Table 2. *Lattice parameters and thermal-expansion data of the compound* $Ni_{11}Zr_9$ *at different temperatures*

Heat treatment and water quenching		a (Å)		c (Å)		$\alpha_a \times 10^6$ (K^{-1})	$\alpha_c \times 10^6$ (K^{-1})
Temperature (K)	Time (min)	Observed	Calculated from linear equation	Observed	Calculated from linear equation		
298 (As cast)	–	9·9646 (58)	9·9661	6·6940 (42)	6·6944	28·05 (1)	29·71 (4)
1003	70	10·1626 (58)	10·1631	6·8357 (42)	6·8346	27·50 (1)	29·10 (4)
1093	60	10·1892 (58)	10·1883	6·8538 (42)	6·8525	27·43 (1)	29·02 (4)
1223	50	10·2250 (58)	10·2246	6·8758 (42)	6·8783	27·33 (1)	28·93 (4)
1293	40	10·2558 (58)	10·2442	6·8950 (42)	6·8923	27·25 (1)	28·85 (4)
1423	60	10·2703 (58)	10·2805	6·9125 (42)	6·9181	27·21 (1)	28·77 (4)
1493	30	10·2996 (58)	10·3001	6·9359 (42)	6·9320	27·14 (1)	28·68 (4)

Kirkpatrick & Larsen (1961) have shown the existence of this phase with a b.c.t. structure but the reported parameters appear to be tentative. The correctness of the crystal structure of this phase has to be decided by comparison with the phase $Pt_{11}Zr_9$ (which has 40 atoms per unit cell and is b.c.t. with $a = 10\cdot257$ and $c = 6\cdot888$ Å) reported by Panda & Bhan (1974). Comparison shows that $Ni_{11}Zr_9$ is isomorphous with the $Pt_{11}Zr_9$ phase. This is expected as Ni and Pt are both members of the T^{10} group with ground-state electron configurations of their free atoms of $3d^8 3s^2$ and $5d^8 6s^2$ respectively and both have similar alloying behavior (Panda & Bhan, 1973).

Thermal-expansion coefficient

The X-ray photographs of the alloy $Ni_{55}Zr_{45}$ at each temperature were indexed and cell dimensions were determined using a least-squares treatment (Cohen, 1935, 1936). The standard errors in the lattice parameters so obtained were calculated by the method suggested by Jette & Foote (1935).

The lattice parameters vary linearly with temperature and the dependence may be expressed analytically as $a_T = 9\cdot8828$ (14) $+ 2\cdot795$ (13) $\times 10^{-4} T$; and $c_T = 6\cdot6351$ (34) $+ 1\cdot989$ (31) $\times 10^{-4} T$; where a_T and c_T are the lattice parameters at TK.

The linear coefficients of thermal expansion for both parameters are calculated by $\alpha_a = (1/a)(da_T/dT)$ and $\alpha_c = (1/c)(dc_T/dT)$ and are listed in Table 2.

The *American Institute of Physics Handbook* (1972) only gives the values of α for pure Ni and Zr at 293 K, but the thermal-expansion coefficient of an alloy cannot be predicted from those of its constituents (Lonsdale, 1968).

References

American Institute of Physics Handbook (1972). Edited by E. G. Dwight, pp. 119–142. New York: McGraw-Hill.
Cohen, M. U. (1935). *Rev. Sci. Instrum.* **6**, 68.
Cohen, M. U. (1936). *Rev. Sci. Instrum.* **7**, 155.
Jette, E. R. & Foote, F. (1935). *J. Chem. Phys.* **3**, 605.
Kirkpatrick, M. E. & Larsen, W. L. (1961). *Trans. Am. Soc. Met.* **54**, 580–590.
Lonsdale, K. (1968). *International Tables for X-ray Crystallography*, Vol. III, pp. 125–129. Birmingham: Kynoch Press.
Panda, S. C. & Bhan, S. (1973). *Z. Metallkd.* **64**, 793–799.
Panda, S. C. & Bhan, S. (1974). *J. Less-Common Met.* **34**, 344–347.

On the 'riding-model' correction for bond lengths.
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Abstract

It is usual in structural reports based on X-ray or neutron diffraction methods to correct bond lengths for thermal-

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motion effects. Two common procedures adopted are the riding model [Busing & Levy (1964). *Acta Cryst.* **17**, 142–146], and the rigid-body model [Schomaker & Trueblood (1968). *Acta Cryst.* B24, 63–76], the specific choice being dependent on the circumstances. It would appear that no critical assessment is available in the literature as to how

sound and reliable these corrections are. This paper attempts to provide such an assessment, specifically for the riding-model correction, purely from an empirical point of view, by comparing neutron diffraction data with wide-line proton magnetic resonance (PMR) and microwave data.

We recently examined the neutron diffraction data for a number of small organic molecules with a view to arriving at the most appropriate geometry of groups such as NH_3^+, CH_3 and CH_2. This was undertaken in connection with the theoretical calculation of second moments for the interpretation of wide-line PMR absorption spectra. The internuclear distances enter the expression for the second moment as the inverse sixth power (Van Vleck, 1948) and hence precise coordinates of the protons (in the case of PMR) are important in these calculations. One of the assumptions in the riding-model correction for a bond length is that one of the atoms is light compared to the other to justify the riding concept. H attached to C, N or O in organic molecules would seem to qualify well in this respect. H-atom location from X-ray data tends to be less precise and there have been several instances where unrealistically large values of the second moment for organic compounds were estimated by use of X-ray coordinates (Watton, Reynhardt, Sandhu & Petch, 1977; Jagannathan & Srinivasan, 1982a). This obviously results from the fact that X-ray data normally yield lengths which are too short for bonds such as C—H and N—H, especially in groups such as CH_3 and NH_4^+ (Tomiie, 1958; McDonald, 1960; Banyard & March, 1961; Nahringbauer, 1967; Khan, Boux & James, 1972). Our analysis thus concentrates on neutron diffraction data, since these yield more reliable coordinates. Also we shall confine ourselves to riding-model corrections, since the data available on rigid-body corrections are rather meagre for a critical analysis.

Initial statistical analysis (Jagannathan & Srinivasan, 1982b) carried out on about 80 organic compounds containing these groups gave bond-length averages for C—H of about 1·090 Å, if only uncorrected values are used. In many cases, bond lengths corrected by the riding model were also available and the average corrected C—H length was about 1·126 Å. The standard deviations in these averages were, however, rather large ($\sim$ >0·015 Å). This was obviously because no special effort was made to screen the structures in relation to accuracy of analysis and applicability of the riding-model correction. The latter aspect has been discussed by Brown (1968).

Thus, to make the analysis more effective the current investigation is restricted to a select group of 16 carbohydrates which have been studied by neutron diffraction. These are reasonably accurate structures as judged by the final R factors and the e.s.d.'s in bond lengths and other parameters (Table 1). Also, the analysis is restricted to the three groups CH_3, CH_2 and CH. An additional factor governing the choice of these compounds is that wide-line PMR studies are available for three sugars, and these studies show that the structures are essentially 'rigid' even at room temperature. This reduces the possible inaccuracy in the second moment as would be the case if group rotations exist. Thus the experimental second moment is interpreted more reliably in terms of the model geometry from the statistical analysis.

Table 1. *Compounds included in the statistical analysis*

Serial number	Compound	R factor	Reference
(1)	α-L-Xylopyranose	0·036	(a)
(2)	β-D-Fructopyranose	0·053	(b)
(3)	β-L-Lyxopyranose	0·048	(c)
(4)	3-Amino-1,6-anhydro-3-deoxy-β-D-glucopyranose	0·056	(d)
(5)	Methyl α-D-mannopyranoside	0·030	(e)
(6)	Methyl α-D-glucopyranoside	0·046	(e)
(7)	β-D,L-Arabinopyranose	0·058	(f)
(8)	Methyl α-D-galactopyranoside monohydrate	0·055	(g)
(9)	Methyl β-D-galactopyranoside	0·058	(g)
(10)	α-L-Sorbopyranose	0·044	(h)
(11)	α-D-Glucose	0·048	(i)
(12)	α-L-Rhamnose monohydrate	0·042	(j)
(13)	β-L-Arabinose	0·035	(k)
(14)	Methyl β-D-xylopyranoside	0·045	(k)
(15)	Methyl α-D-altropyranoside	0·089	(l)
(16)	Sucrose	0·033	(m)

References: (a) Takagi & Jeffrey (1979c); (b) Takagi & Jeffrey (1977b); (c) Nordenson, Takagi & Jeffrey (1978); (d) Noordik & Jeffrey (1977); (e) Jeffrey, McMullan & Takagi (1977); (f) Takagi & Jeffrey (1979b); (g) Takagi & Jeffrey (1979a); (h) Nordenson, Takagi & Jeffrey (1979); (i) Brown & Levy (1979); (j) Takagi & Jeffrey (1978); (k) Takagi & Jeffrey (1977a); (l) Poppleton, Jeffrey & Williams (1975); (m) Brown & Levy (1973).

Table 2. *Average bond lengths (Å) and bond angles (°) for different groups (values in parentheses are e.s.d.'s)*

Group	Type	Uncorrected	Minimum riding	Riding
CH	(C—H)	1·100 (4)	1·104 (4)	1·123 (3)
CH_2(ring)	(C—H)	1·093 (5)	1·097 (5)	1·118 (5)
	(H—C—H)	109·0 (5)	–	–
CH_2(free)	(C—H)	1·090 (7)	1·097 (6)	1·127 (6)
	(H—C—H)	108·0 (7)	–	–
CH_3	(C—H)	1·054 (16)	1·082 (9)	1·142 (17)
	(H—C—H)	108·6 (19)	–	–
	(X—C—H)	110·3 (16)	–	–

Table 2 shows that the uncorrected C—H bond length in the CH_3 group has a mean value of 1·054 Å (with a standard error of ±0·016 Å) as against means of 1·092 Å (±0·004 Å) and 1·100 Å (±0·004 Å) for CH_2 and CH groups. This would seem reasonable since the CH_3 group is a terminal group and is likely to be affected by rotational and other motional effects.

In the case of the CH_2 group a minor subdivision was felt necessary depending upon whether or not the group occurs in the sugar ring. The mean C—H bond lengths are not different, but there appears to be a significant difference in the angle H—C—H.

It is of interest to note that the mean corrected values are 1·142 Å for the CH_3 group and 1·123 Å for CH_2 and CH groups, although one would have expected that the corrected values would be the same. However, the indication is clear that the corrected value for the CH_3 group (which has larger motional effects) is higher than for the other groups. This

Table 3. *Observed second moments for some sugars compared with theoretical values*

The units for second moment are G^2 ($1\,G \stackrel{\wedge}{=} 10^{-4}\,T$).

| Compound | Second moment using actual neutron diffraction data | | Theoretical second moment with $C-H = 1\cdot127\,\text{Å}$ | Observed experimental second moment |
	Average $C-H$ in the structure (Å)	Theoretical second moment		
D-Glucose	1·097	8·9	7·6	8·5 (0·5)*
L-Xylose	1·099	14·1	10·6	13·1 (0·4)
L-Sorbose	1·095	14·5	13·6	13·9 (0·7)

* Values in the parentheses are e.s.d.'s.

Table 4. $C-H$ *bond lengths for various groups from microwave data*

Values in parentheses are e.s.d.'s.

Group	Bond length
CH_3	1·095 (3) Å
CH_2	1·090 (3)
CH	1·094 (4)
Overall	1·093 (3)

itself might be attributed to the fact that the correction is overdone. However, additional evidence arises as follows.

The wide-line PMR results for three of the sugars are given in Table 3. The theoretical values of the second moment listed correspond to two geometries for the CH_2 and CH groups, namely $C-H$ lengths with and without correction. The uncorrected set corresponds to the actual neutron diffraction results for these compounds, while for the corrected set the $C-H$ bond lengths were changed uniformly to $1\cdot127\,\text{Å}$. The angles were kept as observed in the neutron diffraction analyses. This corresponds to using $1\cdot097$ and $1\cdot127\,\text{Å}$ respectively for the $C-H$ bond lengths. It is clear from Table 3 that the agreement is poor for the corrected set and very much better for the uncorrected one.

Further independent evidence is obtained from microwave data. Table 4 lists the average $C-H$ values in different groups derived from about 25 simple organic compounds. The geometry of these groups is more precisely determined from microwave data as is evident from the quoted e.s.d.'s. The overall mean of $1\cdot093$ (3) Å (Table 4) also indicates that the values in column 5 of Table 2 are overcorrected. Although we have not discussed angles, the microwave data broadly support the general results from diffraction data (for example, the $H-C-H$ angle in the CH_3 group is $\sim108\cdot7°$, less than the tetrahedral value).

As regards column 4 of Table 2 where minimum corrected $C-H$ lengths are listed, these are also rather unsatisfactory and inconsistent. For instance, the average for CH_3 is $1\cdot082$ (9) Å, distinctly less than $1\cdot093$ (3) Å (which may, for the present, be taken as standard), whereas the average taken over the CH_2 and CH groups is $1\cdot099$ (5) Å.

From these considerations we may conclude that bond lengths corrected by the riding model tend to yield overcorrected values. The uncorrected values, particularly for groups such as CH_2 and CH which are relatively rigid, should be preferred and are probably close to the true values than values for groups such as CH_3 where motional effects are large. The conclusion drawn above, although based on data for CH_3, CH_2 and CH groups, may be expected to hold good in general for other groups such as NH_4^+, NH_3^+, NH_2 and OH.

References

BANYARD, K. E. & MARCH, N. H. (1961). *Acta Cryst.* **14**, 357–361.
BROWN, G. M. (1968). *Acta Cryst.* B**24**, 294–295.
BROWN, G. M. & LEVY, H. A. (1973). *Acta Cryst.* B**29**, 790–797.
BROWN, G. M. & LEVY, H. A. (1979). *Acta Cryst.* B**35**, 656–659.
BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
JAGANNATHAN, N. R. & SRINIVASAN, R. (1982a). *Indian J. Pure Appl. Phys.* In the press.
JAGANNATHAN, N. R. & SRINIVASAN, R. (1982b). *J. Cryst. Mol. Struct.* In the press.
JEFFREY, G. A., McMULLAN, R. K. & TAKAGI, S. (1977). *Acta Cryst.* B**33**, 728–737.
KHAN, A., BOUX, J. P. & JAMES, W. J. (1972). *Acta Cryst.* B**28**, 2065–2069.
McDONALD, J. R. R. (1960). *Acta Cryst.* **13**, 113–124.
NAHRINGBAUER, I. (1967). *Acta Cryst.* **23**, 956–965.
NOORDIK, J. H. & JEFFREY, G. A. (1977). *Acta Cryst.* B**33**, 403–408.
NORDENSON, S., TAKAGI, S. & JEFFREY, G. A. (1978). *Acta Cryst.* B**34**, 3809–3811.
NORDENSON, S., TAKAGI, S. & JEFFREY, G. A. (1979). *Acta Cryst.* B**35**, 1005–1007.
POPPLETON, B. J., JEFFREY, G. A. & WILLIAMS, G. J. B. (1975). *Acta Cryst.* B**31**, 2400–2404.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
TAKAGI, S. & JEFFREY, G. A. (1977a). *Acta Cryst.* B**33**, 3033–3040.
TAKAGI, S. & JEFFREY, G. A. (1977b). *Acta Cryst.* B**33**, 3510–3515.
TAKAGI, S. & JEFFREY, G. A. (1978). *Acta Cryst.* B**34**, 2551–2555.
TAKAGI, S. & JEFFREY, G. A. (1979a). *Acta Cryst.* B**35**, 902–906.
TAKAGI, S. & JEFFREY, G. A. (1979b). *Acta Cryst.* B**35**, 991–993.
TAKAGI, S. & JEFFREY, G. A. (1979c). *Acta Cryst.* B**35**, 1482–1486.
TOMIIE, Y. (1958). *J. Phys. Soc. Jpn*, **13**, 1030.
VAN VLECK, J. H. (1948). *Phys. Rev.* **74**, 1168–1183.
WATTON, A., REYNHARDT, E. C., SANDHU, R. S. & PETCH, H. S. (1977). *J. Chem. Phys.* **67**, 887–892.