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Bond-Length Corrections for External and Internal Vibrations in Urea

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Abstract

Bond-length corrections for external and internal vibrations of the urea molecule were carried out at 293 and 123 K. The corrections for the external vibrations were performed by means of the rigid-body model after the vibration tensors of the internal vibrations had been subtracted from the observed vibration tensors. The corrections for the internal vibrations were calculated from the vibration and coupling tensors for urea which were recently determined by a spectroscopic analysis. If the external and internal vibrations in the crystal are not mixed, as is likely for the small urea molecule, the total correction can be calculated as the sum of the external and internal corrections. Since the internal vibrations contribute strongly to the vibrations of the H atoms, large total corrections for the N—H bonds are found; 0·030 and 0·027 Å for 293 K. The agreement of the corrected bond lengths for the C—N and N—H(1) bonds at 293 and 123 K is excellent (within 0·003 Å), for the N—H(2) bond (within 0·005 Å) and the C—O bond (within 0·010 Å) it is a little less satisfactory. The corrected N—H lengths are also in good agreement (within 0·003–0·005 Å) with those in the free ammonia molecule determined by gas electron diffraction and infrared spectroscopy. The correction with the rigid-body model alone, applied to the observed vibration tensors obtained from diffraction data, cannot be considered to be a satisfactory substitute for the correction obtained by the joint analysis. The riding model provides better corrections, but they are still too small for the N—H bonds. Most of the corrected bonds with terminal H atoms reported in the crystallographic literature were probably determined too short by about 0·01 Å or even more.

1. Introduction

It is well known that, for the calculation of a bond-length correction, dynamic models of motion are needed. A model which can be easily handled, and is most frequently used, is the model of rigid-body motion for (nearly) rigid molecules. Its exclusive use for calculating the correction, however, implies that the contributions from the internal modes of the molecules are neglected or, at best, are taken inappropriately into account. A better correction can be obtained when the internal modes of the molecules are known. Then the observed vibration tensors can be divided according to the contributions from the external and internal vibrations; the corrections can be calculated separately and finally added together. By comparison, such a procedure would make obvious to what extent the rigid-body model alone can also represent the contributions of the internal modes, and thus can lead to an acceptable correction. Since we have recently determined the internal vibrations of urea (Ishii & Scheringer, 1979) we can here apply such a procedure. For the vibration tensors of the atomic nuclei we use the parameters of Guth, Heger, Klein, Treutmann & Scheringer (1980) which were recently determined at 293 and 123 K by means of neutron diffraction.

In § 2 we discuss the separation of the bond-length correction according to the contributions from the external and internal vibrations. In the determination of the external vibrations considerable differences are observed, depending on whether or not the H atoms are included. This will be discussed in § 3. In § 4 we calculate the corrections for the external vibrations by means of the rigid-body model, and for the internal vibrations by means of the vibration and coupling tensors. In § 5 we calculate the values of the corrected bond lengths and compare them for two temperatures.

2. Corrections for external and internal vibrations

The external vibrations of the molecule will be determined by means of the rigid-body vibration tensors **TLS**; the tensors of the internal vibrations, $\mathbf{U}_{\rm int}$, are taken from the spectroscopic analysis of Ishii & Scheringer (1979). This procedure implies that a corresponding division of the vibration tensors into those for external and internal vibrations is possible and permitted. The lattice-dynamical assumptions for such a division were recently discussed (Scheringer & Fadini, 1979). The most important assumption is that the normal modes of the crystal can be separated according to external and internal modes. Then we

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obtain for the vibration and coupling tensors according to (2.2) of Scheringer (1972)

$$\mathbf{U}_r = \mathbf{U}_{r,\,\mathrm{ext}} + \mathbf{U}_{r,\,\mathrm{int}}, \quad \mathbf{U}_{rs} = \mathbf{U}_{rs,\,\mathrm{ext}} + \mathbf{U}_{rs,\,\mathrm{int}}. \quad (1)$$

If the above assumption does not hold for a large part of the lattice modes, *i.e.* if there are many mixed modes in the crystal, then the separation (1) can no longer be defined (in terms of lattice dynamics). The $\mathbf{U}_{\mathrm{int}}$ tensors, determined by spectroscopic methods, would no longer be representative for the crystal. As a rule, for smaller molecules, the frequencies of the external and internal modes are sufficiently split so that only a small part of the lattice modes is mixed. With urea this assumption appears to be justified, since the smallest observed internal-mode frequency (500 cm^{-1}) is high compared to the external-mode frequencies ($<$150 cm^{-1}). For transferring the spectroscopic results on isolated molecules to the crystal, we have to make two further assumptions [Scheringer & Fadini (1979), assumptions (2) and (3)], the validity of which we cannot examine for urea. The violation of these assumptions can lead to small errors in the $\mathbf{U}_{\mathrm{int}}$ tensors used for describing the crystal.

With metric tensor $\mathbf{g}$ and bond vector $\mathbf{d}$ between the mean positions of two atoms r and s, we have for the thermally corrected bond length

$$d_{\mathrm{corr}} = d + \frac{1}{2d}\,[\mathrm{trace}\,(\mathbf{A}_{rs}\mathbf{g}) - \mathbf{d}^T\mathbf{g}\mathbf{A}_{rs}\mathbf{g}\mathbf{d}/d^2], \quad (2)$$

where

$$\mathbf{A}_{rs} = \mathbf{U}_r + \mathbf{U}_s - \mathbf{U}_{rs} - \mathbf{U}_{sr}, \quad (3)$$

and $\mathbf{U}_{sr} = \mathbf{U}_{rs}^T$ [*cf.* Scheringer (1972), equations (3.1), (3.6) and (3.7)]. From (1) and (3) we obtain $\mathbf{A}_{rs} = \mathbf{A}_{rs,\,\mathrm{ext}} + \mathbf{A}_{rs,\,\mathrm{int}}$, and this, applied to (2), gives

$$d_{\mathrm{corr}} = d + \mathrm{corr}\,(\mathbf{A}_{rs,\,\mathrm{ext}}) + \mathrm{corr}\,(\mathbf{A}_{rs,\,\mathrm{int}}), \quad (4)$$

where corr stands for the correction term in (2). Thus, if we assume that the separation (1) holds, the correction can be separated accordingly. This, incidentally, means that the corrections for the external and internal vibrations can be calculated in different coordinate systems.

The corrections for the internal vibrations are calculated in a coordinate system which is specified in Table 3, from the vibration and coupling tensors derived by Ishii & Scheringer (1979). To obtain the corrections for the external vibrations, we first calculate the tensors $\mathbf{U}_{\mathrm{ext}} = \mathbf{U}_{\mathrm{obs}} - \mathbf{U}_{\mathrm{int}}$ from the observed vibration tensors $\mathbf{U}_{\mathrm{obs}}$. With the tensors $\mathbf{U}_{\mathrm{ext}}$ the rigid-body vibration tensors **TLS** are then determined. With **TLS** we could first calculate the coupling tensors $\mathbf{U}_{rs,\,\mathrm{ext}}$ and then the correction according to (2) and (3). We shall use another, more direct approach for which only the libration tensor $\mathbf{L}$ is needed. We have shown earlier that the second term in the correction, $\mathbf{d}^T\mathbf{g}\mathbf{A}_{rs}\mathbf{g}\mathbf{d}/d^2$, is zero for rigid-body motions, and that the tensor $\mathbf{A}_{rs}$ can be expressed as a function of $\mathbf{L}$ and the positional coordinates of the atoms r and s [Scheringer, 1972, equation (4.5)]. If we define $\mathbf{L}$ doubly covariant with respect to the crystal axes (in lattice units $\mathrm{rad}^2\mathrm{Å}^2$), we obtain for the first term of the correction

$$\mathrm{trace}\,(\mathbf{A}_{rs}\mathbf{g}) = \mathbf{d}^T\mathbf{g}\mathbf{d}\,\mathrm{trace}\,(\mathbf{g}^{-1}\mathbf{L}) - \mathbf{d}^T\mathbf{L}\mathbf{d}, \quad (5)$$

in agreement with equation (4.10) of Scheringer (1978), where this result was derived in another manner.

3. Determination of the libration tensor

Our main concern is the determination of the libration tensor $\mathbf{L}$ from the tensors of the external vibrations $\mathbf{U}_{\mathrm{ext}} = \mathbf{U}_{\mathrm{obs}} - \mathbf{U}_{\mathrm{int}}$. Since the H atoms participate strongly in the internal vibrations of the molecule, which can be eliminated in our procedure, we can also use the H atoms for determining the rigid-body motions (in contradistinction to common practice). Since, in principle, the four C,N,O atoms would be sufficient for determining $\mathbf{L}$, we also determine $\mathbf{L}$ with the U_{ij} of these four atoms alone. Furthermore, we determine $\mathbf{L}$ with the observed vibration tensors $\mathbf{U}_{\mathrm{obs}}$, and can thus examine to what extent the values of L_{ij} deviate from those which are obtained with the (more appropriate) tensors $\mathbf{U}_{\mathrm{ext}}$.

Although only $\mathbf{L}$ is needed for the correction, we have to determine all components of the rigid-body vibration tensors **TLS**. The site symmetry $mm2$ of the urea molecule in the crystal (space group $P\bar{4}2_1m$) restricts the number of independent components to eight. Referred to the crystal axes, these are: T_{11} ($= T_{22}$), T_{33}, T_{12}, L_{11} ($= L_{22}$) L_{33}, L_{12}, S_{11} ($= -S_{22}$), S_{12} ($= -S_{21}$); all other components are zero. Furthermore, we have generally used the restriction $\mathbf{S} = \mathbf{0}$, because the refinement became unstable with S_{11} and S_{12} (negative eigenvalues occurred), particularly when only the ten independent components U_{ij} of the four C,N,O atoms were used. The numerical

Table 1. *Components L_{ij} of the libration tensor determined from various sets of nuclear vibration components U_{ij}*

The L_{ij} are in $(°)^2$ and refer to a Cartesian coordinate system parallel to the crystal axes.

Set of components U_{ij}	L_{11}	L_{12}	L_{33}
293 K, $\mathbf{U}_{\mathrm{obs}}$, 8 atoms	31·1	11·8	68·9
293 K, $\mathbf{U}_{\mathrm{ext}}$, 8 atoms	14·3	2·1	40·0
293 K, $\mathbf{U}_{\mathrm{obs}}$, 4 CNO atoms	25·1	5·5	156·4
293 K, $\mathbf{U}_{\mathrm{ext}}$, 4 CNO atoms	26·8	6·9	158·3
123 K, $\mathbf{U}_{\mathrm{obs}}$, 8 atoms	21·4	9·5	47·5
123 K, $\mathbf{U}_{\mathrm{ext}}$, 8 atoms	6·0	0·6	20·8
123 K, $\mathbf{U}_{\mathrm{obs}}$, 4 CNO atoms	7·9	0·8	77·8
123 K, $\mathbf{U}_{\mathrm{ext}}$, 4 CNO atoms	9·5	2·1	79·5
123 K, $\mathbf{U}_{\mathrm{int}}$, 8 atoms	15·5	8·9	26·6

calculations were performed with the program of Schomaker & Trueblood (1968). The results are listed in Table 1.

With the U_{ij}'s of only the four C,N,O atoms, smaller values of L_{11} are obtained than with the U_{ij}'s of all eight atoms, but larger values of L_{33}. We do not consider these large rotational amplitudes about the C—O axis ($\sqrt{L_{33}} = 8{\cdot}8°$ at 123 K and $12{\cdot}5°$ at 293 K) to be correct. The fit of **T** and **L** to the U_{ij} is much better for the C,N,O atoms alone than for all eight atoms, but, at the same time, the fit of **T** and **L** to the errors in the U_{ij}'s is also improved. Even with the smaller azide ion in the structure of NaN_3 at room temperature such large rotational amplitudes were not observed, but only about 7° (Stevens & Hope, 1977).

With the tensors $\mathbf{U}_{ext}$, smaller values of L_{ij} are obtained than with the tensors $\mathbf{U}_{obs}$ (the H atoms being included). This shows that, in determining **T** and **L** from the $\mathbf{U}_{obs}$, the fit occurs in such a way that the rigid-body motions also express part of the internal vibrations. We demonstrate this purely numerical but physically meaningless fit more explicitly by fitting **T** and **L** to the tensors $\mathbf{U}_{int}$ of the internal vibrations. Substantial values are obtained for **L** (see last row of Table 1) whereas we would expect $\mathbf{L} = \mathbf{0}$; however, one eigenvalue of **T** is negative. With the $\mathbf{U}_{int}$ of the four C,N,O atoms alone, all three eigenvalues of **L** are negative. This shows that a part of the bond-length correction, that due to the internal vibrations, is picked up and represented by the external vibrations, but, as we shall see, not in the proper manner.

With the U_{ij} of the four C,N,O atoms alone, we would also expect a corresponding reduction of **L** when we use the tensors $\mathbf{U}_{ext}$. Table 1 shows that this is not the case; we even obtain values of **L** that are a little larger. This is, however, outweighed by correspondingly smaller values of **T**. Thus, in the two cases – with and without H atoms – **T** and **L** are fitted in a completely different manner to the components $\mathbf{U}_{ij}$. As already stated, we do not consider the values of **T** and **L** obtained by a fit to the U_{ij} of the four C,N,O atoms alone to be correct.

The positive values of L_{12} mean that the librations about the axis perpendicular to the molecular plane are smaller than those about the second axis (not the C—O axis) in the molecular plane. Thus, the librations about the plane normal are the smallest altogether. This corresponds to the fact that the moment of inertia about the plane normal is the largest.

4. Corrections for external and internal vibrations

We calculated the corrections for the external vibrations not only with those **L** tensors which we considered to be most correct, **L**(ext), 8 atoms, but with all **L** tensors of Table 1. The corrections obtained are remarkably scattered, Table 2. This shows that a careful selection of the components U_{ij} is important. The rigid-body motions yield the largest corrections for the C—N and N—H(1) bonds (Table 2), because the L_{33} components are the largest and because these bonds are nearly perpendicular to **z**. Since, on the other hand, the N—H(2) bond is nearly parallel and the C—O bond is parallel to **z**, contributions to the corrections for these bonds only arise from L_{11} and L_{22}. Thus, the corrections for the C—O and N—H(2) bonds are correspondingly smaller.

The coupling tensors needed to correct for the internal vibrations are predominantly negative. For pairs C—O and C—N they have only negative components, for pairs N—H they are given in Table 3. Negative components of the coupling tensors mean that the antiphase vibrations of the two atoms concerned prevail. The $U_{rs,22}$ components of the N—H bonds have particularly large absolute values. These components refer to the motions of the N and H atoms perpendicular to the molecular plane, *i.e.* they arise mainly from the low-frequency out-of-plane modes of the molecule. Thus, in these modes, the N and H atoms vibrate predominantly antiphased, which gives rise to a large correction, Table 4. For comparison, we have also calculated the corrections for the internal vibrations with the model of uncorrelated motion ($\mathbf{U}_{rs} = \mathbf{0}$), and, for the N—H bonds, with the model of riding motion (H rides on N, $\mathbf{U}_{NH} = \mathbf{U}_N$). The results are given in Table 4 for 123 K; for 293 K the values are 8·6% larger on average and are not given. The corrections obtained with the coupling tensors of Ishii & Scheringer (1979) are in all cases larger than those obtained with the two other models, since, with them, the antiphase vibrations of the two atoms are less well

Table 2. *Bond-length corrections* (Å) *for the libration tensors of Table* 1

Model	C—O	C—N	N—H(1)	N—H(2)
293 K, **L**(obs), 8 atoms	0·0115	0·0162	0·0124	0·0093
293 K, **L**(ext), 8 atoms	0·0053	0·0091	0·0071	0·0043
293 K, **L**(obs), 4 CNO atoms	0·0093	0·0283	0·0224	0·0075
293 K, **L**(ext), 4 CNO atoms	0·0099	0·0288	0·0228	0·0080
123 K, **L**(obs), 8 atoms	0·0082	0·0111	0·0085	0·0066
123 K, **L**(ext), 8 atoms	0·0023	0·0045	0·0035	0·0018
123 K, **L**(obs), 4 CNO atoms	0·0030	0·0134	0·0105	0·0024
123 K, **L**(ext), 4 CNO atoms	0·0036	0·0139	0·0108	0·0029

represented ($\mathbf{U}_{rs} \geq \mathbf{0}$). Moreover, a comparison with Table 2 shows that, with the N—H bonds, the corrections for the internal vibrations are much larger than those for the external vibrations (the only exception: N—H(1), 293 K, C,N,O atoms). For the C—O and C—N bonds, the corrections for the internal vibrations are small because the tensors $\mathbf{U}_{\rm int}$ are already very small.

In Table 5, rows 1 and 4, the total corrections for external and internal vibrations are given. By comparison with Table 2, models **L** (obs, 8 atoms), we see that the rigid-body model, applied with the tensors $\mathbf{U}_{\rm obs}$, yields quite different corrections. For the C—O and C—N bonds they are too large, and for the N—H bonds they are too small by 0·0153–0·0178 Å. Thus, we conclude that, at least for urea, the rigid-body model alone, applied with the observed vibration tensors, cannot appropriately pick up and represent the contributions to the corrections for the internal vibrations. For comparison, we have also calculated the corrections for the models of uncorrelated motion ($\mathbf{U}_{rs} = \mathbf{0}$) and riding motion (H rides on N, $\mathbf{U}_{\rm NH} = \mathbf{U}_{\rm N}$) from the observed vibration tensors, Table 5. Uncorrelated motion yields corrections which are much too large. With the riding model better corrections are obtained which are, however, too small (for 293 K by 0·006–0·011 Å, for 123 K by about 0·004–0·008 Å).

Table 3. *Sums of the coupling tensors* $\mathbf{U}_{rs} + \mathbf{U}_{sr}$ ($\text{Å}^2 \times 10^6$) *for the pairs* N—H(1) *and* N—H(2) *at* 123 K

The x axis is parallel to the C—O bond, the y axis perpendicular to the plane of the molecule. The absolute values of the coupling components may be compared to the vibration components given by Ishii & Scheringer (1979, Table 2).

N—H(1)

$$\begin{pmatrix} 462 & 0 & 100 \\ 0 & -3926 & 0 \\ 100 & 0 & 936 \end{pmatrix}$$

N—H(2)

$$\begin{pmatrix} 738 & 0 & -96 \\ 0 & -4032 & 0 \\ -96 & 0 & 756 \end{pmatrix}$$

Table 4. *Bond-length corrections* (Å) *for the internal vibrations of the urea molecule at* 123 K

IS = Ishii & Scheringer (1979)

Model	C—O	C—N	N—H(1)	N—H(2)
Coupling tensors, IS	0·0022	0·0018	0·0213	0·0208
Uncorrelated motion	0·0014	0·0013	0·0196	0·0192
Riding motion			0·0183	0·0178

5. Corrected bond lengths

To obtain accurate values of the corrected bond lengths, accurate lattice constants are needed. Unfortunately, for 293 K the lattice constants of Guth *et al.* (1980) and Pryor & Sanger (1970) do not agree very well. Similarly, for 123 K, the lattice constants of Guth *et al.* (1980) and Mullen & Hellner (1978) also deviate from each other. To make obvious the effect of the inaccuracy in the lattice constants, we calculated the corrected bond lengths with both sets of lattice constants, Table 6. The observed deviations in the lattice constants give rise to a maximum deviation of 0·002 Å in the bond lengths for 123 K, and to a maximum deviation of 0·003 Å for 293 K.

For the temperatures of 123 and 293 K, we expect the corrected bond lengths essentially to be equal.

Table 5. *Bond-length corrections* (Å) *for the total of external and internal vibrations, and for the models of uncorrelated motion and riding motion* (H *rides on* N)

Model	C—O	C—N	N—H(1)	N—H(2)
293 K, **L**(ext) + $\mathbf{U}_{\rm int}$, 8 atoms	0·0077	0·0111	0·0302	0·0269
293 K, uncorrelated motion	0·0690	0·0703	0·1559	0·1536
293 K, riding motion			0·0246	0·0159
123 K, **L**(ext) + $\mathbf{U}_{\rm int}$, 8 atoms	0·0045	0·0063	0·0238	0·0226
123 K, uncorrelated motion	0·0313	0·0355	0·0834	0·0806
123 K, riding motion			0·0196	0·0149

Table 6. *Lattice constants and corrected bond lengths* (Å) *for urea*

GHKTS refers to Guth *et al.* (1980), MH to Mullen & Hellner (1978) and PS to Pryor & Sanger (1970).

Source of parameters	Source of lattice constants	a	c	C—O	C—N	N—H(1)	N—H(2)
123 K, GHKTS	GHKTS	5·578	4·695	1·263	1·346	1·036	1·037
123 K, GHKTS	MH	5·576	4·686	1·260	1·345	1·036	1·035
293 K, GHKTS	GHKTS	5·645	4·704	1·253	1·345	1·035	1·032
293 K, GHKTS	PS	5·662	4·716	1·257	1·348	1·038	1·035
293 K, PS	PS	5·662	4·716	1·260	1·352	0·998	1·003

Kuchitsu & Cyvin (1972, p. 191) point out that, with very low-frequency internal modes, the corrected bond lengths may depend upon temperature. Since, with urea, the lowest internal frequency is 500 cm^{-1}, we can well exclude this situation here. Thus, the comparison of the corrected bond lengths, on the one hand, may serve as a hint concerning the accuracy of the parameters obtained for the two temperatures and, on the other hand, may be used to judge the appropriateness of our procedure. The agreement of the corrected C—N and N—H(1) lengths within 0·003 Å for 123 and 293 K is excellent and could even be improved by more accurate lattice constants. A little worse is the agreement for the N—H(2) bond (within 0·005 Å) where one value (293 K, GHKTS), 1·032 Å, deviates more strongly. The C—O length appears to be the least accurately determined one (within 0·010 Å). This is probably because the z parameters are the least accurately determined ones and are the only positional parameters for the C—O bond.

A comparison of our corrected bond lengths with those of Pryor & Sanger (1970), last row of Table 6, shows that only for the least accurately determined C—O length an adequate agreement is obtained. We consider the fact that Pryor & Sanger have corrected the bond lengths only with the rigid-body model (**L** tensor) to be the cause of these deviations. From the data of their $C + R$ refinement we calculate $L_{11} = L_{22} = 21{\cdot}34$, $L_{33} = 128{\cdot}0$, $L_{12} = 1{\cdot}64\ (°)^2$. The very large value of L_{33} gives rise to too large a correction of the C—N bond (0·0241 Å), and neglecting the correction for the internal vibrations gives rise to corrections for the N—H bonds which are too small (0·0189 and 0·0066 Å). Moreover, even the uncorrected N—H distances of Pryor & Sanger (1970) appear to be too small (0·979 and 0·996 Å).

The corrected N—H lengths from Table 6 can be compared with the thermally averaged bond lengths r_g which are obtained by gas electron diffraction and spectroscopic methods. No data are available for urea, though they exist for ammonia and hydrazine. For the N—H bond in ammonia, $r_g = 1{\cdot}0302\ (20)$ Å was found by electron diffraction (Landolt-Börnstein, 1976). Morino, Kuchitsu & Yamamoto (1968) determined $r_g = 1{\cdot}0332$ Å from infrared data and anharmonic calculations. Primarily, the infrared investigation yields the distance between the mean positions of the atoms at 0 K, r_z; the authors give $r_z = 1{\cdot}0240$ Å. Hence, the bond-length correction in the free ammonia molecule is only 0·0092 Å and is less than half of the correction for urea (for the internal vibrations). The correction is smaller because the internal frequencies in ammonia (950, 1628, 3336 and 3415 cm^{-1}, see Alpert, Keiser & Szymanski, 1970, p. 156) are much larger than those in urea. Thus, although the distances between the mean positions of the N and H atoms in the free ammonia molecule (1·0240 Å) and in the urea crystal (on average, 1·013 Å for 123 K and 1·007 Å for 293 K) are quite different, a good agreement is obtained for the corrected bond lengths. For the N—H bond in hydrazine, $r_a = 1{\cdot}022\ (6)$ Å was determined by gas electron diffraction (Landolt-Börnstein, 1976) and, since $r_g = r_a + \langle \Delta r^2 \rangle / r$, a value of r_g well above 1·030 Å may also be assumed for hydrazine. Thus, our N—H lengths in Table 6 are in substantial agreement with the r_g values in other molecules. It may be that the N—H bonds in the urea crystal are stretched a little due to the presence of hydrogen bonds. This, then, would explain the remaining difference of 0·003–0·005 Å by which the N—H bonds in urea are found to be longer than those in ammonia.

Our investigation has shown that a bond-length correction with the rigid-body model is not satisfactory for the N—H bonds in urea and cannot replace the correction for the internal vibrations. The riding model gives better corrections which are, however, still too small. Since, as a rule, the internal vibrations of the molecules are not known and a corresponding correction cannot be calculated, we presume that most of the corrected bonds with terminal H atoms reported in the literature were determined too short by about 0·01 Å or even more when the correction was calculated with the rigid-body model.

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