

Getting More out of Crystal-Structure Analyses

by Hans-Beat Bürgi* and Silvia C. Capelli

Laboratorium für Kristallographie, Universität Bern, Freiestr. 3, CH-3012 Bern
(phone: +41 31 631 4282; fax: +41 31 631 3996; e-mail: hans-beat.buergi@krist.unibe.ch)

To Jack Dunitz, our teacher and mentor

Motion and disorder in the crystal structures of benzene, (D₆)benzene, and the clathrate C₆₀·(HQ)₃ (HQ = hydroquinone = benzene-1,4-diol) are studied. The observed temperature evolution of their atomic displacement parameters (ADPs) is analyzed in terms of a physical model that explicitly accounts for effects of temperature. The major part of the ADPs of (D₆)benzene is explained by rigid-body normal modes. The small but significant fraction that remains is shown to be due to zero-point intramolecular motion. Comparison of the ADPs of D- and H-isotopomers of benzene confirms the expected isotopic relationship. These findings, which leave no room for disorder between two *Kekulé* structures, corroborate the validity of the physical model. An analogous treatment of the ADPs of the hydroquinone part of the clathrate compound reveals a distinctive disposition of displacements related neither to rigid-body nor to zero-point motion. The pattern is interpreted nearly quantitatively in terms of orientational and positional disorder of the hydroquinone molecule amounting to a few degrees and hundredths of an Ångström, respectively. The model of disorder accounts for unusual bond angles in the average structure and suggests a chemically sensible pattern of locally ordered H-bonds.

Introduction. – More than 300000 entries in the organic- and inorganic-crystal-structure databases attest to the success of single-crystal structure analysis as an analytical method. The technique and the underlying theory are extremely well understood, so well that it has become feasible to code the procedures of data collection, data processing, structure solution, structure refinement, and – to some extent – chemical interpretation and structure validation into suites of computer programs. These tools allow experts as well as nonexperts to determine crystal structures of low-molecular-mass compounds with minimal user intervention within a few hours. The method is not only fast, it also provides results of high precision: standard uncertainties of a few thousandths of an Ångström in interatomic distances and a few hundredths of a degree in bond angles are not uncommon.

Given these successes, the takers of crystal structures tend to forget that the results of a structure analysis are subject to two important limitations: 1) it is not the chemically interesting bond lengths and angles that are determined in a single-crystal diffraction experiment but the probability distributions of the atoms in the unit cell, and 2) it is not the ‘crystal structure’ that is determined, but rather an *average unit cell*, *i.e.*, the time and space average of the distribution of atoms over the entire crystal. Both limitations may have serious repercussions on the deduction of molecular geometries from the observed electron or nuclear densities. The distribution of an atom in a crystal is characterized by a mean position as well as by the dynamic excursions and static displacements from this position. The latter determine the shape of the distribution,

which is usually approximated with the help of atomic displacement parameters (ADPs). The widths of such distribution functions are substantial, on the order of a tenth of an Ångström, up to two orders of magnitude larger than the precision reported for interatomic distances. The latter is derived from the precision of atomic positions with the implicit assumption that uncertainty related to ADPs can be largely ignored. This assumption is justified for well-ordered, rigid molecules or rigid parts of flexible molecules. Note however, that the justification usually depends entirely on information not coming from diffraction experiments, *e.g.*, on information from vibrational spectroscopy and high-level quantum-mechanical calculations. The second limitation, namely averaging over unit cells, presents no difficulties as long as the vast majority of unit cells look alike during most of the time it takes to perform a diffraction experiment. It may become a problem if different unit cells look different, *i.e.*, if a crystal is disordered. The extent of the problem depends on the type and degree of disorder: if a given atom is distributed over several, partially occupied but well-resolved positions in the unit cell, a chemical interpretation of the disorder is usually not very difficult. If distances between disordered atoms become smaller than the resolution of a typical diffraction experiment, *ca.* 0.8 Å, the resulting average distribution no longer has a straightforward interpretation in terms of molecular geometry. Frequently, the two types of disorder occur together in the same crystal structure. Given that the molecules in a crystal are flexible, fluxional, or disordered, the nature of atomic distributions has to be taken into account if erroneous conclusions about molecular geometries are to be avoided.

The limitations described in the preceding paragraph have interfered significantly with conclusive crystal-structure analyses of several important organic molecules. Some of the difficulties are illustrated with selected examples: C₆₀ fullerene, cyclobutadiene, [18]annulene, and benzene. In its low-temperature modification, the C₆₀ fullerene molecule assumes two different, superimposed molecular orientations with different populations. Of the 60 atoms, 18 do not coincide in the two orientations, whereas 42 of them have nearly but not exactly the same positions. Initially, the non-overlapping atoms belonging to the minor orientation were overlooked. The lengths of the formal double bonds were found to be in the range between 1.340(7) and 1.391(6) Å, those of the formal single bonds extended all the way from 1.378(9) to 1.561(10) Å! Several ADPs looked somewhat unusual [1]. Once the nature of the problem was recognized, it was relatively easy to do a directed search for the small residual electron densities representing the non-coinciding atoms of the minor orientation¹). The model including both orientations is consistent with equal bond distances in each of the two groups (1.387(3) and 1.450(3) Å), although it provides no proof of these equalities [2].

A subtler kind of problem was encountered with tetra-(*tert*-butyl)cyclobutadiene and a closely related derivative [3][4]. The first X-ray analysis on the tetra-(*tert*-butyl) compound performed at room temperature showed nearly equal C–C distances in the four-membered ring (1.464(2) and 1.482(2) Å) [3] rather than the distinctly rectangular structure observed for less symmetrically substituted cyclobutadiene molecules (1.344(2) and 1.600(2) Å) [5]. Initially, this discrepancy has been interpreted in terms

¹) Contrary to naïve intuition, these densities increase in magnitude with increasing temperature because the population of the minor orientation increases.

of steric strain due to the *tert*-butyl groups. Later diffraction experiments at temperatures down to -150° showed noticeably larger differences in bond distances [6]. This observation has been explained in terms of a superposition of two rectangular molecules rotated by 90° relative to each other and with increasingly different populations as the temperature decreases [5][7]. In this arrangement, the disordered C-atoms are 0.1–0.2 Å apart. The mean atomic position is somewhere between the real equilibrium positions at distances well within the width of atomic distributions and too small to be resolved by the diffraction experiment. A similar type of disorder was observed for [18]annulene: two molecular orientations were found rotated by *ca.* 30° relative to each other and with unequal populations. Upon modelling the disorder, the lengths of the inner and outer bonds changed from 1.382(3) and 1.419(4) Å [8] to 1.385(2) and 1.405(3) Å, respectively [9]. Although the changes are small, the comparison of the distances with their uncertainties still shows that the high precision derived from average positions can be quite deceiving.

At about the time cyclobutadiene was studied, *Ermer* raised the question whether the crystal structure of benzene could be interpreted similarly, namely in terms of a centrosymmetric superposition of two *Kekulé* structures with localized single and double bonds. *Ermer* did not doubt the hexagonal structure of benzene; nevertheless, he argued convincingly and correctly that a crystal structure analysis could not distinguish between a superposition of *Kekulé* structures and a hexagonal structure of the benzene molecule [10]. His arguments are recollected in more detail in the next section.

These episodes raise several related problems: 1) how are molecular flexibility and fluxionality recognized from diffraction experiments? 2) How is disorder recognized? 3) How are the two phenomena distinguished? 4) Under which circumstances is it mandatory to include the widths of atomic distributions, *i.e.*, the atomic displacement parameters, in the determination of molecular geometry?

In the following, we give some answers in terms of a recently developed physical model describing the temperature evolution of ADPs. The discussion is introduced by summarizing the path to the hexagonal structure of the benzene molecule with due consideration of crystallographic evidence and *Ermer*'s reasoning. Our model is then introduced in general lines and applied to the interpretation of the ADPs of (D_6)benzene measured by neutron diffraction and of hydroquinone in a clathrate structure measured by X-ray diffraction. Results for benzene corroborate the hexagonal structure of the molecule and demonstrate the performance of our model; those for the hydroquinone molecule reveal a detailed picture of disorder and of the difference between the average and the real structure of the molecule.

Do Diffraction Data Provide Evidence for D_{6h} Symmetry of Benzene? – The concept of the hexagonal structure of the benzene molecule was formulated without the help of diffraction experiments. About 140 years ago, *Kekulé* reconciled the observed numbers of substituted benzene isomers with the tetravalency of the C-atom by placing the six C–H fragments at the vertices of a regular hexagon. In an *ad hoc* assumption, the remaining valency on each C-atom was assumed to pair up with that of one of its neighbors, leading to alternating C–C and C=C bonds that oscillate between the two *Kekulé* structures (see **1**). After *Lewis*'s interpretation of valency in terms of electrons

centrosymmetric superposition of two *Kekulé* structures with C–C single-bond and C=C double-bond lengths of 1.45 and 1.35 Å, respectively, two atoms from different *Kekulé* structures would be only 0.058 Å apart (*Fig. 1*), too close to be resolved by single-crystal-diffraction experiments whose resolution rarely exceeds 0.5 Å. Such disorder would, therefore, be reflected by an apparent atomic position midway between the two C-atoms and a slight increase in the ADPs of 0.0008 Å² [10]. Even at the lowest experimental temperature (15 K), this is still smaller by an order of magnitude than the observed average mean-square displacement of 0.0088 Å² [17]. This observation beautifully reveals the problems arising when apparent atomic positions are interpreted as equilibrium positions. It also illustrates the questions concerning the interpretation of ADPs mentioned above. In the case at hand, they may be rephrased as follows: which fraction of the ADPs of benzene is to be attributed to disorder and which fraction to atomic motion? Assuming that there is no disorder and that the ADPs are due entirely to motion, how do the atoms move relative to each other? Could the ADPs be the result of significant out-of-phase motions of neighboring C-atoms in the benzene ring, as if the atoms were oscillating between two *Kekulé* structures?

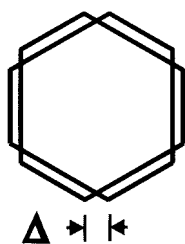


Fig. 1. D_{6h} -Symmetric superposition of two D_{3h} -symmetric hexagons. For short and long distances of 1.35 and 1.45 Å, the distance Δ between alternative positions of the C-atoms is 0.058 Å (difference between bond lengths exaggerated).

ADPs: Motion vs. Disorder and Kinematic vs. Dynamic Interpretations. –

Interpretations of ADPs are complicated by two problems. First, as mentioned already, the usual diffraction experiment performed at a single temperature does not distinguish between the effects of motion and disorder. Second, since ADPs represent *mean square displacements* of atoms from their most probable position, they do not disclose the relative phases of atomic motions or of atomic displacements in disordered structures. These limitations are not only responsible for the problems encountered in the structure determinations of benzene, cyclobutadiene, C₆₀ fullerene, and of many other molecules, they are intrinsic to any chemical interpretation of ADPs [18].

In view of these difficulties, it is usually *assumed* that there is no disorder and that the ADPs are simply the result of translational and librational oscillations of *rigid molecules* about their mean position and orientation in the unit cell (rigid-body model). This assumption fixes the relative phases and magnitudes of atomic displacements within molecules²⁾. The mean-square molecular translation, libration, and screw-motion amplitudes, also called the *T*, *L*, and *S* tensors, are extracted from the observed ADPs through a least-squares procedure [19]. The rigid-body model has been extended to include soft intramolecular motion, albeit at a penalty: the distinction between

²⁾ Note that the ‘rigid-body model’ says nothing about the correlation of motion between different molecules.

internal and external motions is partially lost [20]. In any case, if T , L , and S represent ADPs well and if the mean-square atomic displacements for pairs of atoms along their internuclear vectors are equal [21], it is usually concluded that the rigid-body assumption holds and that the librations and translations are physically meaningful [22]. While the above conditions are necessary for such conclusions to hold, they are obviously not sufficient as they do not exclude the possibility of partial corruption of T , L , and S by intramolecular motion and disorder.

This nuisance may be avoided by following the evolution of the atomic distribution functions with temperature. As described above for several examples, populations of disordered sites and the resulting apparent atomic positions may change substantially with temperature, thus providing a clear caveat to indiscriminate interpretations. Alternative atomic sites that are symmetry-related and close to each other have equal populations and cause a temperature-independent contribution to the ADPs. At a qualitative level, these facts have been recognized long ago [22]. However, to detect effects as small as the ones hypothesized for benzene, a quantitative physical treatment is needed.

We have recently developed a model of the temperature dependence of ADPs as far as they are due to vibrations with low frequencies on the order of kT . It accounts for the mean-square amplitudes of zero-point motion and for the increase of these amplitudes with increasing temperature. The model also includes terms to represent temperature-independent disorder and amplitudes due to vibrations with high frequencies, which are not significantly excited in the temperature range of the experiment and merely add a constant contribution to the ADPs [23].

The harmonic oscillator provides a physically plausible and mathematically simple illustration of the basic principles of this model. Consider an atom of mass μ moving with frequency ω in the harmonic mean field of its crystal lattice. The mean-square displacement amplitude $\langle u^2 \rangle$ of the atom is given by Eqn. 1, wherein T is the absolute temperature, \hbar is Planck's constant, and k_B is the Boltzmann constant. The temperature dependence of $\langle u^2 \rangle$ is shown in Fig. 2. Displacements are particularly large for light atoms moving at low frequency. In the high-temperature limit ($T \rightarrow \infty$), a harmonic oscillator behaves classically, as expressed by Eqn. 2. Displacements measured in this

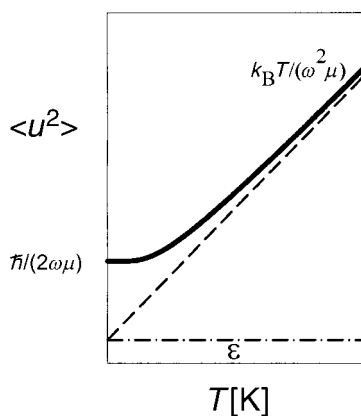


Fig. 2. Mean-square displacement amplitude of a harmonic quantum oscillator (—; the dependence of the zero-point motion and of the classical, temperature-dependent behavior on the frequency ω and the mass μ of the oscillator are given), classical harmonic oscillator (---), and temperature-independent contribution ϵ (-·-·-).

regime have to extrapolate to zero at 0 K because $\langle u^2 \rangle$ varies linearly with temperature. In the low-temperature limit ($T \rightarrow 0$), $\langle u^2 \rangle$ is independent of temperature (see Eqn. 3). In this limit, $\langle u^2 \rangle$ equals the zero-point motion amplitude and reminds us that an atomic system at very low temperature follows quantum-mechanical rules. A temperature-independent term ε is added to the expression of Eqn. 1 to account for the zero-point amplitudes of additional vibrations with very much higher frequencies or for disorder that does not depend on temperature (see Eqn. 4). The more-general theory behind the harmonic-oscillator example derives from normal-mode analysis for molecules in their crystal field. In its most concise representation, the theory takes the form of Eqn. 5.

$$\langle u^2 \rangle = \hbar/(2\mu\omega)\coth(\hbar\omega/2k_{\text{B}}T) \quad (1)$$

$$\langle u^2 \rangle = k_{\text{B}}T/(\omega^2\mu) \quad (2)$$

$$\langle u^2 \rangle = \hbar/(2\omega\mu) \quad (3)$$

$$\langle u^2 \rangle = \hbar/(2\mu\omega)\coth(\hbar\omega/2k_{\text{B}}T) + \varepsilon \quad (4)$$

$$\Sigma^x = \mathbf{A} \cdot \mathbf{g} \cdot \mathbf{V} \cdot \delta(\omega, T) \cdot \mathbf{V}' \cdot \mathbf{g}' \cdot \mathbf{A}' + \varepsilon^x \quad (5)$$

The experimentally observed ADPs are the 3×3 diagonal blocks of the matrix of mean-square displacements, Σ^x . The essential quantities defining the model of motion are $\delta(\omega, T)$ and ε^x . The former are mean-square displacements of normal modes, each of which depends on a vibration frequency ω , a reduced mass μ , and on temperature T , as shown in Eqn. 1. The quantities ε^x describe the temperature-independent part of the ADPs. The matrices \mathbf{V} , \mathbf{g} , and \mathbf{A} and their transposes \mathbf{V}' , \mathbf{g}' , and \mathbf{A}' represent the tricks of the trade. The eigenvector matrix \mathbf{V} transforms the normal-mode displacements into displacements along chemical coordinates, *e.g.*, translation along or libration about the crystallographic axes; \mathbf{g} accounts for the mass dependence of vibrational motions, and \mathbf{A} transforms to atomic mean-square displacements along the crystallographic axes, *i.e.*, to the ADPs and to the interatomic mean-square codisplacements hosted by the off-diagonal blocks of Σ^x . The latter contain the information on the correlations of atomic motions, but, unlike the former, they cannot be obtained from a diffraction experiment. This is one of the reasons preventing straightforward solution of Eqn. 5 by diagonalization of Σ^x . To compensate for this deficiency, ADPs measured at several temperatures are introduced, and the elements of $\delta(\omega, T)$, \mathbf{V} and ε^x determined by a least-squares procedure [23].

Models based on Eqn. 5 are dynamic in the sense that they refer directly to molecular motions, their vibrational frequencies, and force constants (see below), whereas the rigid-body models imply a purely kinematic parameterization of ADPs with no direct relationship to forces. In the following section, the new tool is used to test different models of motion and disorder, and to discriminate between them.

Obtaining Diffraction Evidence for D_{6h} Symmetry of Benzene is Possible! – In their report on ‘the crystal structure of deuterated benzene’, Jeffrey *et al.* remark that ‘benzene is a compound of central importance in organic chemistry. It is fitting

therefore that it should be repeatedly investigated by each scientific method whenever there is a significant advance with respect to the detail or accuracy that the method can offer' [17]. In an article entitled 'Why does Benzene Possess a D_{6h} Symmetry?', *Hiberty, Shaik*, and co-workers similarly state that 'benzene is not simply a molecule; it is a paradigm which has played a central role in the development of the theory of organic chemistry. . . As such, benzene deserves repeated reexamination whenever there is an advance in the probing power of our scientific methods. . . ' [24]. We reverse the motivation of *Jeffrey, Hiberty, Shaik* and their co-workers and take advantage of the well-established structure of benzene for testing the probing power of the ADP analysis described in the preceding section.

In analysing *Jeffrey's* two sets of ADPs pertaining to 15 and 123 K [17], we assume, as others did before, a rigid-body undergoing three low-frequency translations and three low-frequency librations. These motions account for the temperature dependence of the ADPs. We also allow for temperature-independent contributions ϵ^* to the ADPs of C- and D-atoms. The details of the calculations are given elsewhere [25].

The eye-catching result, given in *Table 1*, is the in-plane displacement ϵ_{ip} of the C-atom. It is 0.0007(1) Å², almost exactly the value *Ermer* expects for two superimposed *Kekulé* structures. Does this imply disordered cyclohexatriene molecules after all? There are two ways to argue this question: 1) if ϵ_{ip} signifies disorder, there is no room for zero-point motion, or 2) if ϵ_{ip} signifies zero-point motion, there is no room for disorder. Since the first option contradicts the laws of physics, ϵ_{ip} as well as all the other displacements listed in *Table 1* must be due to zero-point intramolecular motion, thus excluding disorder. At a quantitative level, this conclusion is confirmed by comparing the experimental values of ϵ^* for the C-atom with the ones calculated from an *ab initio* force field [26]. Agreement is unexpectedly perfect. An analogous comparison for the D-atom is not quite as good. The difference in the values along the C–D bond is probably due to anharmonic stretching motion, which is not included in the model. The difference in the out-of-plane displacement might indicate a constraint of this motion by the crystal lattice³).

Table 1. *Temperature-Independent Contributions ϵ to the ADPs of (D_6)Benzene along the C–D Bonds (ϵ_{bond}), in the Ring Plane (ϵ_{ip}) and out of the Ring Plane (ϵ_{oop})*

	C-Atom			D-Atom		
	$\epsilon_{bond} \cdot 10^4 [\text{Å}^2]$	$\epsilon_{ip} \cdot 10^4 [\text{Å}^2]$	$\epsilon_{oop} \cdot 10^4 [\text{Å}^2]$	$\epsilon_{bond} \cdot 10^4 [\text{Å}^2]$	$\epsilon_{ip} \cdot 10^4 [\text{Å}^2]$	$\epsilon_{oop} \cdot 10^4 [\text{Å}^2]$
Diffraction [25]	14(1)	7(1)	15(1)	52(1)	83(1)	110(2)
Force field [26]	13	8	16	44	89	133

We also tested the possibility of a large-amplitude '*Kekulé* vibration' by considering a corresponding ring-deformation coordinate in addition to the librational and

³) Translation (*T*) and libration amplitudes (*L*) at 15 and 123 K were calculated from *Eqn. 5* [25]. These amplitudes, especially those at 15 K, differ significantly from those obtained by *Jeffrey et al.* [17]. The latter are the result of *two* independent rigid-body fits (one each for the 15 and 123 K data) to the observed ADPs after an approximate correction for zero-point motion of the ADPs of the D-atoms. Although *Jeffrey's* two sets of *T* and *L* tensors parameterize the observed ADPs well, they lack the physical consistency between different temperatures implicit in the dynamic model presented in this work.

translational degrees of freedom. Various assumptions concerning the associated displacements of the D-atoms were made: 1) no displacement, 2) equal displacement vectors for C- and D-atoms in the same, or 3) in opposite directions. Corresponding least-squares optimizations lead to two stable solutions. The one with a low frequency ‘Kekulé vibration’ always shows much poorer agreement between observed and modelled ADPs than the alternative one, which is very similar to the simpler model given above.

Our analysis yields not only ϵ^* but also a dynamic model of the temperature-dependent part of the motion of C_6D_6 in terms of ω_D and V_D . The word ‘dynamic’ implies that ω_D and V_D , together with g_D , which depends on molecular geometry and atomic masses, define the force constants F according to Eqn. 6, where λ_D is a diagonal matrix whose elements are the squares of the frequencies ω_D of (D_6) benzene.

$$\lambda_D = g_D \cdot V_D \cdot F \cdot V_D' \cdot g_D' \quad (6)$$

As a further test of our method of analysis, the ADPs of C-atoms in the isotopomer C_6H_6 at 110 K were calculated from those of C_6D_6 measured at 15 and 123 K. Since F is independent of the isotopic composition of the molecule, Eqn. 6 with the subscripts D replaced by H also applies to C_6H_6 . Diagonalization of F yields the quantities V_H , ω_H , and thus $\delta_H(\omega_H, T)$, since g_H is known. This is the information needed to calculate the ADPs of C_6H_6 from Eqn. 5 [27]. The calculated elements U_{ij} of the three symmetry-independent C-atoms are compared in Table 2 with those determined from an X-ray diffraction experiment at ca. 110 K. The agreement between the two sets of U_{ij} further endorses our interpretation of the ADPs of benzene. An analogous comparison for the H- and D-atoms would not be meaningful because the displacement parameters of the H-atoms from X-ray diffraction are too inaccurate.

Table 2. ADPs of C_6H_6 at 110 K ($\cdot 10^4 \text{ \AA}^2$). Comparison of ADPs Measured at 110 K by X-Ray Diffraction (X-ray; s.u. $< 0.0001 \text{ \AA}^2$) with Those Calculated at the Same Temperature from ADPs of C_6D_6 Measured at 15 and 123 K by Neutron Diffraction (calc.; s.u. $0.0002\text{-}3 \text{ \AA}^2$).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1), X-ray	212	181	236	12	-12	-10
calc.	211	186	240	13	-7	-9
C(2), X-ray	197	237	221	13	29	-18
calc.	195	236	222	13	27	-17
C(3), X-ray	211	215	214	-21	10	20
calc.	206	215	217	-17	11	18

In summary, a dynamic interpretation of the ADPs of C_6D_6 and of C_6H_6 1) excludes an interpretation of the crystal structure of benzene in terms of two superimposed Kekulé structures, 2) excludes a low-frequency ‘Kekulé vibration’, and 3) confirms the regular hexagonal structure of benzene and provides a measure of its zero-point motion amplitudes. Although this is not a new result, the qualitative and excellent quantitative agreement between neutron- and X-ray-diffraction results measured at different temperatures and those from *ab initio* calculations suggests that investigating ADPs over a large temperature range provides a general tool for studying and distinguishing

motion and disorder in crystals. In the next section, we illustrate this conclusion with an example in which disorder dominates.

When Symmetry Hides Disorder. – The clathrate $C_{60} \cdot (HQ)_3$ (HQ = dihydroquinone = benzene-1,4-diol) was conceived, synthesized, and structurally characterized by Ermer [28]. The HQ molecules form a three-dimensional H-bonded network with large cages of symmetry D_{3d} that are occupied by C_{60} molecules (space group $R\bar{3}m$; Fig. 3). At room temperature, the crystal structure shows several kinds of disorder that have not been resolved in the initial structure determination. Additional diffraction experiments at 100, 200, 293, and 373 K revealed orientational disorder of the C_{60} molecules about the threefold axes [29]. The hydroxy H-atoms of HQ are disordered over two mirror-symmetric sites within bonding distance of their O-atoms (Fig. 3). The HQ molecule itself has crystallographic C_{2h} symmetry and very nearly D_{2h} symmetry with the crystallographic twofold axis bisecting the unsubstituted C–C bonds. This symmetry implies, among other things, equal O–C–C angles. A comparison with data from the *Cambridge Structural Database (CSD)* [30] shows that the two exocyclic O–C–C angles in ordered HQ molecules differ by *ca.* 2–6°, the one on the side of the hydroxy proton being larger (Fig. 4). The unusual geometry of HQ is the result of a more-subtle kind of disorder, albeit one that is not uncommon in crystal-structure analysis.

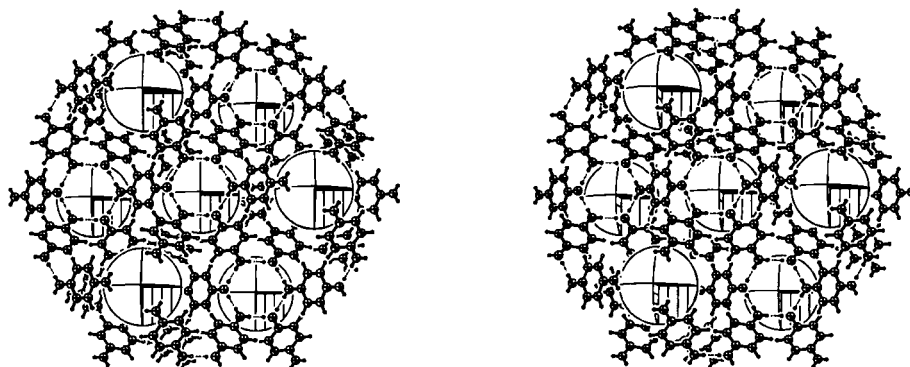


Fig. 3. Stereoscopic packing diagram of $C_{60} \cdot (HQ)_3$. Disordered C_{60} molecules are shown as big spheres.

The ADPs decrease in magnitude with decreasing temperature as expected. At first sight, they show no obvious anomalies (Fig. 5). If the rigid-body tensors \mathbf{L} and \mathbf{T} are considered instead and the six eigenvalues followed as a function of temperature, four of them extrapolate to zero at zero temperature, as expected. The remaining two, namely libration about the normal to the molecular plane (L_z) and translation in the molecular plane perpendicular to the C–O bonds (T_y), extrapolate to distinctly positive values indicative of disorder [29]. However, L_z and T_y also include the effects of motion. To distinguish between the two, the ADPs from the four temperatures were analyzed simultaneously by the approach illustrated above for benzene.

Experimental. – The temp.-dependent part of the model incorporates six coordinates, three translations (t_x , t_y , t_z) and three librations (l_x , l_y , l_z). The working coordinate system is right-handed Cartesian with the x -axis

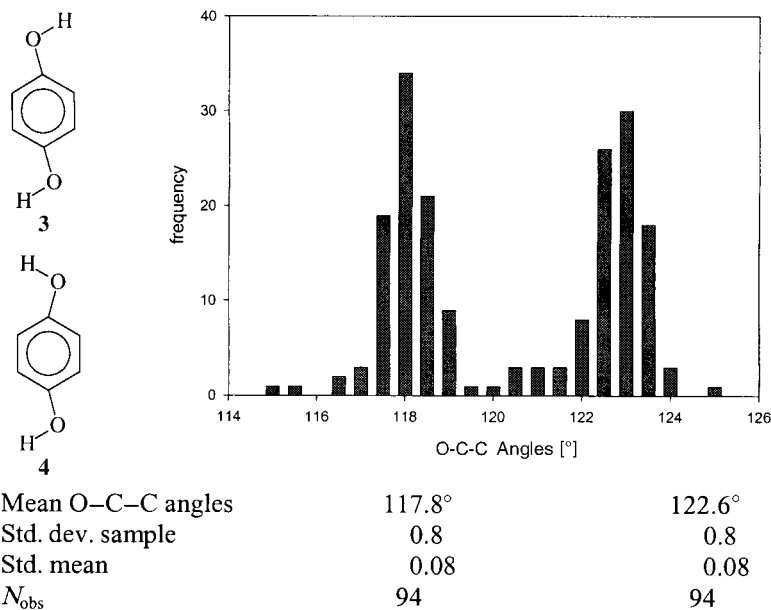


Fig. 4. Distribution of geminal O–C–C angles in hydroquinone molecules: 88 molecules show anti-conformation **3** and 6 show syn-conformation **4**

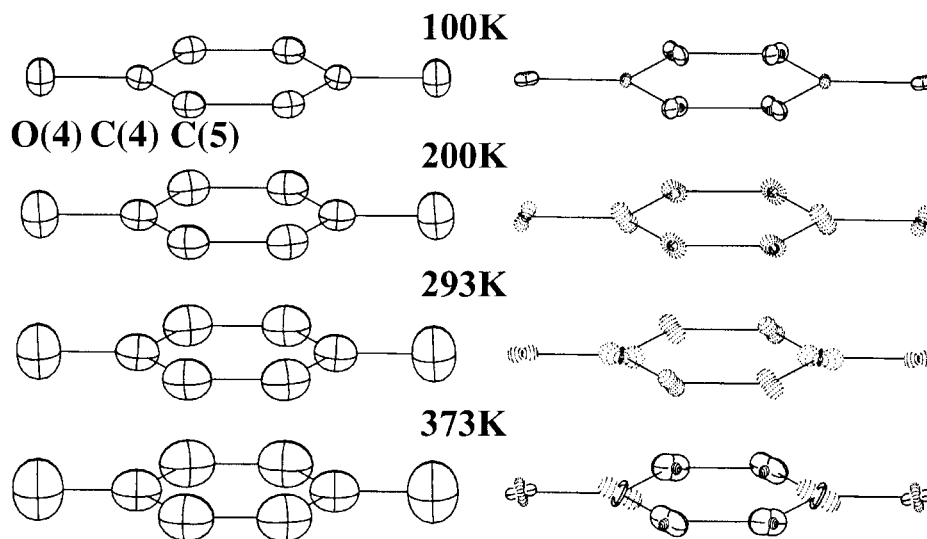


Fig. 5. ADPs of hydroquinone molecules as a function of temperature (left) and differences $4 \cdot [U_{obs} - U_{calc}]^{1/2}$ (right; positive differences: solid shapes; negative differences: dotted shapes; PEANUT plot [35])

along the C–O bond direction and the y-axis in the molecular plane, coincident with the two-fold axis. The origin is at the molecular centre of mass. Three temperature-independent ϵ -tensors with local coordinate systems were also included, one for the O-atoms, one for the C-atoms bonded to O-atoms, and one for the

remaining C-atoms. The local x -axes point along the C–O and C–H bonds, respectively, the local y -axes are perpendicular to the x s and in the molecular plane, the z -axes complete a right-handed Cartesian coordinate system. H-Atoms, for which anisotropic displacements are not available, were included only in the calculation of the molecular mass and of the inertial tensors [23]. The agreement factor, $[\Sigma w(U_{\text{obs}} - U_{\text{calc}})^2 / \Sigma w U_{\text{obs}}^2]^{1/2}$ is 0.023. The goodness-of-fit ($Gof = [\Sigma w(U_{\text{obs}} - U_{\text{calc}})^2 / (n_{\text{obs}} - n_{\text{par}})]^{1/2}$) is 4.3 for 22 parameters and 56 independent observations. The weighting factor w is $1/\sigma^2(U_{\text{obs}})$. The exper. standard uncertainties of the ADPs are *ca.* 0.0002 \AA^2 at all temp. [29]. The average difference $(U_{\text{obs}} - U_{\text{calc}})$ is *ca.* 0.0004 \AA^2 . Fig. 5 shows a comparison between $U_{\text{obs}}^{1/2}$ and the difference tensors $(U_{\text{obs}} - U_{\text{calc}})^{1/2}$ at the four temp. To be visible, the difference tensors are represented at 4 times their actual magnitude. Fig. 5 and the numbers show that the model accounts well for the observations.

The dynamic part of the model is pleasingly simple as it reflects the noncrystallographic D_{2h} symmetry. There are three normal modes at $85(3)$, $59(1)$, and $96(3) \text{ cm}^{-1}$ corresponding very closely to librations l_x , l_y , and l_z about the molecular x -, y -, and z -axes. The corresponding force constants are 0.37, 0.72, and $2.3 \text{ mdyn \AA rad}^{-2}$. The l_x motion corresponds to teetering of the benzene ring on the surface of C_{60} at little cost in energy, as one would expect. The l_y and in particular the l_z motion strain the H-bonds and are more costly. The three translational normal modes are at $39(1)$, $62(1)$, and $64(2) \text{ cm}^{-1}$, corresponding very closely to translations t_x , t_y , and t_z along the molecular x -, y -, and z -axes. The corresponding force constants are 0.10, 0.26, and $0.28 \text{ mdyn \AA}^{-1}$. All six normal-mode frequencies are in the expected range between *ca.* 20 and *ca.* 100 cm^{-1} .

As in the case of benzene, the temperature-independent mean-square amplitudes ε are the result of primary interest (Table 3). The ε_{22} values of O(4), C(4), and C(5) are highly significant, they account for a large percentage of the observed ADPs (73% for O(4) and 65% for C(4) at 100 K). Other ε values are smaller but still positive, whereas some are slightly negative. The meaning of these numbers is gauged with respect to two criteria: 1) negative residuals ε are physically meaningless and indicate inaccurate ADPs or an inadequate model of motion. Some systematic error in the ADPs is expected because the diffraction data were refined with standard, spherical-atomic-form factors that do not account for deformation of atomic electron densities due to

Table 3. Temperature-Independent Portion of the ADPs of C- and O-Atoms in the HQ Molecule (X-ray), Zero-Point-Motion Amplitudes Calculated ab initio (Z.p. motion), Difference between Temperature-Independent Portion of the ADPs and Zero-Point Motion in Units of s.u. of the Former (Δ/σ , dimensionless), and Temperature-Independent Portion of the ADPs Calculated from a Disorder Model (see text)

	$\varepsilon_{11} \cdot 10^4 [\text{\AA}^2]$	$\varepsilon_{22} \cdot 10^4 [\text{\AA}^2]$	$\varepsilon_{33} \cdot 10^4 [\text{\AA}^2]$	$\varepsilon_{12} \cdot 10^4 [\text{\AA}^2]$	$\varepsilon_{13} \cdot 10^4 [\text{\AA}^2]$	$\varepsilon_{23} \cdot 10^4 [\text{\AA}^2]$
O(4): X-ray	-4(3)	297(5)	59(5)	0	-8(3)	0
Z.p. motion	13	14	32	0	0	0
Δ/σ	-5.7	56.6	5.4	0	-2.7	0
Disorder model	-	297	-	-	-	-
C(4): X-ray	-6(4)	127(3)	9(6)	0	-6(3)	0
Z.p. motion	12	12	22	0	0	0
Δ/σ	-4.5	38.3	-2.2	0	-2.0	0
Disorder model	-	131	-	-	-	-
C(5): X-ray	34(3)	93(3)	19(4)	18(2)	4(2)	4(3)
Z.p. motion	13	14	26	2	0	0
Δ/σ	7.0	26.3	-1.8	8.0	2.0	1.3
Disorder model	31	100	-	18	-	-

chemical bonding [31]. 2) Comparison of the ε values with the amplitudes of intramolecular zero-point motion provides a second test. These quantities were calculated at 100 and 373 K from an *ab initio* force field determined by density-functional methods (*Table 3* lists only the values at 100 K; the ones at 373 K are insignificantly different) [32]. The difference between the zero-point-motion amplitudes, which are similar in magnitude to those of benzene, and the negative ε_{11} and ε_{13} components of C(4) and O(4) provide a more-conservative assessment of the errors in the ADPs. These reservations notwithstanding, six ε values clearly exceed the values due to zero-point motion and are highly significant in terms of their standard uncertainties: ε_{22} of O(4), C(4), and C(5), ε_{11} and ε_{12} of C(5), and ε_{33} of O(4). They encrypt information on disorder.

The in-plane components ε_{11} , ε_{22} , and ε_{12} show a distinctive pattern: the maximum displacements are tangential to the benzene ring or nearly so (*Fig. 6*). This arrangement is suggestive of an in-plane orientational disorder about the z -axis. The slight tilt

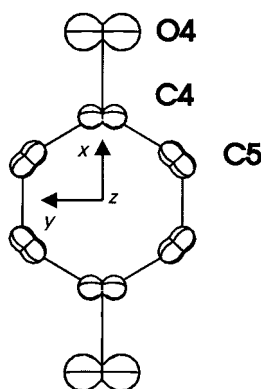
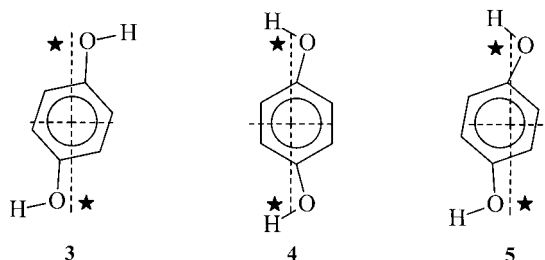


Fig. 6. Temperature-independent part ε of the ADPs. The (nearly) tangential orientation of the rms-displacement surfaces relative to the benzene ring indicates orientational disorder about the z -axis. The tilt of the rms-displacement surface of C(5) towards the y -axis indicates an additional displacive disorder along the y -axis. A crystallographic two-fold axis coincides with the y -axis, a mirror plane with the xz plane (PEANUT plot [35]).

of the root-mean-square surface of C(5) away from the tangential orientation towards the y -axis suggests additional disorder, namely displacement along the y -axis. These findings correspond to those suspected from the temperature evolution of L_z and T_y (see above). The degree of disorder, as estimated from the in-plane amplitudes of C(4) and C(5), amounts to a mean-square displacement along y of $0.0045(1) \text{ \AA}^2$ and a mean-square rotation of $0.0042(1) \text{ rad}^2$ (13.8 deg^2). The in-plane displacement of O(4) expected from this disorder is $0.0045(6) \text{ \AA}^2 + 0.0042 \text{ rad}^2 \cdot (2.8 \text{ \AA})^2 = 0.0374 \text{ \AA}^2$ (2.8 \AA is the distance of O(4) from the origin). The value derived from the observed ADPs is much smaller, $0.0297(5) \text{ \AA}^2$ (*Table 3*).

The observations on the unusual temperature dependence of the ADPs of HQ, on the apparent discrepancy between ε_{22} of C(4), and C(5) and ε_{22} of O(4), on the unusual geometry of HQ in $C_{60} \cdot \text{HQ}_3$, and on the normal geometry of the HQ molecule from

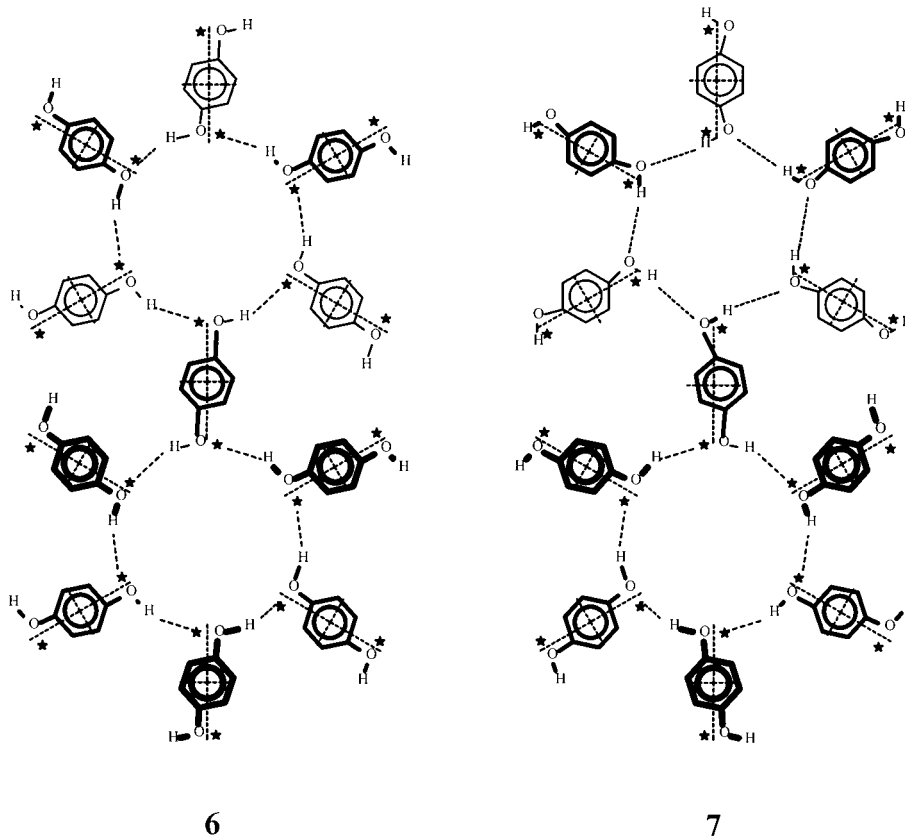
the *CSD* may now be assembled into a model of disorder of the HQ molecules including the hydroxy protons. The HQ molecules assume two conformations, *anti* (see **3**) and *syn* (see **4**), which differ in energy by only *ca.* 0.5 kJ mol⁻¹ [33]. The O–C–C angles on the side of the hydroxy protons exceed their geminal partners by *ca.* 5° as found in the *CSD*. The O-atoms O(4) are displaced from the local, crystallographic mirror plane along the *y*-axis by $\pm 0.172(2)$ Å as indicated by the symbols O or ★. The benzene rings connect pairs of O-positions in different ways (see **3–5**). The three arrangements imply a rotation of the benzene ring by 4.8° for **3**, a shift of the benzene ring by 0.11 Å for **4**, and a rotation of 3.5° coupled with a shift of 0.06 Å for **5**. In the simplest model, occupations of **3**, **4**, and **5** are 0.67, 0.33, and < 0.01, respectively. The resulting ϵ values are given in *Table 3* ('disorder model'). They agree well with the ϵ values derived from the experimental ADPs ('X-ray').



The O-atoms and H-bonds in the structure form six-membered rings with HQ molecules alternately above and below the rings (thick and thin lines in **6** and **7**). The C₆₀ molecules are embedded in the resulting cavities (*Fig. 3*). H-Bonds within the rings, which are separated from each other by HQ molecules, must be largely homodromic as shown in **6** and **7** [34]. There are two possible patterns; in one of them, the H-bonds point away from the local mirror plane (**6**, top), in the other they cross it (**7**, top). To ensure the connection between the two different patterns, an intermediary is required. An HQ molecule with the orientation shown in **5** takes on this role, as illustrated in the center of **7**. A very small concentration of **5** is sufficient to equalize the populations of the two H-bond arrangements and of the two O-sites (O and ★) and, thus, to explain the observed disorder of the HQ molecules and the hydroxy protons.

Summary and Discussion. – A model of the temperature dependence of atomic displacement parameters (ADPs) is described that discriminates between the static and dynamic displacements of atoms from their average positions in the crystal. The approach is generally applicable as it is based on a physical model of the dependence of ADPs on temperature. The results presented here illustrate the potential of such analyses in revealing new information on crystal structures that is not obtainable from a classical structure analysis at a single temperature.

In a case study performed on (D₆)benzene and benzene, the zero-point-motion amplitudes of the deuterated molecule and the isotope effects on the molecular librations and translations were determined. This study also demonstrates that the diffraction data cannot be interpreted in terms of a superposition of two *Kekulé* structures but require a D_{6h}-symmetric structure of the benzene molecule.



The same analysis applied to a hydroquinone (HQ) clathrate, $C_{60} \cdot (HQ)_3$, uncovers significant disorder of the HQ molecule. The ADPs include a large temperature-independent portion, implying displacements of the atoms from their mean position by 0.1–0.2 Å. They are the key for interpreting the average D_{2h} symmetry of the HQ molecule in terms of orientational and positional disorder. The resulting model of disorder requires unequal O–C–C bond angles, in agreement with the distribution of geminal O–C–C bond angles found in the *Cambridge Structure Database* for HQ molecules with symmetry 1 and $\bar{1}$.

The experiments required for this kind of structure analysis are straightforward: several conventional crystal-structure determinations over as large a temperature range as possible, preferably between *ca.* 10 K and the melting point of the substance under investigation. With *CCD* detectors and modern cryo-techniques using a free-flowing stream of cold helium, the necessary multi-temperature diffraction data may now be collected in a matter of a day or two. These technological advances together with specially developed software⁴⁾ establish ADP analysis as a new tool for the study of the structure and dynamics of molecules in crystals.

⁴⁾ The computer programs for analyzing ADPs are available from the authors on request.

We thank Dr. Jürg Hauser for help with the *Cambridge Structural Database* and *Therese Lüthi Nyffeler* for calculations.

REFERENCES

- [1] S. Liu, Y.-J. Lu, M. M. Kappes, J. A. Ibers, *Science (Washington, D.C.)* **1991**, 254, 408.
- [2] H.-B. Bürgi, E. Blanc, D. Schwarzenbach, S. Liu, Y.-J. Lu, M. M. Kappes, J. A. Ibers, *Angew. Chem., Int. Ed.* **1992**, 31, 640; *Angew. Chem.* **1992**, 104, 667; W. I. F. David, R. M. Ibberson, T. J. S. Dennis, J. P. Hare, K. Prassides, *Europhys. Lett.* **1992**, 18, 219.
- [3] H. Irngartinger, N. Riegler, K.-D. Malsch, K.-A. Schneider, G. Maier, *Angew. Chem., Int. Ed.* **1980**, 19, 211.
- [4] L. T. J. Delbaere, M. N. G. James, N. Nakamura, S. Masamune, *J. Am. Chem., Soc.* **1975**, 97, 1973.
- [5] H. Irngartinger, H. Rodewald, *Angew. Chem., Int. Ed.* **1974**, 13, 740.
- [6] H. Irngartinger, M. Nixdorf, *Angew. Chem., Int. Ed.* **1983**, 22, 403.
- [7] J. D. Dunitz, C. Krüger, H. Irngartinger, E. F. Maverick, Y. Wang, M. Nixdorf, *Angew. Chem., Int. Ed.* **1988**, 27, 387; H. Irngartinger, M. Nixdorf, N. H. Riegler, A. Krebs, H. Kimling, G. Maier, K.-D. Malsch, K.-A. Schneider, J. Pocklington, *Chem. Ber.* **1988**, 121, 673; H. Irngartinger, M. Nixdorf, *Chem. Ber.* **1988**, 121, 679.
- [8] J. Bregman, F. L. Hirshfeld, D. Rabinovich, G. M. J. Schmidt, *Acta Crystallogr.* **1965**, 19, 227.
- [9] S. Gorter, E. Rutten-Keulemans, M. Krever, C. Romers, D. W. J. Cruickshank, *Acta Crystallogr., Sect. B* **1995**, 51, 1036.
- [10] O. Ermer, *Angew. Chem., Int. Ed.* **1987**, 26, 782; *Angew. Chem.* **1987**, 99, 791.
- [11] J. Gauss, J. F. Stanton, *J. Phys. Chem. A* **2000**, 104, 2865.
- [12] S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty, *Chem. Rev.* **2001**, 101, 1501.
- [13] J. S. Siegel, *Angew. Chem., Int. Ed.* **1994**, 33, 1721; H.-B. Bürgi, K. K. Baldrige, K. Hardcastle, N. L. Frank, P. Gantzel, J. S. Siegel, J. Ziller, *Angew. Chem., Int. Ed.* **1995**, 34, 1454.
- [14] S. G. Brush, *Stud. Hist. Phil. Sci.* **1999**, 30, 21; *Stud. Hist. Phil. Sci.* **1999**, 30, 263.
- [15] K. Lonsdale, *Trans. Faraday Soc.* **1929**, 25, 352; *Proc. R. Soc. Lond., Sect. A* **1929**, 123, 494.
- [16] E. G. Cox, J. A. S. Smith, *Nature (London)* **1954**, 173, 75.
- [17] G. A. Jeffrey, J. R. Ruble, R. K. Mullan, J. A. Pople, *Proc. R. Soc. Lond., Sect. A* **1987**, 414, 47.
- [18] H.-B. Bürgi, *Annu. Rev. Phys. Chem.* **2000**, 51, 275.
- [19] V. Schomaker, K. N. Trueblood, *Acta Crystallogr., Sect. B* **1968**, 24, 63.
- [20] V. Schomaker, K. N. Trueblood, *Acta Crystallogr., Sect. B* **1998**, 54, 507.
- [21] M. Harel, F. L. Hirshfeld, *Acta Crystallogr., Sect. B* **1975**, 31, 162; F. L. Hirshfeld, *Acta Crystallogr., Sect. A* **1976**, 32, 239.
- [22] J. D. Dunitz, V. Schomaker, K. N. Trueblood, *J. Phys. Chem.* **1988**, 92, 856; J. Dunitz, E. F. Maverick, K. N. Trueblood, *Angew. Chem., Int. Ed.* **1988**, 100, 910; *Angew. Chem.* **1988**, 27, 880.
- [23] H.-B. Bürgi, S. C. Capelli, *Acta Crystallogr., Sect. A* **2000**, 56, 403; H. B. Bürgi, M. Förtsch, *J. Mol. Struct.* **1999**, 485–486, 457.
- [24] P. C. Hiberty, D. Danovich, A. Shurki, S. Shaik, *J. Am. Chem. Soc.* **1995**, 117, 7760.
- [25] S. C. Capelli, M. Förtsch, H.-B. Bürgi, *Acta Crystallogr., Sect. A* **2000**, 56, 413.
- [26] L. Goodman, A. G. Ozkabak, S. N. Thakur, *J. Phys. Chem.* **1991**, 95, 9044.
- [27] H.-B. Bürgi, S. C. Capelli, A. E. Goeta, J. A. K. Howard, M. A. Spackman, D. S. Yufit, *Chem.–Eur. J.* **2002**, 8, 3512.
- [28] O. Ermer, *Helv. Chim. Acta* **1991**, 74, 1339.
- [29] E. Blanc, R. Restori, D. Schwarzenbach, H.-B. Bürgi, M. Förtsch, P. Venugopalan, O. Ermer, *Acta Crystallogr., Sect. B* **2000**, 56, 1003.
- [30] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, 58, 380.
- [31] C. P. Brock, J. D. Dunitz, F. L. Hirshfeld, *Acta Crystallogr., Sect. B* **1991**, 47, 789; V. Pichon-Pesme, C. Lecomte, H. Lachekar, *J. Phys. Chem.* **1995**, 99, 6242.
- [32] M. Nonella, *J. Phys. Chem.* **1997**, 101, 1235.
- [33] K. Kim, K. D. Jordan, *Chem. Phys. Lett.* **1995**, 241, 39.
- [34] G. A. Jeffrey, W. Saenger, 'Hydrogen Bonding in Biological Structures', 2nd edn., Springer-Verlag, Berlin-Heidelberg, 1994.
- [35] W. Hummel, J. Hauser, H.-B. Bürgi, *J. Mol. Graph.* **1990**, 8, 214.

Received March 14, 2003