

effects. The Ce—P distances are only slightly shorter than the corresponding distances in $\text{La}_6\text{Ni}_6\text{P}_{17}$, which indicates that Ce is in its trivalent state.

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The O—H vs O...O Distance Correlation, the Geometric Isotope Effect in OHO Bonds, and Its Application to Symmetric Bonds

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On the basis of recent accurate crystal-structure data, the correlation between O—H and O...O distances and the geometric isotope effect in OHO bonds have been investigated. The average correlation curve of asymmetric bonds appears to coincide with that of symmetric bonds only at the shortest limit of O...O length, around 2.4 Å. On deuteration an expansion can be seen in the O...O distance range 2.44–2.64 Å, with a maximum value of 0.027 Å. Factors smearing the correlation are discussed. The equilibrium position of H in symmetric bonds is considered using the correlation curve of O—H vs O...O distance and the geometric isotope effect as an empirical basis, under the assumption that the potential curve can be expressed as the superposition of two asymmetric bonds. The isotope effect on the distance between the two equilibrium positions is discussed in connexion with an anomalous isotope effect on the transition temperature of hydrogen-bonded crystals which undergo ferro-, antiferroelectric, and other structural phase transitions.

Introduction

It is well known that there exist some correlations between hydrogen-bond parameters; as Nakamoto, Margoshes & Rundle (1955) have pointed out, the

O—H bond length decreases with increasing O...O distance (Iwasaki, Iwasaki & Saito, 1967; Hamilton & Ibers, 1968; Pimentel & McClellan, 1971; Speakman, 1972). However, it seems that the details of the correlation remain uncertain in the short and very short

regions of O...O length, especially with respect to the dependence on the O...O distance, surroundings and symmetry of the hydrogen-bond system.

The other important phenomenon for the understanding of the nature of hydrogen bonding is a geometric isotope effect. Since the studies by Ubbelohde and co-workers (Robertson & Ubbelohde, 1939; Ubbelohde, 1939; Ubbelohde & Woodward, 1942) it seems to have been established that an expansion of the hydrogen-bond length is observed when deuterium is substituted for hydrogen in crystals. However, there is still uncertainty about the following aspects: is the size of the geometric isotope effect a function of the hydrogen-bond length and how large is its maximum, and what are the factors influencing the isotope effect. This mainly seems to result from the fact that the magnitude of the effect is as small as $\sim 10^{-2}$ Å. Thus, the results obtained from indirect information of lattice-spacing measurement, which assumes that any changes from isotopic substitution are confined to the hydrogen-bond system, may not be regarded as the real effect with sufficient reliability. Even with recent direct structure analysis an accuracy of $\sim 10^{-3}$ Å in hydrogen-bond lengths is not always attained. However, since the accuracy of crystal structure determinations has greatly increased, particularly in the past ten years, several hundred accurate structures have been published, thus giving us the opportunity to reinvestigate the correlation between structural data in detail.

On the other hand, it is well known that some hydrogen-bonded crystals, which undergo ferro-, antiferroelectric, or other types of phase transition, exhibit an anomalous isotope effect. For example, in a series of KH_2PO_4 -type crystals, the transition temperature T_c rises by a maximum of about 100 K on deuteration. The role of the hydrogen bond in the phase transition and the origin of the isotope effect in these crystals seems to be not yet fully understood. The phase-transition mechanism and the isotope effect in hydrogen-bonded ferro-, antiferroelectrics and other materials are expected to be closely associated with the characteristics of the hydrogen bond. Obtaining further knowledge on the nature of the hydrogen bond seems indispensable for a deeper understanding of these problems in hydrogen-bonded crystals.

The purpose of this paper is to establish the correlation between the hydrogen-bond parameters and the geometric isotope effect, and to discuss the relation of the structural isotope effect on the symmetric hydrogen bond to the anomalous increase in T_c by using these correlation curves as an empirical basis (Ichikawa, 1976). Brown (1976) discussed the geometry of OHO bonds, mainly in the medium and long regions, in connexion with the bond valence. When this manuscript was almost completed the author became aware that Olovsson & Jönsson (1976) had

recently surveyed X-ray and neutron crystal structural data and referred to the correlation between hydrogen-bond parameters and the geometric isotope effect independently. Hence, the results obtained on the O—H vs O...O correlation and the geometric isotope effect are summarized in the discussion and their application is stressed.

Data collection

Crystal structure data obtained by X-ray and neutron diffraction have been taken from the literature. Some of the literature used was retrieved with the *TOOL-IR* system (Yamamoto, Negishi, Ushimaru, Tozawa, Okabe & Fujiwara, 1975). Hydrogen-bond parameters were recalculated with *UNICS* (1967) if they and their estimated standard deviations were not specified in the literature. The data were used for a discussion of correlations between hydrogen-bond parameters only if the e.s.d.'s of all the relevant lengths were equal to or less than 0.010 Å, the O...O distance was less than 3 Å, and the O—H...O angle larger than 150°. The data used consisted of 227 bonds and 79 compounds,* including the data of Brown (1976) and Olovsson & Jönsson (1976). Values not corrected for thermal motion were used. If two or more studies were made on the same compound, the data with the smaller e.s.d.'s were adopted.

For discussion of the geometric isotope effect, the threshold value of a combined standard deviation of 0.005 Å was taken; the combined standard deviation is defined as $\sigma = (\sigma_H^2 + \sigma_D^2)^{1/2}$, where σ_H and σ_D are the e.s.d.'s of O...O distances in the hydrogen and corresponding deuterium compound. The remaining data include those from X-ray as well as neutron diffraction. If both were available, both are listed,* but the data with the smallest e.s.d.'s are plotted (Fig. 2), as no systematic difference could be found within experimental error.

The symmetric hydrogen bond

For the following discussion, the term 'symmetric hydrogen bond' should first be defined because its implication seems equivocal in the literature, as pointed out by Olovsson & Jönsson (1976). As far as the author is aware one definition refers to the type of H atom potential curve: (i) a hydrogen bond is said to be symmetric when the potential is of single-minimum type

* A list of the compounds with their hydrogen-bond parameters and references has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33436 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

whether there is crystallographic equivalence between donor and acceptor atom or not. The second refers to crystallographic symmetry: (ii) a hydrogen bond is said to be symmetric if the donor and acceptor atom are crystallographically equivalent, regardless of the type of potential curve.

Speakman and co-workers (*e.g.* Shrivastava & Speakman, 1961; Speakman, 1972) classified acid salts of carboxylic acids using criterion (ii). Catti & Ferraris (1974, 1976) took a somewhat different position and introduced the word 'symmetry restricted' (SR) for (ii). In this paper the description 'symmetric' is confined to (ii), the terms 'single' or 'double minimum' being added if necessary to describe the bonding situation. It is possible to express all probable types of hydrogen bond by using these terms. The terms 'symmetric' and 'centred' proposed by Olovsson & Jönsson (1976) are mostly consistent with our standpoint if 'symmetric' is restricted within (ii), and 'centred' is replaced by 'single-minimum'.

Correlation between O—H vs O...O distance

The correlation diagram of O—H vs O...O distance is shown in Fig. 1.

Symmetric bond

Symmetric bonds are continuously distributed, at least up to about 2.6 Å. Though only one point can be found in the region between 2.468 Å (KH malonate) (Currie & Speakman, 1970) and 2.602 Å [$\text{NaH}_3(\text{SeO}_3)_2$] (Kaplan, Kay & Morosin, 1970), many more examples would be found if less accurate neutron data and a large amount of X-ray data were taken into consideration.

The shape of the H atom potential curve seems to vary continuously from single- to double-minimum type

with increasing O...O distance, retaining the symmetry requirement. This is supported by: (i) in the region less than 2.47 Å the conclusion drawn from a thermal ellipsoid analysis agrees with the theory that the curve is effectively of single-minimum type; (ii) for $\text{KH}_3(\text{SeO}_3)_2$ (2.566 Å), Lehmann & Larsen (1971) reached the conclusion that the disordered description is significantly better than the ordered, after performing least-squares refinement with two models, *i.e.* one that distributes the H atom statistically on two sides of a special position (disordered model) and one that locates it in a special position (ordered model); (iii) for $\text{NaH}_3(\text{SeO}_3)_2$ (2.602 Å), Kaplan, Kay & Morosin (1970) reported that the difference synthesis indicates disorder. It is worth mentioning that the O—H length refined with a disordered model falls on the correlation line of the asymmetric bonds. Because of the above situation regarding symmetric bonds it appears extremely difficult to distinguish between single and double minima for hydrogen-bond lengths around 2.5 Å.

Asymmetric bond

The average correlation curve does not jump discontinuously or approach very rapidly the 'symmetric' straight line at a particular O...O length, but appears to coincide with it at the shortest limit, near 2.4 Å.

The deviation of each point from the average correlation curve becomes large when the O...O distance is less than about 2.55 Å. In the longer-bond region more than 90% of the points are within 0.02 Å of the smooth curve, whereas in the shorter-bond region this figure is only 40%. This seems to indicate that the potential curve becomes flat when the O...O distance is shorter than 2.55 Å, and the equilibrium position of the H atom shifts from the average according to the characteristics of the differing environment of the hydrogen bond.

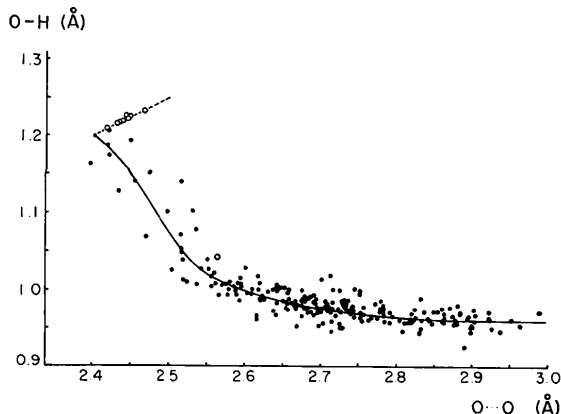


Fig. 1. A diagram of the correlation between O—H and O...O distances in OHO hydrogen bonds. Open circle: symmetric bond; filled circle: asymmetric bond.

Geometric isotope effect

The difference in the O...O distance caused by substituting deuterium for hydrogen, ΔR , is called the geometric isotope effect in this paper; $\Delta R = R(\text{O}\cdots\text{O})_{\text{D}} - R(\text{O}\cdots\text{O})_{\text{H}}$ where $R(\text{O}\cdots\text{O})_{\text{H}}$ and $R(\text{O}\cdots\text{O})_{\text{D}}$ denote the hydrogen and corresponding deuterium bond lengths. The $(\text{O}\cdots\text{O})_{\text{H}}$ and $(\text{O}\cdots\text{O})_{\text{D}}$ notation is used only if it is necessary to distinguish between them, otherwise O...O is used. ΔR is plotted against O...O distance in Fig. 2.

There exists a correlation between ΔR and $R(\text{O}\cdots\text{O})_{\text{H}}$: the positive isotope effect, *i.e.* expansion can be seen only in the O...O region of about 2.44–2.64 Å, with a maximum value of 0.027 Å. This corresponds to the correlation between the isotope ratio of antisymmetric OH stretching frequency $\nu_{\text{OH}}/\nu_{\text{OD}}$ and

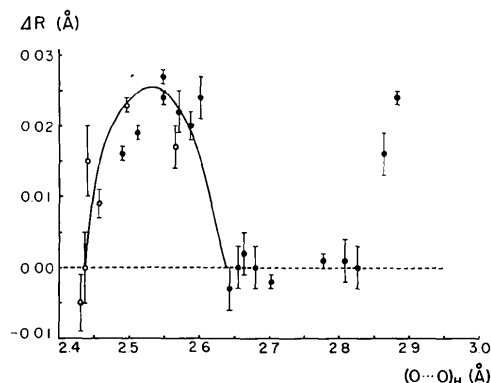


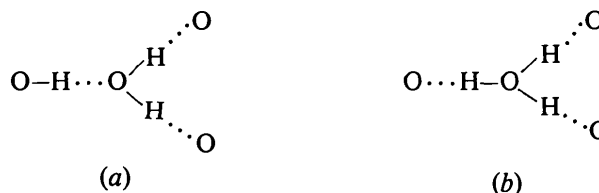
Fig. 2. The geometric isotope effect, ΔR , as a function of $(\text{O}\cdots\text{O})_{\text{H}}$ length.

$R(\text{O}\cdots\text{O})_{\text{H}}$ (Novak, 1974). Further definite conclusions cannot be drawn at present for lack of sufficient data.

It may be worth while to consider here what factors smear the correlation, since there seems to be room for argument as to whether a correlation between ΔR and $R(\text{O}\cdots\text{O})_{\text{H}}$ is present or not. Finholt & Williams (1973) state that no correlation seems to exist. Thomas (1972) and Olovsson & Jönsson (1976) considered that in a crystal with more than one species of hydrogen bond only short bonds (up to 2.6 Å) exhibit the genuine isotope effect and long bonds do not, since changes in the latter are exerted by the influence of the structural rearrangement induced by the genuine isotope effect on the short bonds.

The following may be pointed out as possible factors smearing the correlation. (i) Insufficient accuracy. The geometric isotope effect is of the order of $\sim 10^{-2}$ Å at most and it should be emphasized that only collection of accurate data revealed the correlation. (ii) Incomplete deuteration. Perfect deuteration cannot be achieved in spite of repeated recrystallization in D_2O and precautions to prevent H_2O contamination (Finholt & Williams, 1973). From the average of the real deuterium contents (0.899) in the crystals quoted in Table 1 as perfectly deuterated, which were obtained from least-squares refinement of the deuterium scattering amplitude for neutrons, deuterated crystals are considered to involve usually about 10% incomplete deuteration. (iii) Direct coupling of the geometric isotope effect of an individual bond in a crystal with two or more species of hydrogen bond. Deviation from the general trend of the isotope effect can be recognized in $\alpha\text{-(COOH)}_2 \cdot 2\text{H}_2\text{O}$ (Delaplane & Ibers, 1969; Sabine, Cox & Craven, 1969; Coppens & Sabine, 1969) and in crystalline $\text{H}_3\text{O}^+\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ (Lundgren & Williams, 1973; Finholt & Williams, 1973); in the former the two longer bonds as well as the short bond show a large positive effect, whereas in the latter three short bonds in the region expected to show a large isotope effect

exhibit only a much smaller effect. However, a common feature of the hydrogen-bond arrangement may be pointed out for the two cases. It may be denoted schematically for (a) $\alpha\text{-(COOH)}_2 \cdot 2\text{H}_2\text{O}$ and (b) $\text{H}_3\text{O}^+\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ as follows.



In the two cases three hydrogen bonds are directly coupled to each other through the central O, and each of them is crystallographically independent. This situation would seem to make it difficult to obtain the genuine isotope effect of the individual bond separately. We believe that for long bonds the geometric isotope effect is equally as genuine as for short bonds though, strictly speaking, the effect cannot be confined to the hydrogen-bond system and more or less necessarily leads to structural changes in its neighbourhood or throughout the unit cell.

Symmetric bond and phase transition

Let us consider the structure of a linear symmetric hydrogen bond on the basis of the assumption that the potential curve of the symmetric bond can be expressed as a superposition of the curves of two asymmetric bonds, and the correlation curve between O—H and O \cdots O distance can be used as an empirical basis for the equilibrium position of the H atom. This seems plausible since the symmetric bonds exist continuously at least up to about 2.6 Å and the values of O—H length refined with a disordered model agree with those of the asymmetric bond. Catti & Ferraris (1976) discussed the disordered nature of symmetric bonds in the very short region, which is compatible with the present assumption. Then the distance between the two equilibrium positions of the H atom, δ , is written as

$$\delta = R(\text{O}\cdots\text{O}) - 2R(\text{O}-\text{H}).$$

As shown in Fig. 3, δ increases, with a maximum slope around 2.48 Å, as the O \cdots O distance increases, and gradually approaches a straight line. It is noted here that δ does not mean immediately the distance between the two minima in a double-minimum potential well since the shape of the basic potential-energy surface and the vibrational level are not known from diffraction data alone.

If the O \cdots O distance expands by an amount ΔR according to the ΔR vs $R(\text{O}\cdots\text{O})$ correlation curve when a D atom is substituted for H, the O—D distance will be equal to the O—H value corresponding to the

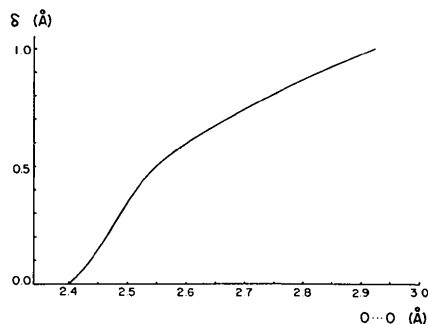


Fig. 3. The distance between two equilibrium positions in a symmetric hydrogen bond, δ , as a function of O...O length.

length $R(\text{O}\cdots\text{O})_{\text{H}} + \Delta R$ from the O—H *vs* $R(\text{O}\cdots\text{O})_{\text{H}}$ curve; $R(\text{O—D}) = R(\text{O—H}) - \Delta R(\text{O—H})$, where $\Delta R(\text{O—H})$ denotes a contraction of the O—H distance due to an expansion of $R(\text{O}\cdots\text{O})$ by ΔR . Then the distance between the two equilibrium positions of the corresponding D bond is expressed as

$$\begin{aligned}\delta_{\text{D}} &= R(\text{O}\cdots\text{O})_{\text{D}} - 2R(\text{O—D}) \\ &= \delta_{\text{H}} + 2\Delta R(\text{O—H}) + \Delta R,\end{aligned}$$

where the subscripts H and D are used only if it is necessary to distinguish between the H and D bond. This situation is illustrated in Fig. 4. The isotope effect on the distance between the two equilibrium positions $\delta_{\text{D}} - \delta_{\text{H}}$ consists of two terms: in the short-bond region where the O—H length varies rapidly with O...O distance, $2\Delta R(\text{O—H})$ contributes mainly to the total $\delta_{\text{D}} - \delta_{\text{H}}$ and amounts to about three times ΔR at maximum, whereas in the long-bond region, where O—H varies more slowly with O...O, ΔR is the more dominant. With increasing O...O, $\delta_{\text{D}} - \delta_{\text{H}}$ increases rapidly and reaches its maximum value around 2.49 Å and then decreases more slowly, as shown in Fig. 5.

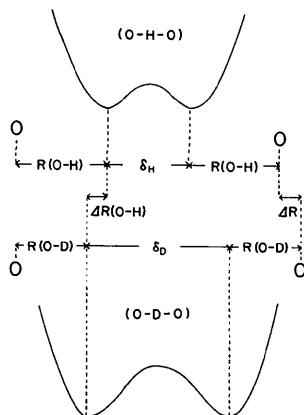


Fig. 4. Schematic illustration of the geometric isotope effect in a symmetric bond.

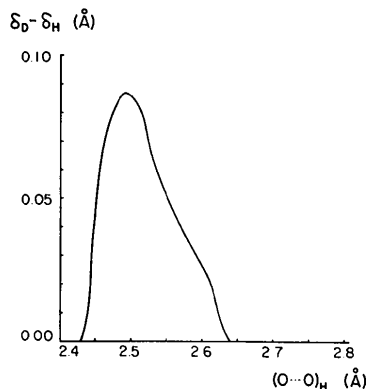


Fig. 5. The isotope effect on the distance between the two equilibrium positions in a symmetric bond, $\delta_{\text{D}} - \delta_{\text{H}}$, as a function of $(\text{O}\cdots\text{O})_{\text{H}}$ length.

The functional behaviour of δ_{H} and $\delta_{\text{D}} - \delta_{\text{H}}$ should not be regarded as being fully established at the present stage because it largely depends on the accuracy of the correlation curve of $R(\text{O—H})$ *vs* $R(\text{O}\cdots\text{O})$ and ΔR *vs* $R(\text{O}\cdots\text{O})$. However, it should be emphasized that if ΔR itself is small, $\delta_{\text{D}} - \delta_{\text{H}}$ induced by ΔR becomes four times as large as ΔR . The effect of ΔR seems to have been overlooked or underestimated so far (Samara, 1973).

The role of the hydrogen bond in hydrogen-bonded crystals which exhibit ferroelectric, antiferroelectric and other structural phase transitions seems closely associated with the characteristics of the hydrogen bond, *i.e.* those of the potential curve. Therefore, an anomalous isotope effect in physical quantities, such as the transition temperature T_c , is likely to be closely related to differences between the features of the potential curve of the hydrogen bond and that of the corresponding deuterium bond; it may be reflected in the magnitude of ΔR and $\delta_{\text{D}} - \delta_{\text{H}}$. A large shift of T_c may be expected when the crystal has a symmetric hydrogen bond in a paraelectric or high-temperature phase, and its O...O length is in a region of $\Delta R > 0$ and is longer than that expected for a single-minimum type bond. The relevant values of some ferro-, antiferroelectric, and other materials are listed in Table 1. The data are compatible with the above statement. ΔT_c is large when the hydrogen bond is symmetric and O...O is in the range of about 2.5–2.6 Å. ΔT_c is only about 10 K or negative when the O...O length is around 2.44 Å, even if symmetric, or when the hydrogen bond is asymmetric even if O...O is in a range of 2.5–2.6 Å. However, in order to confirm this relation, further examinations may be necessary both by structural and dielectric studies.

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Table 1. O...O distance in the paraelectric phase, Curie temperature, T_c , and its shift on deuteration, ΔT_c , in some crystals which exhibit ferro-, antiferroelectric, and other structural phase transitions

The O...O distance is the room-temperature value if not specified. F and AF denote ferro- and antiferroelectric respectively. The references to structural data are marked with an asterisk and dielectric data are quoted from *Landolt-Börnstein* (1969) if not mentioned expressly.

Compound	References	O...O (Å)	Type of bond	T_c (K)	ΔT_c (K)
NH ₄ H(ClCH ₂ COO) ₂	1,* 2	2.432 (5)	symmetric	120	11 F
TGS at 330 K	3*	2.443 (7)	symmetric	322	11 F
KH ₂ PO ₄	4*	2.496 (1)	symmetric	123	90 F
NH ₄ H ₂ PO ₄	5*	2.490 (1)	symmetric	148	94 AF
NH ₄ H ₂ AsO ₄	5*	2.512 (2)	symmetric	216	88 AF
NaH ₃ (SeO ₃) ₂	6*	2.556 (6)	asymmetric	194	75 F
		2.602 (9)	symmetric		
RbHSO ₄	7,* 8,	2.53 (1)	asymmetric	264	-11 F
	9	2.62 (1)	asymmetric		
NH ₄ HSO ₄	10,* 11	2.514 (6)	asymmetric	270	-8 F
		2.598 (5)	asymmetric		
KH ₃ (SeO ₃) ₂	11, 12*	2.566 (1)	symmetric	201	70

References: (1) Ichikawa (1972). (2) Chihara, Inaba, Nakamura & Yamamoto (1973). (3) Itoh & Mitsui (1973). (4) Nakano, Shiozaki & Nakamura (1973). (5) Khan & Baur (1973). (6) Kaplan, Kay & Morosin (1970). (7) Ashmore & Petch (1975). (8) Kasahara & Tatsuzaki (1975). (9) Kasahara (1976). (10) Nelmes (1971). (11) Subbarao (1973). (12) Lehmann & Larsen (1971).

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The Crystal Structure of Sodium Cyanide Dihydrate, NaCN·2H₂O

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The crystal structure of NaCN·2H₂O has been refined from X-ray data collected at room temperature ($22 \pm 2^\circ\text{C}$). It is monoclinic with $a = 6.622$ (3), $b = 10.561$ (4), $c = 6.064$ (3) Å, $\beta = 103.06$ (4)°, $Z = 4$, space group $P2_1/a$. Least-squares refinement of 1533 independent diffractometer data converged at a conventional R value of 0.056. The results are generally in agreement with those in a recent study at 150 K [Bats (1977). *Acta Cryst.* **B33**, 466–472] except that the CN group appears to be partially disordered at room temperature.

Introduction

Bats (1977) has reported the structure of NaCN·2H₂O using data collected at 150 K. His determination was undertaken, among other reasons, to look at the electron density in the CN ion. Prior to the report of his work we had undertaken a similar study at room temperature for the same reason. His study is more accurate than ours could possibly be since at the lower temperature there is less thermal motion, which improves the situation both directly and also indirectly by allowing meaningful data to be collected at larger Bragg angles. We did, however, find an apparent disorder in the CN group, a disorder that appears to be absent at the lower temperature. We shall discuss this aspect of our results in some detail.

Experimental

NaCN from Mallinkrodt was recrystallized from a 50% ethanol–water mixture. One of the large, thick plates so obtained was cut and ground to a sphere with a radius of 0.715 mm, which was used for data collection. It was necessary to coat the sphere with a layer of Apiezon L grease to prevent the loss of water on exposure to air.

Data were collected on a four-circle Hilger & Watts automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The unit-cell dimensions, determined from a least-squares fit of the Bragg angles of 12 reflections carefully measured on the diffractometer (θ between 16 and 26°) are: $a = 6.622$ (3), $b = 10.561$ (4), $c = 6.064$ (3) Å, $\beta = 103.06$ (4)° and $V = 413.1$ Å³. The space group, following Le Bihan (1958), is $P2_1/a$; for $Z = 4$ our calculated density, 1.367 g cm⁻³, agrees with her observed value, 1.361 g cm⁻³.

Intensity data for 1533 independent reflections were collected using a moving-crystal moving-counter scan with one hundred 0.01° steps in θ and ω for all reflections; step times were 1 s and background counts were 50 s at each end of the scan. Two check reflections were measured every 25 regular reflections; these check reflections increased by 10% over the course of the data collection, presumably owing to a long-term drift in the X-ray power supply; this was corrected for in the subsequent calculations. Extinction was present (see below). The calculated extinction corrections for the check reflections were 3.5% and 1.6% of the intensities. Thus, it would not appear that the variation in the check reflection intensities arose from a change in the extinction with time. To avoid coincidence losses in the counter, the high intensity reflections were measured using filters in the diffracted X-ray beam. For $0 < \theta \leq 10^\circ$, data were collected for