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A Model for the Hydrogen-Bond-Length Probability Distributions in the Crystal Structures of Small-Molecule Components of the Nucleic Acids

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Abstract

The probability distributions of the N—H...O=C and O—H...O=C hydrogen-bond lengths observed in the crystal structures of the purines, pyrimidines, nucleosides and nucleotides have been fitted to a one-dimensional hydrogen-bond potential-energy function. In order to obtain a quantitative correspondence between the experimental and theoretical distributions, it is necessary to include with the usual hydrogen-bond-type potential-energy function, an effective crystal-packing force and two thermodynamical parameters of the crystal lattice, the Debye temperature and the Gruneisen constant.

Introduction

The statistical analysis of results of crystal structure determinations has had some notable successes. Examples are the exploration of the permitted regions of polypeptide chain conformations by Ramachandran & Sasisekharan (1968) and the determination of the permitted ring conformations and glycosidic torsion angles in the components of the nucleic acids by Altona & Sundaralingam (1972). Over the past five years, a number of statistical studies have been made of the hydrogen-bond geometry observed in the crystal structures of small biological molecules. These studies have been made possible by access to crystal structural data through the computer-readable Cambridge Structural Database (Allen, Kennard & Taylor, 1983).

Taylor, Kennard & Versichel (1983, 1984*a,b*) studied the geometry of 1509 N—H...O=C and N⁺—H...O⁻—C bonds in a variety of compounds.

Ceccarelli, Jeffrey & Taylor (1981) examined the O—H...O bonds in the pyranose and pyranoside sugars using neutron diffraction data. A similar study was made by Jeffrey & Maluszynska (1982) of neutron diffraction analyses of amino acids. The analyses have been extended to the small-molecule components of nucleic acids, nucleosides and nucleotides, and purines and pyrimidines by Jeffrey, Maluszynska & Mitra (1985) and Jeffrey & Maluszynska (1986). The following general observations were made from these studies.

(i) Hydrogen-bond lengths are group-pair properties, rather than atom-pair properties. Based on the observed hydrogen-bond lengths, acceptor and donor groups can be ordered according to the strengths of the hydrogen bonds that they form (Taylor, Kennard & Versichel, 1984*b*). In the nucleosides and nucleotides, for example, the hydrogen-bond strengths of the donor groups are P—OH > C—OH > >NH > O_wH > N(H)H, whereas for the acceptor groups, they are O=P > O_wH₂ > O=C > O(H)C > N << > O < (Jeffrey, Maluszynska & Mitra, 1985).

(ii) For any particular group pair, the observed hydrogen-bond lengths, *i.e.* H...A, have a distribution which is qualitatively 'an inverse' of a Morse type of hydrogen-bond potential-energy curve, *i.e.*, ρ_{exp} vs V_{hb} in Fig. 1.

In this paper, we seek to obtain a relationship between the bond-length probability distribution, ρ_{exp} , and an effective potential-energy relationship for the two-centered† N—H...O=C and O—H...O=C hydrogen bonds observed in the crystal structures of the

† A two-centered hydrogen bond is defined as a configuration in which there is only one electronegative acceptor atom within 3.0 Å from the H atom in the forward direction with respect to the covalent X—H bond, *i.e.*, with $D—H...A \geq 90^\circ$.

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small-molecule components of the nucleic acids, *i.e.* the purines, pyrimidines, nucleosides and nucleotides. We will show that the effective potential-energy curve which can reproduce the experimental hydrogen-bond-length distribution must be different from the Morse-type V_{hb} curve shown in Fig. 1. To reproduce the experimental distributions, additional terms are necessary to take into account the other intra- and intermolecular forces and the thermal motion of the atoms in the crystal. Such terms are specific to each crystal structure. Some hydrogen bonds may be compressed, while others are expanded with respect to the equilibrium lengths for a particular isolated hydrogen-bond donor/acceptor pair. A remarkable example of this is observed in the crystal structure of D-glucitol, where the O—H...O—H bonds form two infinite chains. In one the hydrogen-bond lengths are significantly shorter than average, 1.691 to 1.729 Å, while in the other they are longer, 1.914 to 2.218 Å (Park, Jeffrey & Hamilton, 1971).

In the distribution, ρ_{exp} , shown in Fig. 1, the averaged effect of many different, but related, crystal structures is observed. As we will show later, this averaged crystal field has an overall compression effect, such that the experimental distribution curves are compressed at distances longer than the most probable value, when compared with theoretical distributions obtained without taking into account the other forces in the crystal lattice and the thermal motion. The maxima of the bond-length distribution curves are also at different values than the minima of the hydrogen-bond atom-pair potential functions.*

*The suggestion that hydrogen-bond lengths in molecular crystals would be shortened owing to compression from the long-range attractive forces was made by Pedersen (1974).

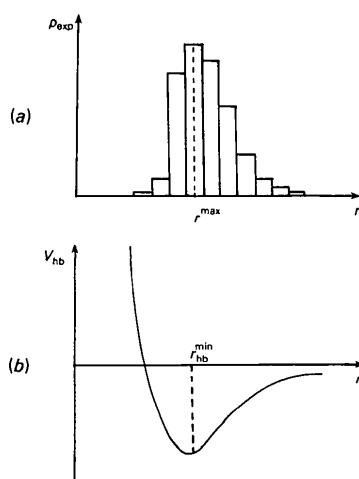


Fig. 1. Qualitative relationship between the hydrogen-bond-length distribution in the crystal state (a), and (b) the hydrogen-bond potential.

Experimental data

The experimental distribution curves for the N—H...O=C and O—H...O=C hydrogen-bond lengths were those reported in the survey of hydrogen bonds in the crystal structures of the nucleosides and nucleotides (Jeffrey, Maluszynska & Mitra, 1985) and barbiturates, purines and pyrimidines (Jeffrey & Maluszynska, 1986). This survey was based on the 1985 issue of the Cambridge Database. It would have been preferable to use only neutron diffraction data, since these have a smaller component of spread due to experimental errors, but there are insufficient neutron diffraction crystal structure analyses available for this class of compound.

In order to combine X-ray and neutron data and to reduce the X-ray bond-shortening errors, the covalent O—H and N—H bond lengths from the X-ray analyses were normalized to the standard internuclear distances of N—H = 1.03 and O—H = 0.97 Å (Jeffrey & Lewis, 1978; Taylor & Kennard, 1983). The experimental distributions, which contained 151 C=O...HN bonds and 47 C=O...HO bonds, were normalized to unity at the maximum.

Theoretical model

The model for the experimental system is an idealized ensemble of two-center hydrogen bonds located in an isotropic crystalline lattice. We assume that the hydrogen-bond-length distributions, $\rho(r, T)$, are determined by the Helmholtz free-energy function, A , which depends on the distance between the donor and the acceptor group, r , and on the temperature, T :

$$\rho(r, T) = \exp[-\Delta A(r, T)/kT] \quad (1)$$

where

$$\Delta A(r, T) = A(r, T) - A(r^{\text{min}}, T) \quad (2)$$

and

$$A(r, T) = V_{\text{eff}}(r, T) - TS(r, T). \quad (3)$$

V_{eff} is an effective interatomic potential between the interacting groups, and r^{min} is the distance at which the free energy attains its minimum.

In our first attempt to reproduce the experimental distribution, we used for $\Delta A(r, T)$, the (6-12) Lennard-Jones-type hydrogen-bond potential function, ΔV_{hb} , of Lifson, Hagler & Dauber (1979) and Dauber & Hagler (1980):

$$V_{\text{hb}} = \sum_A^{\text{acceptor}} \sum_D^{\text{donor}} \frac{q_A q_D}{r_{AD}} + \varepsilon_{AD} \left[-2 \left(\frac{r_{AD}^*}{r_{AD}} \right)^6 + \left(\frac{r_{AD}^*}{r_{AD}} \right)^{12} \right]. \quad (4)$$

This function is known to give reasonable hydrogen-bond energies when appropriately parameterized for the

Table 1. *Initial and optimized hydrogen-bond potential-energy-function parameters*

The charges have been fixed at their initial values (Lifson, Hagler & Dauber, 1979; Dauber & Hagler, 1980): $q_{\text{O}_{\text{keto}}} = -0.38$, $q_{\text{C}(\text{O}_{\text{keto}})} = 0.38$, $q_{\text{O}_{\text{hydroxy}}} = -0.38$, $q_{\text{H}(\text{O}_{\text{hydroxy}})} = 0.35$, $q_{\text{N}} = -0.28$, $q_{\text{H}(\text{N})} = 0.28$. Note the unrealistic values of the optimized ϵ parameters, obtained from fitting the theoretical to the experimental distribution (Figs. 2*a,b*), excluding thermodynamical lattice parameters.

r^* (Å)		O _{keto} ...N	O _{keto} ...O _{hydroxy}	C...N	C...O _{hydroxy}
	Initial	3.57	3.21	4.14	3.78
	Optimized	2.98	2.84	4.07	2.86
ϵ (kcal mol ⁻¹)†	Initial	-0.195	-0.228	-0.081	-0.094
	Optimized	-3.2	-14.8	-26.0	-27.5

† 1 kcal mol⁻¹ \equiv 4.187 kJ mol⁻¹.

partial charges on the acceptor and donor atoms, q_D and q_A , the Lennard-Jones constant ϵ_{AD} and the equilibrium distance r_{DA}^* (i.e. r_{CN}^* and r_{OO}^* for these bonds).

Using the initial parameters given in Table 1 for the N-H...O=C and O-H...O=C bonds, the theoretical bond-length distributions, ρ_{theo} , gave a very poor fit to the experimental results. The most important feature of this misfit was that the experimental distributions were much narrower and somewhat more symmetrical, as shown in Figs. 2*a,b*. A non-linear regression method *BMDP* (Dixon, 1985) was used to optimize the values

of ϵ_{DA} and r_{DA}^* in (4) to obtain the better fits shown by ρ_{opt} in Figs. 2*a,b*. The weighted residual sum of squares $\sum_i w_i (\rho_{\text{exp}}^i - \rho_{\text{theo}}^i)^2$ was minimized using the pseudo-Gauss-Newton algorithm (Dixon, 1985) with the weights $w_i = (\rho_{\text{exp}}^i)^{1/2}$. In this way more-populated regions of the experimental distribution contribute preferentially to the shape of the analytical function. The residual sum of squares was 0.02 and 0.16 for the N-H...O=C and O-H...O=C bonds, respectively. The initial and optimized parameters are given in Table 1. These are dimensionless quantities because the experimental distributions were normalized. Even though the Lennard-Jones parameters in (4) could be adjusted to make the maxima coincide and induce a better fit in the shape of the distribution curves, the required values of the ϵ parameters were highly unrealistic. The depth of the Lennard-Jones potential functions was 1–2 orders of magnitude greater than the initial value.

In order to check this result with another type of hydrogen-bond potential function, a bond-length distribution was calculated using the hydrogen-bond potential derived from the *ab-initio* molecular orbital calculation for the water dimer by Singh & Kollman (1985), and compared with the O_wH...O_w bond distribution reported from neutron diffraction data on hydrated crystals by Chiari & Ferraris (1982). This gave a similar result† to that from the semi-empirical function, as shown in Fig. 3.

A more sophisticated model was then derived for the effective interaction potential function in (3), which would account for a compression on the hydrogen bond by the other forces in the crystal lattice and for thermal lattice energy and entropy terms.

† It is worth noting that the theoretical O...O equilibrium distance for the hydrogen bond in the isolated water dimer at rest, 2.95–3.00 Å, is longer than the O_w...O_w distances of ~2.75 Å observed in the ices and crystalline hydrates, by the same order of magnitude as between the maxima of ρ_{theo} and ρ_{exp} in Fig. 2*a*.

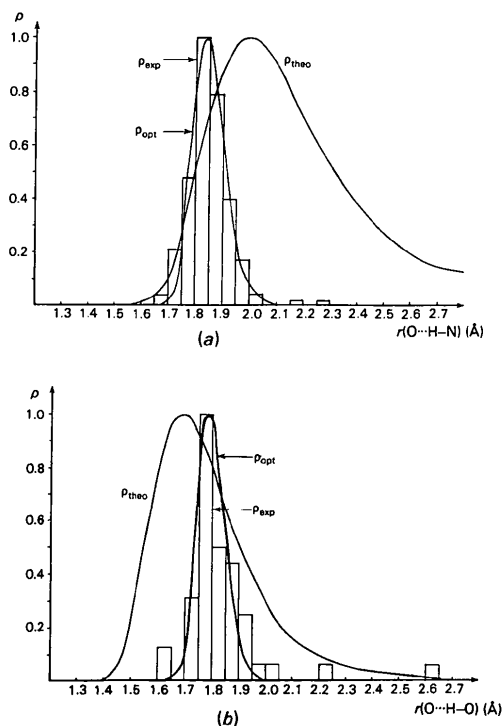


Fig. 2. Experimental (ρ_{exp}) and theoretical (ρ_{theo} , ρ_{opt}) hydrogen-bond-length distribution. (a) For C=O...H-N, (b) for C=O...H-O. ρ_{opt} determined with optimization of the (6–12) Lennard-Jones potential function.

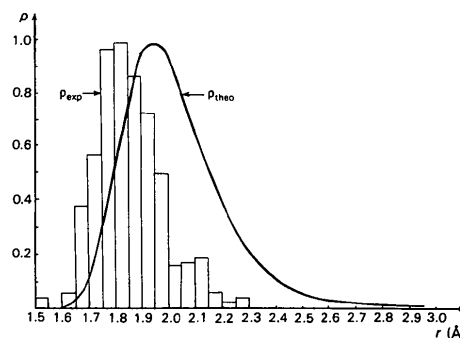


Fig. 3. Theoretical hydrogen-bond-length distribution, ρ_{theo} , calculated using the potential-energy function for the linear water dimer of Singh & Kollman (1985), with ρ_{exp} for O_wH...O_w distribution from neutron diffraction data on hydrated crystals (Chiari & Ferraris, 1982).

This model of a hydrogen bond in an isotropic crystal lattice is illustrated in Fig. 4. The effect of the crystal forces on the hydrogen bond is described by three constants: a mean compression force, f , the Debye temperature, Θ , and the Gruneisen constant, γ . The physical interpretation of the last two constants is described by Meyer (1975), Tabor (1980) and McQuarrie (1973).

The function $A(r, T)$ in (3) is then given by

$$A(r, T) = V_{\text{hb}}(r) + V_{\text{comp}}(r) + E_{\text{vib}}(r, T) - TS_{\text{vib}}(r, T) \quad (5)$$

where the first three terms correspond to V_{eff} in (3). $V_{\text{hb}}(r)$ is calculated, as before, using (4). $V_{\text{comp}}(r)$ is the simple compression potential:

$$V_{\text{comp}}(r) = f(r - r_{\text{hb}}^{\text{min}}) \quad (6)$$

where f is a constant representing the mean compression force of the crystal lattice and $r_{\text{hb}}^{\text{min}}$ is the equilibrium hydrogen-bond distance $\text{H}\cdots\text{O}$ in $V_{\text{hb}}(r)$.

$E_{\text{vib}}(r, T) - TS_{\text{vib}}(r, T)$ is the vibrational free energy $A_{\text{vib}}(r, T)$. (It is assumed that the total entropy can be approximated by the vibrational entropy.)

Within the limits of the Debye heat-capacity theory:

$$A_{\text{vib}}(r, T) \approx \frac{3}{8}R\Theta + 3RT\{\ln[1 - \exp(-\Theta/T)] - \frac{1}{3}D(\Theta/T)\} \quad (7)$$

where D is the Debye function, and Θ is the Debye temperature for the hydrogen-bond ensemble in the crystal lattice:

$$D(\Theta/T) = [3/(\Theta/T)^3] \int_0^{\Theta/T} [x^3/\exp(x) - 1] dx. \quad (8)$$

In this form, $A_{\text{vib}}(r, T)$ is not a function of a hydrogen-bond length, r . It has been shown, however (see McQuarrie, 1973), that normal-mode vibrational frequencies, ν_j , of atoms near their equilibrium positions are a function of the density or volume, V , of the system, and satisfy the relationship:

$$\partial \ln \nu_j / \partial \ln V = -\gamma \quad (9)$$

where γ is the Gruneisen constant. We assume that the same functional dependence describes the Debye frequency, $\nu_D = k\Theta/h$.

Under these circumstances, in the one-dimensional case shown in Fig. 4, the following dependence of the

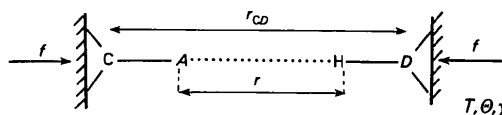


Fig. 4. One-dimensional model of the hydrogen bond in the solid state, perturbed by the compression force f . A and D denote the acceptor and donor atoms, respectively. The temperature, T , the Debye temperature, Θ , and the Gruneisen constant, γ , are the macroscopic thermodynamical parameters of the ensemble. In this study, $C-A$ is $\text{C}=\text{O} = 1.22 \text{ \AA}$, $D-H$ is $\text{O}-\text{H} = 0.97 \text{ \AA}$ and $\text{N}-\text{H} = 1.03 \text{ \AA}$.

Debye temperature on the hydrogen-bond length is satisfied (see Appendix):

$$\Theta = \Theta^{\text{min}} \left(1 - \gamma \frac{r - r_{\text{hb}}^{\text{min}}}{r_{\text{hb}}^{\text{min}} + r_{\text{CA}} + r_{\text{DH}}} \right) \quad (10)$$

where Θ^{min} is a reference Debye temperature in the hydrogen-bond energy minimum.

Substituting equation (10) into (7), we obtain $A_{\text{vib}}(r, T)$, and this allows us to determine the total free-energy function $A(r, T)$ (5) and consequently the probability distribution function $\rho(r, T)$ (1).

This probability distribution function contains too many parameters for an unconstrained optimization against the available experimental data. Therefore, we fixed the partial charges (q 's) and the Lennard-Jones potential depths (ϵ 's) at the realistic initial values given in Table 1. The other parameters (r 's, f , Θ^{min} and γ) were optimized with the aid of the non-linear regression procedure used previously.

As shown in Fig. 5, a close correspondence with the experimental bond-length distributions was obtained using the optimized parameters given in Table 2. The final residual sum of the squares was 0.016 and 0.139 for the $\text{N}-\text{H}\cdots\text{O}=\text{C}$ and $\text{O}-\text{H}\cdots\text{O}=\text{C}$ bonds, respectively.

Discussion

The contraction of the theoretical bond-length distribution at the larger values of r necessary to fit the experimental data is obtained by an increase of the r_{ON}^* and r_{OO}^* equilibrium distances by about 0.4 and 0.5 Å from the initial values. This can be interpreted as an increase in the effective van der Waals radii of the atoms adjacent to the H atom of the hydrogen bond. The r_{CN}^* and r_{CO}^* parameters are even larger than the initial values, by 1.3 and 1.5 Å respectively, but these

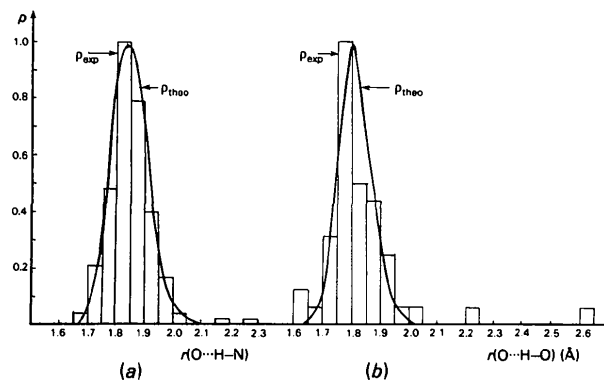


Fig. 5. Experimental (ρ_{exp}) and theoretical (ρ_{theo}) hydrogen-bond-length distributions. ρ_{theo} is obtained with optimization of the free-energy parameters. (a) For $\text{C}=\text{O}\cdots\text{H}-\text{N}$, (b) for $\text{C}=\text{O}\cdots\text{H}-\text{O}$. Number of experimental data are 151 and 47 for (a) and (b), respectively.

Table 2. *Optimized parameters used to obtain ρ_{opt} in Fig. 5*

(a) Optimized equilibrium distances in the Lennard-Jones interaction potential functions. The ϵ parameters and the charges were fixed at their initial values (see Table 1). Standard deviations are given in parentheses.

r_{AB}^* (Å)	O _{keto} ...N	O _{keto} ...O _{hydroxy}	C...N	C...O _{hydroxy}
	3.90 (0.41)	3.73 (0.25)	5.49 (3.96)	5.32 (1.47)

(b) Optimized thermodynamical crystal-state parameters. f is the mean crystal compression force; $k\Theta^{\min}$ is the Debye temperature in the hydrogen-bond energy minimum multiplied by the Boltzmann constant; γ is the Gruneisen constant. Standard deviations are given in parentheses.

	C=O...H-N	C=O...H-O
F (kcal mol ⁻¹ Å ⁻¹)	29.8 (15.4)	30.3 (5.3)
$k\Theta^{\min}$ (kcal mol ⁻¹)	0.50 (0.25)	0.52 (0.27)
γ	0.98 (0.87)	1.00 (0.33)

changes are not significant in relation to the standard deviations (see Table 2*a,b*). The experimental distributions do not provide any reliable information relating to these second-neighbour parameters, since the interactions between these more remote atom pairs contribute much less to the potential energy and have little effect on the shape of the hydrogen-bond-length distributions.

This result is consistent with the observation by Savage & Finney (1986) and Savage (1986) that the hydrogen-bonding patterns of the water structure in the crystals of macromolecules can be more readily interpreted by concentrating on the repulsion characteristic of the O atoms in order to define the excluded regions of configurational space.* In this study the effective van der Waals radii of the O atoms had also to be increased by about 0.2–0.3 Å beyond the traditionally accepted values.

The optimized values for the mean compression forces, f , are close to 30 kcal mol⁻¹ Å⁻¹. This corresponds to reasonable values of 3 to 6 kcal mol⁻¹ for the distortions of 0.1 to 0.2 Å from the most stable configurations in the vapour state. It would be more realistic to use a distribution function to describe a dispersion of the crystal-packing forces and to include nonlinearity of the hydrogen bonds in the statistical analysis. The latter correction would probably result in a decrease of the compression-force dispersion. However, this would require additional optimizations and the present experimental data do not justify this additional complexity.

The model correctly predicts the order of magnitude for the Debye temperature. The optimal $k\Theta^{\min}$ parameter is equal to about 0.5 kcal mol⁻¹ (Table 2). This is a

reasonable value when compared with $kT = 0.582$ kcal mol⁻¹.

The Gruneisen constants are close to 1.0 (Table 2) with large standard deviations, 0.87 and 0.33 for the C=O...H-N and C=O...H-O hydrogen-bond systems, respectively. The Gruneisen constant cannot be well refined using the present set of data. This constant mainly determines the temperature-dependent properties of the solids (e.g. thermal expansion coefficient), whereas our experimental distributions are based almost entirely on the room-temperature X-ray and neutron data. When more precise temperature-dependent neutron diffraction data become available, this aspect of the model could be examined more critically.

This work was supported by the National Institutes of Health, grant No. GM-24526. BL wishes to acknowledge travel support from the Ministry of Science, Higher Education and Technology (Poland) within the project CPBP 01.06.

APPENDIX

Normal frequencies of vibration of the atoms near their equilibrium position are a function of volume, V , and satisfy the following relation [see McQuarrie (1973)]:

$$\partial \ln \nu_j / \partial \ln V = -\gamma. \quad (A1)$$

We assume that the same relation describes the Debye frequency, ν_D . In addition, in the one-dimensional case, the distance r_{CD} between the most separated heavy atoms in the hydrogen bridge (see Fig. 4) plays a role of volume. This leads to the relation:

$$\partial \ln \nu_D / \partial \ln r_{CD} = -\gamma. \quad (A2)$$

For small displacements, Δr , from the vapour-state equilibrium position, r_{hb}^{\min} , the relation (A2) takes the form:

$$(\Delta \nu_D / \nu_D^{\min}) / (\Delta r / r_{CD}) = -\gamma \quad (A3)$$

where $\Delta r = r - r_{hb}^{\min}$ and $\Delta \nu_D = \nu_D - \nu_D^{\min}$. r_{hb}^{\min} and ν_D^{\min} stand for the vapour-state equilibrium distance and the characteristic Debye frequency in this reference state, respectively.

Because $r_{CD} = r + r_{C-A} + r_{D-H}$, the relation (A3) can be written in the form

$$\nu_D = \nu_D^{\min} \left(1 - \gamma \frac{r - r_{hb}^{\min}}{r_{hb}^{\min} + r_{C-A} + r_{D-H}} \right). \quad (A4)$$

Finally, a similar relation is obtained for the Debye temperature $\Theta = h\nu_D/k$,

$$\Theta = \Theta^{\min} \left(1 - \gamma \frac{r - r_{hb}^{\min}}{r_{hb}^{\min} + r_{C-A} + r_{D-H}} \right). \quad (A5)$$

Θ^{\min} is a reference Debye temperature at the hydrogen-bond energy minimum, in a vapour reference state.

* Because the protein and nucleic acid crystals contain such a large proportion of 'unbound' water, it is debatable which hydrogen bonds should be regarded as being in a crystal lattice and which could be adequately represented by a liquid-phase potential-energy curve.

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SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.

Acta Cryst. (1988). **B44**, 198

The structure and absolute configuration of (+)-biperiden: a chiral ligand for the pirenzepine binding site.

Erratum. By PENELOPE W. CODDING, *Departments of Chemistry and Pharmacology and Therapeutics, University of Calgary, Calgary, Alberta T2N 1N4, Canada*

(Received 26 October 1987)

Abstract

According to the IUPAC sequence-rule preferences, the absolute configuration of (+)-biperiden at C(1) should be assigned (*R*)-configuration not the (*S*)-configuration reported

in the original manuscript [Coddling (1986). *Acta Cryst.* **B42**, 632–638].

All relevant information is given in the *Abstract*.

Acta Cryst. (1988). **B44**, 198

2,2,4,4-Tetramethyl-1,3-cyclobutanedione. Erratum. By CHARLES D. SHIRRELL and DONALD E. WILLIAMS.

Department of Chemistry, University of Louisville, Louisville, Kentucky 40208, USA

(Received 25 November 1987)

Abstract

There is a typographical error in the paper by Shirrell & Williams [*Acta Cryst.* (1974), **B30**, 245–246]. The correct

space group is *C2/m* and all calculations were performed in this space group.

All relevant information is given in the *Abstract*.

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