Trueblood, 1968), including cumulants to allow for curvilinear atomic motion. No phase transition has been detected in this range of temperatures.

## 2. Experimental

The preparation of  $HQ_3C_{60}$  has been described by Ermer (1991). Table 1 shows the crystal data, data collection and refinement parameters.<sup>1</sup> The dark shiny crystals have well developed faces. Suitable single-crystal domains were cut from the branches of dendrites with a sharp blade and mounted onto quartz fibres with epoxy glue. Low- and high-temperature data were collected using a nitrogen gas-flow cooling device. The crystals crack if cooled rapidly to low temperatures. The temperature was therefore lowered from 200 to 100 K in steps of  $10^\circ$  and of 45 min duration. Temperature fluctuations during the measurement of a data set were less than  $1^\circ$ , while the absolute temperatures are

<sup>1</sup>Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0080). Services for accessing these data are described at the back of the journal.

correct to within  $\sim 5^\circ$ . The lattice constants change linearly with temperature. Thermal expansion coefficients referring to the mean temperature of 250 K are reported in Table 1(a). The intensity data were collected in two portions in order to obtain a suitable number of symmetry-equivalent reflections for averaging: 1/6 of reciprocal space from  $\theta = 0$  to  $30^\circ$ , and 1/2 of reciprocal space from  $\theta = 0$  to  $15^\circ$ . The  $\omega$ -scan angle ( $^\circ$ ) was  $1.00 + 0.35\tan \theta$  and the maximum time spent on a reflection was 2 min. Variations of the intensities of three periodically measured check reflections were negligible, except at 373 K where they decreased linearly by 10% during the experiment. The intensities were rescaled using the average regression line with respect to exposure time. The variance of a net intensity was estimated as  $u^2(I) = u^2(\text{counting statistics}) + (KI)^2$ , where  $K$  was obtained from this formula by analyzing the fluctuations of the standard reflections about their mean. The Laue symmetry  $R\bar{3}m$  of the crystal at 100 K was ascertained with an additional data set containing 955 reflections,  $\theta$  between 0 and  $20^\circ$ , maximum scan time up to 6 min. The systematic absences corresponding to the  $R$  centering were not violated and no significant deviations from trigonal symmetry were detected.

## 3. Structure determination

A model for the orientational disorder of the  $C_{60}$  molecule at 293 K was determined by trial and error. The shape and dimension of  $C_{60}$ , as determined by Bürgi *et al.* (1992a,b), was fixed by distance and angle restraints, and molecular rigid-body displacements (Schomaker & Trueblood, 1968) were imposed by rigid-link restraints on the ADPs (atomic displacement parameters) of C (Didisheim & Schwarzenbach, 1987). The restrained atomic parameters of  $C_{60}$  were refined by least-squares, together with the parameters of the hydroquinone (HQ) molecule, starting with various molecular site symmetries and orientations. Usually,  $R|F|$  values were  $\sim 18\text{--}20\%$  and hardly changed during refinement. No satisfactory solution was found for molecular site symmetry  $\bar{3}$ . For one of the orientations with symmetry  $2/m$ , corresponding to threefold disorder, the agreement indices dropped sharply to a well defined optimum at  $R|F| \simeq 5\%$ . At this point, the alternative possibility of triple twinning was explored. From the optimal disordered structure, an ordered monoclinic structure, space group  $P2_1/m$ , was derived. Domains of this structure with their twofold axes at  $120^\circ$  result in a threefold twin. If the domains are of equal volume, the twinned crystal shows the observed maximum diffraction symmetry  $\bar{3}m$ . This model refined to  $R|F|$  of only 11% and twinning was therefore ruled out.

The disordered model at 293 K was subsequently used as a starting model for the least-squares refinements at all four temperatures. The shape of  $C_{60}$  was fixed only by angle restraints to the icosahedral symmetry, as described below. The two independent bond lengths,  $d_{56}$ , common to a pentagon and a hexagon, and  $d_{66}$ , common to two hexagons, are thus effective free parameters and are determined exclu-

**Table 2**Atomic coordinates and equivalent isotropic  $U$  of hydroquinone.

The numbering of the atoms is shown in Fig. 2. Consecutive rows show data at 100, 200, 293 and 373 K, respectively. For C4 and O4,  $y = x/2$ . The occupation factor of H4 is 0.5.

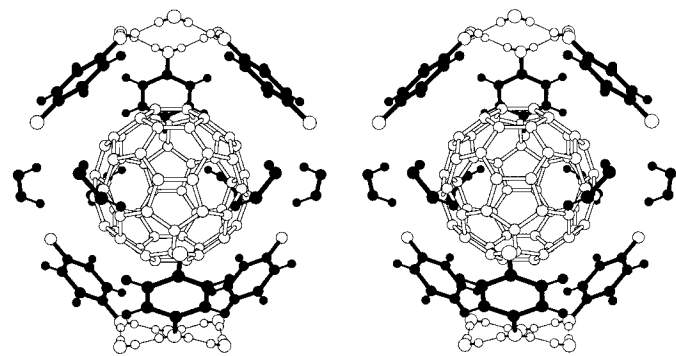
	$x$	$y$	$z$	$U_{\text{eq}}$
C4	0.26185 (2)	0.13093 (1)	0.59647 (2)	0.01469 (12)
	0.26213 (3)	0.13106 (2)	0.59684 (3)	0.02369 (17)
	0.26227 (2)	0.13114 (1)	0.59711 (2)	0.03277 (14)
	0.26248 (2)	0.13124 (1)	0.59748 (2)	0.04114 (15)
O4	0.19128 (2)	0.09564 (1)	0.52590 (2)	0.02748 (9)
	0.19155 (3)	0.09578 (2)	0.52661 (3)	0.04079 (18)
	0.19189 (2)	0.09594 (1)	0.52763 (2)	0.05426 (14)
	0.19225 (3)	0.09612 (2)	0.52840 (2)	0.06608 (15)
C5	0.29761 (2)	0.07461 (2)	0.63151 (2)	0.01634 (10)
	0.29767 (2)	0.07486 (3)	0.63180 (2)	0.02606 (15)
	0.29797 (2)	0.07550 (2)	0.63209 (2)	0.03554 (12)
	0.29812 (2)	0.07592 (2)	0.63244 (2)	0.04538 (13)
H4	0.1641 (4)	0.1213 (5)	0.5139 (5)	0.057 (2)
	0.1631 (6)	0.1196 (6)	0.5187 (7)	0.069 (4)
	0.1651 (4)	0.1201 (4)	0.5140 (5)	0.095 (3)
	0.1686 (5)	0.1220 (4)	0.5112 (5)	0.114 (3)
	0.1686 (5)	0.1220 (4)	0.5112 (5)	0.114 (3)
H5	0.27155 (16)	0.00903 (17)	0.60727 (16)	0.0171 (6)
	0.2710 (2)	0.0101 (3)	0.6083 (2)	0.0339 (10)
	0.27097 (14)	0.01065 (19)	0.60757 (13)	0.0389 (6)
	0.27274 (16)	0.01282 (16)	0.60774 (14)	0.0449 (6)

sively by the experimental data. The corresponding refinements converged easily and smoothly. At 100 K the values obtained for  $d_{56}$  and  $d_{66}$  were close to the expected values (Bürgi *et al.*, 1992*a,b*). However, these lengths changed smoothly by  $\sim 0.03$  Å as functions of temperature between 100 and 373 K: the higher the temperature, the longer was  $d_{56}$  and the shorter was  $d_{66}$ , while the molecular diameter remained almost constant between 7.072 and 7.075 Å. Restraining the bond lengths to the same expected values at all temperatures considerably increased the reliability factors, at 373 K by as much as 2%. Much effort was spent on understanding this very significant effect, which had also been observed in the room-temperature structure of pure  $C_{60}$  (Bürgi *et al.*, 1993). Since the effect is correlated with the size of the displacement parameters, it is probably due to the limited ability of ADP's to describe large-amplitude librations. Although the r.m.s. amplitudes of the molecular librations of  $C_{60}$  do not exceed  $6^\circ$  even at 373 K and are smaller than those obtained for HQ, the corresponding atomic r.m.s. displacements are as large as 0.3 Å. Two types of models were devised to explain this trend in the bond lengths  $d_{56}$  and  $d_{66}$ .

(i) Efforts were first directed at finding additional orientational disorder of the  $C_{60}$  molecules. Several models with molecular site symmetry  $\bar{1}$ , *i.e.* a sixfold disorder defined by a molecule rotated by a few degrees from the  $2/m$  position, resulted in roughly the same agreement factors, and also in the same changes of bond lengths with temperature. Models composed of two inequivalent kinds of orientations, a major set with  $2/m$  or  $\bar{1}$  symmetry and a minor set with  $\bar{3}$ ,  $2/m$  or  $\bar{1}$  symmetry, were not more encouraging. Low  $R$  values could be

obtained for some of them, but convergence was difficult to achieve and the resulting bond lengths were far from expectations,  $d_{56}$  being too long and  $d_{66}$  being too short in all cases.

(ii) The rigid-body TLS model of Schomaker & Trueblood (1968) approximates the atomic displacements by rectilinear movements, and assumes a harmonic isolated-molecule potential for the translational and librational movements of the entire molecule. This model may be generalized with two kinds of anharmonicity, arising respectively from the curvilinear motions of the atoms, and from an anharmonic translation–libration potential. A correction for the first kind, the skewness of the atomic probability density functions arising from harmonic angular large-amplitude librational oscillations, has been proposed by Pawley & Willis (1970). These authors include third-order cumulant terms in the displacement factor expression. The extension to fourth-order cumulant terms is laborious but straightforward. The number of adjustable parameters is thereby not increased since all these cumulant terms are functions of the  $\mathbf{L}$  tensor elements. The resulting atomic parameters do not need to be corrected for the effects of the curvilinear motion. The refinement has to be carried out with respect to the elements of the  $\mathbf{T}$ ,  $\mathbf{L}$  and  $\mathbf{S}$  tensors, *i.e.* the rigid-body motion is imposed by constraints rather than the rigid-link restraints used during structure determination. The program *LSLS* (Blanc & Schwarzenbach, 1992) has been extensively modified to include this type of refinement. The second type of anharmonic motion due to an anharmonic libration potential has been neglected in the present work. It requires the introduction of additional adjustable parameters, specifically four third-order and nine fourth-order parameters in the case of  $2/m$  symmetry. However, the presence of such anharmonic terms may generally be inferred from the temperature dependence of the results of harmonic refinements. In particular, harmonic mean-square libration amplitudes are proportional to temperature, but anharmonic terms would result in a steeper increase with temperature. In addition, the second type of anharmonicity would result in a variation of the apparent equilibrium orientation of the molecule as a linear function of temperature.

**Figure 1**

Coordination of  $C_{60}$  by 12 hydroquinone molecules, six face-on and six edge-on. For clarity, only the H5–C5–C5'–H5' fragments of the edge-on HQ molecules are shown. Program: *ATOMS* (Dowty, 1993).

**Table 3**

Anisotropic displacement parameters of hydroquinone.

Consecutive rows show data at 100, 200, 293 and 373 K, respectively. The ADP expression is  $\exp(-2\pi^2 \sum U^i a_i^* a_j^* h_i h_j)$ . For C4 and O4,  $U^{12} = U^{11}/2$ ,  $U^{23} = U^{13}/2$ .

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C4	0.01174 (17)	0.01716 (13)	0.01337 (16)	0.00587 (9)	0.00208 (14)	0.00104 (7)
	0.0223 (3)	0.0247 (2)	0.0233 (2)	0.01117 (13)	0.0050 (2)	0.00250 (10)
	0.0322 (2)	0.03231 (14)	0.03377 (18)	0.01610 (11)	0.00587 (17)	0.00293 (8)
	0.0425 (2)	0.03971 (16)	0.0421 (2)	0.02123 (11)	0.00834 (18)	0.00417 (9)
O4	0.01988 (15)	0.03597 (15)	0.02123 (14)	0.00994 (8)	-0.00633 (12)	-0.00316 (6)
	0.0345 (3)	0.0460 (2)	0.0380 (2)	0.01724 (13)	-0.00891 (19)	-0.00445 (9)
	0.05011 (19)	0.05688 (17)	0.05353 (19)	0.02506 (10)	-0.01262 (15)	-0.00631 (8)
	0.0648 (2)	0.06576 (17)	0.0673 (2)	0.03242 (11)	-0.01330 (17)	-0.00665 (9)
C5	0.01829 (14)	0.01201 (13)	0.01784 (12)	0.00692 (11)	0.00339 (10)	0.00014 (10)
	0.03045 (19)	0.01829 (17)	0.02925 (16)	0.01205 (16)	0.00530 (15)	0.00083 (14)
	0.04283 (17)	0.02449 (13)	0.04080 (15)	0.01795 (13)	0.00704 (12)	0.00086 (11)
	0.05424 (19)	0.02983 (15)	0.05376 (17)	0.02230 (14)	0.00855 (12)	0.00087 (12)

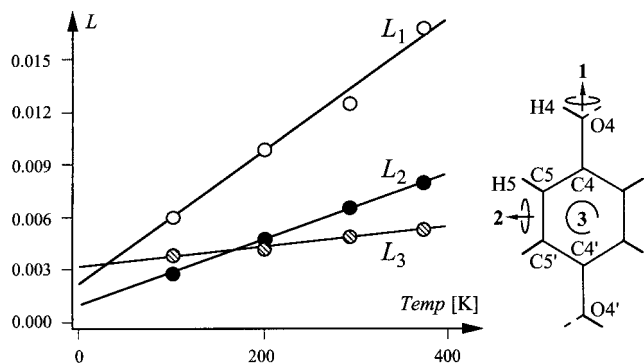
Model (ii) including third- and fourth-order cumulants correcting for curvilinear motion was used for the final refinements, starting from the optimal model with threefold disorder of  $C_{60}$ . Since the molecular site symmetry is  $2/m$ , the thermal displacement of  $C_{60}$  is described by four elements of  $\mathbf{T}$  and four elements of  $\mathbf{L}$ , the elements of  $\mathbf{S}$  being zero. The symmetry of  $C_{60}$  was imposed with a minimum number of angle restraints with weights  $(0.02^\circ)^{-2}$ : 16 angles of  $108^\circ$  and 16 angles of  $36^\circ$  to keep all the pentagons planar and regular; 18 angles of  $120^\circ$  and 18 angles of  $60^\circ$  to keep the hexagons planar and semi-regular with alternating long and short edges. C4, C5 and O4 of HQ were refined anisotropically, H5 (bonded to C5) and H4 isotropically without restraints. H4 forms the hydrogen bonds between the HQ molecules. It is disordered with an occupation factor of 0.5. The weights  $u^{-2}(|F|^2)$  were not modified during the refinements. All refinements converged smoothly. The largest maxima in the final difference-Fourier maps with heights between 0.3 and  $0.4 \text{ e } \text{\AA}^{-3}$  are located near the centers of the C—C and C—O bonds of HQ. The highest features on the  $C_{60}$  sphere are smaller than  $\pm 0.2 \text{ e } \text{\AA}^{-3}$  at all temperatures. Atomic para-

meters are reported in Tables 2–5. Table 6 shows interatomic distances in HQ and  $C_{60}$ . Since the symmetry  $m\bar{3}5$  of  $C_{60}$  was imposed with restraints, symmetry-equivalent bond lengths do not assume exactly the same values; we report average values with s.u.'s calculated from the sample distributions. The lengthening of the  $d_{56}$  bond and the concomitant shortening of the  $d_{66}$  bond with temperature is still evident. Models combining superpositions of more than three molecular orientations (type *a* model) with corrections for curvilinear motion (type *b* model) all show the same trend in  $d_{56}$  and  $d_{66}$ . We cannot offer an explanation of this effect, except that it may be attributable to an anharmonic component of the libration potential.

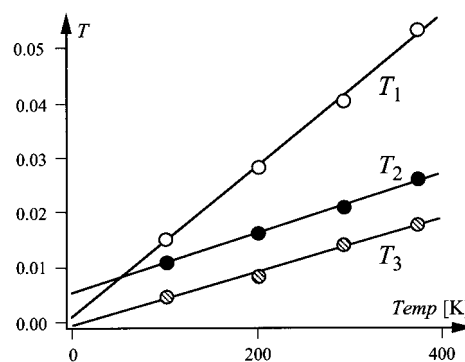
## 4. Discussion

### 4.1. Geometry

The HQ molecule possesses crystallographic  $2/m$  symmetry; the mirror plane is perpendicular to the molecular plane and contains the O atoms (Fig. 2). HQ is planar at all temperatures and therefore has molecular symmetry  $mmm$ : the distances of



**Figure 2** Hydroquinone: identification of the atoms; axes of inertia **1**, **2**, **3**; eigenvalues of the rigid-body libration tensor  $\mathbf{L}$  as a function of temperature. The eigenvectors of  $L_1$  and  $L_3$  are approximately parallel to the respective inertial axes **1** and **3**. The eigenvector of  $L_2$  coincides with the twofold symmetry axis **2**.



**Figure 3** Eigenvalues of the rigid-body translation tensor  $\mathbf{T}$  of hydroquinone as a function of temperature. The eigenvectors of  $T_1$  and  $T_3$  are closely parallel to the respective inertial axes **1** and **3**. The eigenvector of  $T_2$  coincides with the twofold symmetry axis **2**.

**Table 4**Fractional atomic coordinates of  $C_{60}$ .Consecutive rows show data at 100, 200, 293 and 373 K, respectively. For C105 and C106,  $y = x/2$ . Population parameters of all atoms are 1/3.

	x	y	z
C103	0.01121 (3)	-0.03939 (3)	0.25305 (3)
	0.01199 (5)	-0.03911 (4)	0.25161 (4)
	0.01332 (5)	-0.03893 (4)	0.24998 (3)
	0.01414 (5)	-0.03855 (5)	0.24888 (3)
C104	-0.08454 (3)	-0.11505 (3)	0.22847 (3)
	-0.08393 (4)	-0.11486 (5)	0.22746 (4)
	-0.08291 (4)	-0.11488 (4)	0.22624 (3)
	-0.08235 (5)	-0.11472 (5)	0.22536 (3)
C105	-0.14371 (4)	-0.07185 (2)	0.21317 (4)
	-0.14322 (5)	-0.07161 (3)	0.21232 (5)
	-0.14263 (5)	-0.07131 (2)	0.21130 (4)
	-0.14221 (6)	-0.07111 (3)	0.21049 (5)
C106	-0.21277 (4)	-0.10639 (2)	0.14028 (4)
	-0.21195 (5)	-0.10598 (2)	0.14049 (5)
	-0.21049 (5)	-0.10524 (2)	0.14108 (5)
	-0.20948 (5)	-0.10474 (3)	0.14114 (5)
C109	-0.24707 (4)	-0.16842 (4)	-0.01893 (4)
	-0.24667 (5)	-0.16836 (5)	-0.01855 (5)
	-0.24626 (4)	-0.16847 (4)	-0.01840 (5)
	-0.24600 (5)	-0.16852 (4)	-0.01830 (6)
C110	-0.22594 (3)	-0.18566 (3)	0.07958 (3)
	-0.22527 (4)	-0.18550 (4)	0.07979 (4)
	-0.22414 (3)	-0.18546 (4)	0.08018 (4)
	-0.22335 (4)	-0.18530 (4)	0.08024 (5)
C111	-0.16967 (3)	-0.22742 (4)	0.09436 (3)
	-0.16941 (4)	-0.22675 (5)	0.09419 (4)
	-0.16913 (3)	-0.22596 (4)	0.09389 (4)
	-0.16889 (4)	-0.22533 (4)	0.09359 (4)
C112	-0.09723 (3)	-0.19122 (3)	0.17031 (2)
	-0.09670 (4)	-0.19049 (5)	0.16990 (4)
	-0.09587 (4)	-0.18971 (4)	0.16939 (3)
	-0.09530 (4)	-0.18896 (5)	0.16907 (4)
C113	-0.01454 (3)	-0.19459 (4)	0.13371 (4)
	-0.01408 (4)	-0.19412 (6)	0.13335 (5)
	-0.01313 (4)	-0.19330 (5)	0.13225 (4)
	-0.01255 (4)	-0.19277 (6)	0.13192 (5)
C114	-0.03595 (4)	-0.23305 (5)	0.03548 (4)
	-0.03564 (5)	-0.23240 (8)	0.03471 (5)
	-0.03533 (4)	-0.23195 (6)	0.03297 (4)
	-0.03475 (4)	-0.23097 (7)	0.03213 (5)
C115	-0.13185 (3)	-0.25368 (4)	0.01121 (3)
	-0.13181 (5)	-0.25333 (6)	0.01085 (5)
	-0.13145 (4)	-0.25269 (5)	0.00948 (4)
	-0.13117 (4)	-0.25207 (5)	0.00890 (5)
C116	-0.15143 (4)	-0.23647 (4)	-0.08310 (3)
	-0.15124 (5)	-0.23626 (6)	-0.08205 (5)
	-0.15115 (4)	-0.23638 (5)	-0.08097 (4)
	-0.15122 (5)	-0.23640 (5)	-0.08021 (5)
C117	-0.21135 (4)	-0.19410 (5)	-0.09847 (3)
	-0.21124 (5)	-0.19364 (8)	-0.09729 (5)
	-0.21114 (5)	-0.19282 (6)	-0.09600 (4)
	-0.21120 (5)	-0.19238 (7)	-0.09503 (5)
C118	-0.17352 (4)	-0.12978 (5)	-0.18151 (4)
	-0.17363 (6)	-0.12953 (8)	-0.18020 (6)
	-0.17441 (6)	-0.12986 (6)	-0.17879 (5)
	-0.17437 (7)	-0.12934 (8)	-0.17762 (6)
C119	-0.09032 (3)	-0.13267 (5)	-0.21750 (3)
	-0.09029 (5)	-0.13260 (7)	-0.21644 (5)
	-0.09048 (4)	-0.13263 (6)	-0.21489 (4)
	-0.09076 (5)	-0.13255 (7)	-0.21394 (4)
C120	-0.07712 (3)	-0.19902 (4)	-0.15680 (4)
	-0.07688 (4)	-0.19886 (5)	-0.15591 (6)
	-0.07674 (4)	-0.19881 (5)	-0.15422 (5)
	-0.07678 (5)	-0.19835 (5)	-0.15308 (5)

**Table 5****T** and **L** tensors of  $C_{60}$ .The axes of the unitary coordinate system are  $e_3$  along the threefold axis  $c$ ,  $e_2$  along the twofold axis  $a_2$ ,  $e_1$  in the mirror plane perpendicular to  $a_2$ . Consecutive rows show parameters at 100, 200, 293 and 373 K, respectively.

	11	22	33	13
<i>T</i>	0.00807 (12)	0.00663 (12)	0.00795 (11)	0.00031 (10)
	0.01333 (18)	0.01157 (19)	0.01348 (16)	0.00031 (17)
	0.01699 (17)	0.01709 (18)	0.01832 (13)	0.00161 (19)
	0.0216 (2)	0.0227 (2)	0.02433 (15)	0.0033 (3)
<i>L</i>	0.001842 (15)	0.001135 (13)	0.000912 (17)	-0.000112 (11)
	0.00388 (2)	0.00274 (2)	0.00212 (3)	-0.000512 (18)
	0.00628 (3)	0.00581 (2)	0.00369 (3)	-0.001188 (18)
	0.00908 (4)	0.00886 (3)	0.00557 (4)	-0.00174 (2)

its C atoms from the least-squares plane through all non-H atoms are less than 0.001 Å and the distance for O is 0.01 Å. The bond lengths (Table 6) decrease in general with increasing temperature. The correction due to librational motion of the molecule removes this trend for C4–C5 and C4–O4, and results in variations of less than 0.004 Å, while the distance C5–C5' decreases by 0.01 Å between 100 and 373 K even when corrected for libration.

$C_{60}$  also has point symmetry  $2/m$ . Since this is a subgroup of index 3 of the point symmetry  $\bar{3}m$  of the cage,  $C_{60}$  shows threefold orientational disorder. The line connecting the midpoints of two 5–6 bonds through the molecular center is nearly parallel to the threefold axis. The angle between these directions varies linearly with temperature: it is 2.5° at 100 K, 2.8° at 200 K, 3.1° at 293 K and 3.3° at 373 K. At 100 K, the bond lengths  $d_{56}$  and  $d_{66}$  are within 3 s.u.'s of the values of 1.448 and 1.391 Å reported by Bürgi *et al.* (1992a,b), see Table 6. The radius of  $C_{60}$  is the same within 0.004 Å at all temperatures, with a mean value of 3.537 (2) Å. This value needs no correction for librational molecular motion, since the refinement includes higher-order cumulant terms (see above).

A geometrical description of the molecular packing of  $HQ_3C_{60}$  and the corresponding stereoscopic figures have been given by Ermer (1991). The HQ molecules form a network with large cages. A cage is bordered by 12 molecules whose O–O axes define the edges of a distorted cube and whose molecular centers form a distorted cuboctahedron. A  $C_{60}$  occupying the cage faces the planes of six phenyl groups (face-on coordination) and the H5–C5–C5'–H5' bonds of another six HQ (edge-on coordination), see Fig. 1. Conversely, the HQ molecule is coordinated by four  $C_{60}$  molecules, two face-on and two edge-on. Distances of the midpoints of the C5–C5' bonds from the centers of the coordinating  $C_{60}$  increase with temperature by 0.06 Å: from 6.625 (1) Å at 100 K to 6.685 (1) Å at 373 K for face-on coordination, and from 6.863 (1) to 6.920 (1) Å for edge-on coordination. In the case of face-on coordination, two 6–6 and four 5–6 bonds of  $C_{60}$  point towards the centers of six phenyl rings. The former are parallel to the O–O axis; the latter are inclined to this axis by ~30° and roughly perpendicular to two C4–C5 bonds. At 100 K, the contact distances between the C atoms of  $C_{60}$  and face-on HQ are: 6–6 bonds to C4 3.0835 (7) and 3.1647 (7) Å;

**Table 6**

Bond lengths in the HQ molecule.

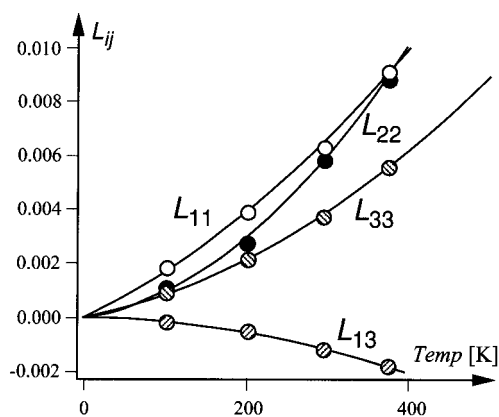
O4—O4'' is the hydrogen bond between HQ molecules; the s.u.'s of the mean distances in C<sub>60</sub>,  $\langle d_{56} \rangle$  and  $\langle d_{66} \rangle$ , are calculated from the sample distribution of equivalent bonds.

	100 K	200 K	293 K	373 K
C5'—C5	1.3859 (3)	1.3839 (5)	1.3763 (3)	1.3710 (3)
C4—C5	1.3819 (5)	1.3804 (7)	1.3772 (5)	1.3756 (5)
C4—O4	1.3796 (4)	1.3809 (6)	1.3760 (5)	1.3750 (5)
C5—H5	0.980 (3)	0.966 (5)	0.974 (3)	0.955 (3)
O4—H4	0.755 (9)	0.739 (13)	0.739 (8)	0.739 (10)
O4—O4''	2.7627 (5)	2.7772 (8)	2.7947 (5)	2.8120 (6)
$\langle d_{56} \rangle$	1.4497 (8)	1.4555 (11)	1.4638 (10)	1.4701 (12)
$\langle d_{66} \rangle$	1.3882 (8)	1.3784 (11)	1.3597 (10)	1.3503 (11)

6–6 bonds to C5 3.2504 (6) and 3.2956 (8) Å; 5–6 bonds to C4 3.1439 (8) and 3.2407 (9) Å; 5–6 bonds to C5 3.1742 (9) and 3.1980 (8) Å. These C···C contacts between C<sub>60</sub> and HQ are very similar to the intermolecular distances in the room-temperature structure of pure C<sub>60</sub> (Bürgi *et al.*, 1993). The edge-on coordination shows C···C distances larger than 3.5 Å and is reminiscent of the contacts observed in crystalline benzene (Jeffrey *et al.*, 1987).

#### 4.2. Analysis of displacement parameters

The anisotropic displacement parameters of HQ (Table 3) can be expressed reasonably well by rigid-body displacement tensors **T** and **L**, whose elements (Table 7) were adjusted to the  $U^{ij}(\text{obs})$  of C4, C5 and O4 with the program *NKA* (Förtsch, 1997; Capelli, 1999). *R* values  $\Sigma|U^{ij}(\text{obs}) - U^{ij}(\text{calc})| / \Sigma|U^{ij}(\text{obs})|$  ranged from 0.017 to 0.032. The eigenvalues at 100 K of the molecular inertial tensor of HQ are 104 g Å<sup>2</sup> mol<sup>-1</sup> for eigenvector **1** along O4—O4', 365 g Å<sup>2</sup> mol<sup>-1</sup> for the twofold axis **2** and 469 g Å<sup>2</sup> mol<sup>-1</sup> for the normal to the ring plane **3** (Fig. 2). The eigenvectors of the



**Figure 4**

Tensor elements of **L** of C<sub>60</sub> (Table 5) as functions of temperature. The curves are  $L_{ij} = aT^2 + bT$ . The coordinate system is **e**<sub>3</sub> along **c**, **e**<sub>2</sub> along **a**<sub>2</sub>, **e**<sub>1</sub> in the mirror plane perpendicular to **a**<sub>2</sub>.

**Table 7**

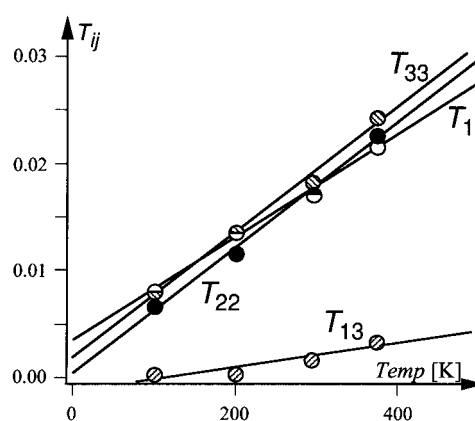
**T** and **L** tensors of hydroquinone, derived from the  $U^{ij}$  of Table 3.

Consecutive rows show parameters at 100, 200, 293 and 373 K, respectively. The uncertainties are derived from the fit of calculated and observed  $U^{ij}$ .

	11	22	33	13
<b>T</b>	0.0094 (2)	0.01102 (17)	0.01051 (7)	0.0052 (2)
	0.0176 (3)	0.0164 (2)	0.0191 (3)	0.0100 (3)
	0.0266 (7)	0.0211 (4)	0.0279 (8)	0.0132 (7)
	0.0355 (10)	0.0263 (7)	0.0359 (12)	0.0179 (10)
<b>L</b>	0.00445 (12)	0.00288 (6)	0.00551 (18)	0.00100 (13)
	0.0061 (2)	0.00482 (10)	0.0081 (2)	0.0027 (2)
	0.0078 (6)	0.0066 (2)	0.0098 (5)	0.0037 (5)
	0.010 (9)	0.0081 (3)	0.0115 (8)	0.0057 (7)

libration and translation tensors **L** and **T** are close to these inertial axes. The angles of the eigenvectors of  $L_1$  and  $L_3$  with the respective axes **1** and **3** decrease from 15 (3)° at 100 K to 3 (3)° at 373 K. The corresponding angles for  $T_1$  and  $T_3$  decrease from 4 (3)° at 100 K to 2 (1)° at 373 K. The eigenvectors of  $L_2$  and  $T_2$  are fixed by symmetry parallel to the twofold axis **2**. Figs. 2 and 3 show that the variation of the eigenvalues with temperature is very close to linear. Except at 100 K, the smaller the inertial moment the larger the m.s. libration amplitude *L*, as expected.  $L_1$  and  $L_2$  extrapolate to relatively small, but not exactly zero, values at 0 K (0.002 and 0.001 arc<sup>2</sup>). In contrast, the behavior of  $L_3$  clearly does not agree with that expected for a harmonic oscillator at high temperatures: its increase with temperature is small and it shows the largest extrapolated value at 0 K [0.003 arc<sup>2</sup> (3.14°)<sup>2</sup>]. Two of the eigenvalues of the **T** tensor,  $T_1$  and  $T_3$ , extrapolate to values very close to zero at 0 K and thus show the expected harmonic behavior with temperature, whereas  $T_2$  extrapolates to 0.005 Å<sup>2</sup>.

The most probable cause for the finite extrapolated values at 0 K is disorder. In particular,  $L_3$  and  $T_2$  suggest disorder with atomic displacements principally in the plane of the HQ



**Figure 5**

Tensor elements of **T** of C<sub>60</sub> (Table 5) as functions of temperature. The coordinate system is as in Fig. 4.

molecule, resulting in split atomic positions due to a rotation of  $ca \pm 3^\circ$  and a translation of the order of  $\pm 0.07 \text{ \AA}$ . The true librational r.m.s. amplitudes around the plane normal would then be only of the order of  $1\text{--}2^\circ$ . Note that in spite of this suggested disorder, the H atoms could be refined. Various models with superimposed images of HQ molecules could be refined at the cost of introducing geometric and displacement factor restraints. They all give very similar reliability indices and no additional insight. Capelli & Bürgi (1997) have found in a literature search that the distribution of C—C—O angles in 37 crystal structures containing ordered HQ molecules show maxima at  $118$  and  $123^\circ$ , and a minimum at  $120^\circ$ , corresponding to an in-plane displacement of O—H from the idealized position on the mirror plane of the phenyl ring. The variation of the displacement parameters of HQ with temperature is then explained by a superposition of two HQ molecules of molecular symmetry  $2/m$  rotated by  $3^\circ$  relative to each other (publication in preparation).

The directions of the eigenvectors of the **L** and **T** tensors of  $C_{60}$  calculated from Table 5 show a larger variation with temperature than those of HQ. The angle between the direction of  $L_3$  and the threefold axis changes from  $6.8 (6)^\circ$  at  $100 \text{ K}$  to  $22.4 (5)^\circ$  at  $373 \text{ K}$ . The molecular inertial tensor is isotropic. For these reasons, Figs. 4 and 5 and Table 5 show the tensor elements as functions of temperature rather than the eigenvalues (note that  $L_{22}$  is an eigenvalue since its eigenvector points along a crystallographic twofold axis). The behavior of the  $L_{ij}$ , and in particular of  $L_{22}$ , is extremely non-linear, but fits reasonably well with parabolae passing through zero at zero temperature. This indicates that the potential for  $C_{60}$  libration may be anharmonic. However, the r.m.s. librational amplitudes of  $C_{60}$  are considerably smaller than those of HQ: at  $373 \text{ K}$  the largest value is  $L_{11}^{1/2} = 5.46 (1)^\circ$  for  $C_{60}$ , compared with  $L_1^{1/2} = 7.4 (2)^\circ$  for HQ. The **T** tensor is roughly isotropic, as evidenced by the similar diagonal terms  $T_{11}$ ,  $T_{22}$  and  $T_{33}$ .  $T_{ij}$  vary linearly with temperature. They extrapolate to small values at zero temperature, of which only  $T_{11}$  might be significant. The r.m.s. amplitudes are rather small, even at  $373 \text{ K}$ , and considerably smaller than  $T_1$  of HQ.

The probability of finding the  $C_{60}$  molecule in a given orientation may be calculated from its libration tensor **L** (Bürgi *et al.*, 1993). **L** is the variance–covariance matrix of a Gaussian distribution, which represents the probability that a molecule librates about a given axis through a certain angle starting from the position obtained in the structure refinement. Owing to the icosahedral symmetry of the molecule (the order of the group of rotations being 60) and the threefold disorder, any orientation of interest can be reached by 180 different rotations and the probability to attain this orientation is therefore a sum of 180 terms. If the Gaussian distribution is narrow, *i.e.* if the  $L_{ij}$  values are small, the resulting probability density function of molecular orientation takes large values only at the positions obtained in the refinements. In  $HQ_3C_{60}$ , this is indeed the case: the probability for all other significantly different orientations is never larger than 0.01. This indicates that the  $C_{60}$  molecules assume well

defined orientations which are not connected by a low-energy reorientation pathway analogous to that found in the room-temperature structure of  $C_{60}$  (Bürgi *et al.*, 1993).

## 5. Conclusions

Although disordered,  $HQ_3C_{60}$  is one of the relatively few structures that allows an experimental determination of the dimensions of the  $C_{60}$  molecule. The bond lengths at  $100 \text{ K}$  (Table 6) agree well with the values of  $1.45$  and  $1.39 \text{ \AA}$  found in the low-temperature structure of pure  $C_{60}$  (Bürgi *et al.*, 1992*a,b*). As for most other structure determinations of  $C_{60}$  from diffraction data, the icosahedral symmetry had to be presupposed. The molecules occupy cages in the HQ framework of just the right dimensions to fit nearly perfectly and tightly. Molecular libration and translation amplitudes are relatively small, and reorientation inside a cage is improbable. The interaction of  $C_{60}$  with HQ is similar to the intermolecular interaction in pure  $C_{60}$  with C—C bonds pointing towards the centers of phenyl rings. The most favorable orientation of  $C_{60}$  is not the one exploiting the  $\bar{3}m$  symmetry of the cage, hence the disorder. A model postulating threefold twinning of ordered domains gave an inferior fit with the observations. Long-range order of the orientations of the  $C_{60}$  molecules in neighboring cages thus appears to be absent. There is no indication that the point symmetry  $2/m$  of  $C_{60}$  results in appreciable distortions of the higher symmetric cages of the HQ framework. Such distortions would be expected to induce correlations and concomitant orientational ordering. Thus, the  $C_{60}$  molecules appear to be isolated in their cages. The dimensions of the cage are roughly spherical. The translational movements of the guests are therefore close to isotropic. The presence of an anharmonic component of the libration potential of  $C_{60}$  is indicated by the non-linear temperature dependence of the elements of the **L**-tensor and the linear temperature dependence of the orientation of the molecule.

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