

Bond lengths in organic and metal-organic compounds revisited: $X-H$ bond lengths from neutron diffraction data¹

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The number of structures in the Cambridge Structural Database (CSD) has increased by an order of magnitude since the preparation of two major compilations of standard bond lengths in mid-1985. It is now of interest to examine whether this huge increase in data availability has implications for the mean bond-length values published in the late 1980s. Those compilations reported mean $X-H$ bond lengths derived from rather sparse information and for rather few chemical environments. During the intervening years, the number of neutron studies has also increased, although only by a factor of around 2.25, permitting a new analysis of $X-H$ bond-length distributions for (a) organic $X = C, N, O, B$, and (b) a variety of terminal and homometallic bridging transition metal hydrides. New mean values are reported here and are compared with earlier results. These new overall means are also complemented by an analysis of $X-H$ distances at lower temperatures ($T \leq 140$ K), which indicates the general level of librational effects in $X-H$ systems. The study also extends the range of chemical environments for which statistically acceptable mean $X-H$ bond lengths can be obtained, although values from individual structures are also collated to further extend the chemical range of this compilation. Updated default 'neutron-normalization' distances for use in hydrogen-bond and deformation-density studies are also proposed for $C-H$, $N-H$ and $O-H$, and the low-temperature analysis provides specific values for certain chemical environments and hybridization states of X .

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1. Introduction

One of the principal advantages of crystal-structure analysis using neutron diffraction is the determination of H-atom positions that are free of the asphericity effects observed in X-ray experiments (see *e.g.* Allen, 1986). The accurate $X-H$ distances obtained using neutrons may then be used, *e.g.* in the construction of accurate models of molecular peripheries in computational procedures, in conjunction with charge-density analyses (see *e.g.* Hoser *et al.*, 2009), and to generate more precise and useful experimental structures when combined with X-ray coordinate information. An obvious example of the latter is the 'neutron normalization' of donor H atoms in systematic studies of hydrogen-bond geometry from crystal structure information, for example using the Cambridge Structural Database (CSD: Allen, 2002) which is dominated by X-ray single-crystal studies. This normalization procedure involves moving an X-ray determined H atom (almost always outwards) along the observed $X-H$ vector to a position that

¹This paper is part of a short series that celebrates the addition of the 500 000th crystal structure to the Cambridge Structural Database in November 2009.

Table 1

Neutron studies in the CSD: comparative statistics for single-crystal studies available in 1985 and 2009.

	Number of structures (N_{str})		N_{str} ratio 2009:1985
	N_{str} (1985)	N_{str} (2009)	
Complete CSD	49 854	495 968	9.95
Neutron studies			
All	538	1213	2.25
Organic	381	811	2.13
With coordinates, $R \leq 0.10$	282	664	2.35
With coordinates, $R \leq 0.10^\dagger$	256	561	2.19
With coordinates, $R \leq 0.075^\dagger$	208	461	2.21
With coordinates, $R \leq 0.05^\dagger$	141	302	2.14
Metal-organic	157	402	2.56
Powder studies	–	217	–

† Structures counted have no disorder and no residual coordinate errors.

corresponds to the mean $X-H$ bond length observed in neutron diffraction studies.

An H-atom normalization procedure has been available within the CSD system for many years, and uses mean neutron $X-H$ distances determined from the CSD more than 20 years ago (Allen *et al.*, 1987). These standard bond lengths were part of two much larger compilations of mean bond lengths in organic (Allen *et al.*, 1987, 1992) and metal-organic systems (Orpen *et al.*, 1989, 1992). Both compilations were derived from the September 1985 release of the CSD which contained a total of 49 854 crystal structures, of which only 538 were neutron diffraction studies (Table 1). By contrast, in November 2009 the 500 000th structure was archived to the CSD, which is now an order of magnitude larger than the 1985 database. Despite this tenfold increase over the last two decades, the number of neutron studies has only risen by a factor of 2.25 to a total of 1213 (Table 1). The massive overall increase in the size of the CSD raises two important questions about the standard bond-length compilations of the late 1980s:

(a) how well do those published values reflect currently available crystal structure data? and

(b) can additional standard values now be derived for chemical-bond types that were either poorly represented or completely absent from the earlier compilations?

The present work addresses these questions with respect to mean $X-H$ distances in neutron structures, since they have specific and important uses, and were originally determined from a rather sparse set of crystal structures. Heavier atom (non-H) geometry will be discussed in a later paper.

2. Methodology

Version 5.31 of the CSD, prepared in late 2009 just before the 500 000th structure was added, contained 495 968 structures and was used in this work, together with the programs *ConQuest* (Bruno *et al.*, 2002), *Vista* (Cambridge Structural Database, 1998) and *Mercury* (Macrae *et al.*, 2006) that comprise the complete CSD system. In the context of neutron studies, some statistics that compare the CSD of 2009 with that of 1985, as used to prepare the earlier bond-length tabulations,

are presented in Table 1. This shows that the amount of neutron data that is useful for the derivation of mean geometry has increased by a factor of *ca* 2.2 over the past 24 years. In selecting CSD entries for analysis, the following filters were applied for organic structures: error-free coordinates after CCDC in-house validation, no disorder, no *catena* structures, no powder studies and $R \leq 0.075$ unless otherwise stated in text or tables. In selecting metal-organic structures, both disordered structures and those with *catena* bonds were accepted, unless the disorder affected the bonding vicinity of the hydride ligands.

$X-H$ distances for the individual substructures identified in Tables 2 and 3 were retrieved from the CSD using *ConQuest*, and

their distributions analysed using *Vista*, with *ConQuest* and *Mercury* graphics being used to check the chemical precision of search queries. These distances were calculated directly from the coordinates stored in the CSD, and are not corrected for thermal motion effects. Each distribution was analysed as described in the earlier published bond-length compilations (Allen *et al.*, 1987, 1992; Orpen *et al.*, 1989, 1992), in particular with respect to:

(i) outlier identification and removal prior to final averaging, and

(ii) use of the unweighted sample mean in all cases.

For each chemically distinct $X-H$ bond, the following parameters are given in Tables 2 and 3: the mean $X-H$ bond length (d); the sample standard deviation (σ_s) [the standard deviation of the mean (σ_m) is then given by $\sigma_s/(n)^{1/2}$]; the number of observations used in the final averaging (n); and the median of the final distribution (m). Also included in Table 2 are a small number of mean $X-D$ ($X = \text{C, N, O}$) distances from the 62 neutron studies in the CSD that contain deuterium. For comparison purposes, Table 2 reports the d , σ_s and n values from the earlier compilation (Allen *et al.*, 1987, 1992), identified using the suffixes (prev). Where these previously determined values do not appear, Table 2 is reporting a new mean value which could not be derived from the 1985 data. Comparison with the earlier metal-organic compilation is not possible in Table 3 since the earlier data on metal hydrides were very sparse and both X-ray and neutron $M-H$ bond lengths were combined in the tables of Orpen *et al.* (1989). In some cases in the current study so few $X-H$ values are available for a particular chemical environment that only values from individual structures can be provided in Tables 2 and 3. Issues connected with the generation and analysis of specific individual distributions are given in §3.

Some of the very simple substructures involved in this work have caused analysis problems owing to their topological symmetry, as discussed at length elsewhere (Allen *et al.*, 1991; Taylor & Allen, 1994). Thus, the fragment $\text{C}-\text{NH}_a\text{H}_b$ can map onto an amino group enumerated as $\text{C}_1-\text{N}_2-\text{H}_3\text{H}_4$ in a crystal structure in two ways, *i.e.* with $\text{H}_a:\text{H}_b$ mapping to either $\text{H}_3:\text{H}_4$ or $\text{H}_4:\text{H}_3$. In its normal operational mode, the CSD search

Table 2

Mean and median $X-H$ and $X-D$ distances (\AA) from single-crystal neutron diffraction studies of organic compounds.

Column headings are as described in §2. In the substructure column, Z is any element except H (subscripts indicate the number of Z atoms) and C(ar) is an aromatic carbon; all σ_s values are multiplied by 10^3 .

Substructure	d	σ_s	n	m	$d(\text{prev})$	$\sigma_s(\text{prev})$	$n(\text{prev})$
$X-H$ bond lengths							
C-H in							
Z_3-Csp^3-H	1.098	11	344	1.099	1.099	7	117
C_3-Csp^3-H	1.099	9	82	1.098	1.099	4	14
$Z_2-Csp^3-H_2$	1.091	17	704	1.094	1.092	12	230
$C_2-Csp^3-H_2$	1.092	17	308	1.095	1.092	13	100
$Z-Csp^3-H_3$	1.077	26	1118	1.085	1.066	28	160
$C-Csp^3-H_3$	1.077	29	827	1.084	1.059	30	83
C(ar)-H	1.083	17	721	1.085	1.083	11	218
$C=Csp^2-H$	1.082	13	109	1.084	1.077	12	14
C(cyclopropyl)-H	1.080	8	9	1.079			
$C\equiv Csp^1-H$	1.042	22	5	1.044			
$C\equiv Csp^1-H$ or D	1.055	9	9	1.059			
O-H† in							
$Z-O-H$	0.983	25	259	0.976			
C(any)-O-H	0.980	21	230	0.974	0.967	10	73
Csp^3-O-H	0.970	12	169	0.971	0.967	10	63
$O=Csp^2-O-H$ (acids)	1.018	22	37	1.014	1.015	17	16
C(ar)-O-H	0.992	17	23	0.988			
N*-H‡ in							
N^+-H	1.036	16	187	1.037	1.033	22	87
$Z-N-H$ (all)	1.015	16	233	1.016	1.009	19	95
Csp^3-N-H_2 §	1.002	10	4	1.002			
Csp^2-N-H_2 (all)	1.013	9	141	1.012			
Csp^2-N-H_2 (amido§)	1.010	8	84	1.009			
Csp^2-N-H_2 (N pl)	1.012	8	129	1.012			
C(ar)-N-H ₂ (all)	1.011	13	30	1.013			
C(ar)-N-H ₂ (N pl)	1.010	14	18	1.012			
C(ar)-N-H ₂ (N py)	1.024	3	5	1.023			
C(ar)-N-H ₂ (N int)	1.010	11	7	1.004			
$Z_2-N-H\ddot{\ddagger}$	1.027	16	74	1.027			
$(Csp^2)_2-N-H\ddot{\ddagger}$	1.030	13	43	1.031			
Other $X-H$							
B-H (terminal)	1.185	18	27	1.189			
B-H (B-H-B bridges)¶	1.338	12	10	1.342			
S-H††	1.338 (2)						
Si-H‡‡	1.506 (2)						
$X-D$ bond lengths							
Z_3-Csp^3-D	1.091	4	4	1.092			
$Z_2-Csp^3-D_2$	1.094	6	40	1.095			
$Z-Csp^3-D_3$	1.084	9	56	1.086			
C(ar)-D	1.084	7	70	1.083			
Csp^1-D	1.058	4	5	1.059			
$Z-O-D$	0.994	14	20	0.998			
N^+-D	1.030	8	32	1.029			
Z_2-N-D	1.026	7	5	1.025			
$Z-N-D_2\ddot{\ddagger}$	1.002	9	10	1.001			

† O-H and O-D values were obtained by removing examples having very short H(D) bonds, as described in the text. ‡ N* is four-coordinate, otherwise N is three-coordinate with a zero formal charge and additional suffixes (pl), (py) and (int) to indicate planar, pyramidal and intermediate N geometry, as defined in the text. § All N in this sample are actually planar, no other geometries were encountered. ¶ Mean value excludes asymmetric bridges [for which see GUNHUS (Fox *et al.*, 2001) and BORMUQ01 (Khan *et al.*, 1986)]. †† From CSD entry NALCYS02 (Takusagawa *et al.*, 1981), the published s.u. of the bond length is in parentheses. ‡‡ From CSD entry COQYUC01 (Gaspar *et al.*, 1999), the published s.u. of the bond length is in parentheses.

require both of the matches to be satisfied, so that both of the chemically equivalent N-H₃ and N-H₄ bond lengths contribute to the same distribution for analysis in *Vista*. For this work, we have modified the released *ConQuest* code to find all permutational matches of topologically symmetric substructures. Care must be taken when topological symmetry interacts with crystallographic symmetry, and this problem was addressed manually in the current analysis. We are continuing to work on problems raised by topological substructure symmetry so that appropriate solutions, in which our current modification will form a part, can be delivered to CSD users.

3. Results and discussion

Mean C-H, N-H, O-H and B-H bond lengths in various organic chemical environments are presented in Table 2, together with individual structure values for S-H and Si-H; the limited information on (C,N,O)-D bond lengths is also included here. Mean transition-metal Tr-H bond lengths are presented in Table 3 for both terminal-H and for Tr-H-Tr bonds in homometallic bridges; individual structure values are again presented in a number of cases.

3.1. C-H bonds

The increase in the number of available neutron studies has led to very significant increases in the numbers of C-H bonds available for analysis. Despite this increase, there is generally excellent correspondence between mean bond lengths derived in 1985 and the new mean values. The only case where some difference exists is for bonds involving methyl-H. As in 1985, the distributions of these bond lengths exhibit a tail towards shorter distances, presumably due to librational effects (not corrected for in the current analysis) and, hence, to a foreshortening of the mean C-H(methyl) bond length of around 0.01 Å by comparison with the median value. The smaller subset of C-D bond lengths agree well with their C-H counterparts, but here the mean $Z-CD_3$ bond length (Z = any non-H atom) is now much closer to the median of the distribution. The increased number of neutron datasets now allows mean distances for C(cyclopropyl)-H and Csp^1-H to be included in Table 2, albeit from rather sparse distributions. Reassuringly, the cyclopropyl-H value is close to that for Csp^2-H , as would be expected from the

$Csp^{2,2}$ hybrids used in exocyclic bond formation (see *e.g.* Allen, 1980, and references therein). The few data for acet-

Table 3

Distribution of structure determination temperature (T in K) for organic structures in the CSD containing selected classes of $X-H$ ($X = C, N, O$) bonds.

N_{obs} (%) are numbers and percentages of CSD entries in each subdivision.

Substructure	Total N_{obs}	$T \leq 60$ K N_{obs} (%)	$60 \leq T \leq 140$ K N_{obs} (%)	$T \geq 240$ K N_{obs} (%)	T (other) N_{obs} (%)
$X-H$ (all)	411	94 (22.9)	100 (24.3)	197 (47.9)	20 (4.9)
Csp^3-H	263	64 (24.3)	63 (24.0)	126 (47.9)	10 (3.8)
Z_3-Csp^3-H	108	21 (19.4)	21 (19.4)	64 (59.3)	2 (1.9)
$Z_2-Csp^3-H_2$	161	28 (17.4)	34 (21.1)	94 (58.4)	5 (3.1)
$Z-Csp^2-H_3$	126	49 (38.8)	30 (23.8)	43 (34.1)	4 (3.2)
Csp^2-H	196	50 (25.5)	50 (25.5)	79 (40.3)	17 (8.7)
$C(\text{ar})-H$	90	27 (30.0)	26 (28.9)	31 (34.4)	6 (6.7)
$O-H$	194	28 (14.4)	40 (20.6)	114 (58.8)	12 (6.2)
$N-H$	111	25 (22.5)	34 (30.6)	48 (43.2)	4 (3.5)
N^+-H	64	4 (6.3)	12 (18.8)	48 (75.0)	0 (0.0)

ylenic $C-H$ have a broad distribution (from 1.015 to 1.064 Å), but the overall $Csp^1-(H \text{ or } D)$ mean of 1.055 (3) Å is close to the 1.0605 ± 0.0003 Å reported for acetylene in the gas phase (Fast & Welsh, 1972).

3.2. O—H bonds

The initial distribution of $Z-O-H$ bond lengths (Fig. 1a) from a simple CSD search shows a long tail towards longer distances. These longer values were observed to arise from short, sometimes symmetrical and frequently intramolecular, $O-H \cdots O$ hydrogen bonds, as studied and discussed by *e.g.* Wilson *et al.* (2001), Vishweshwar *et al.* (2004) and many other authors. It was therefore decided to restrict averaging of $O-H$ bond lengths to those $O-H$ groups that take part in 'normal' intermolecular hydrogen bonding, defined here as having an $O-H \cdots O, N$ hydrogen bond length >1.45 Å based on relevant histograms obtained from CSD data. When the $O-H$ groups associated with very short hydrogen bonds were removed, the more normal distribution of Fig. 1(b) was obtained. This 'short hydrogen-bond removal' procedure was followed in deriving all mean values for $O-H$ and $O-D$ bond lengths cited in Table 2. Once again, the mean values derived from 1985 data are closely comparable with these new values.

3.3. N—H bonds

The availability of more neutron data has allowed us to provide mean $N-H$ bond lengths for a much wider range of chemical environments that was possible from 1985 data, although we note that these earlier values are entirely consistent with our current findings. In deriving the new data, we have routinely removed $N-H$ groups that are involved in very short hydrogen bonds, using the 1.45 Å cut-off discussed above. Also in the current work we have been able to provide realistic separate means for $-NH_2$ and $>NH$, and to classify the geometry around N in terms of pyramidal/planar variations, using criteria based on the sum of valence angles (Σ) around N: $N(\text{planar})$ has $\Sigma \geq 352.5^\circ$, $N(\text{pyramidal})$ has $\Sigma \leq 339.0^\circ$, with some intermediate entries having Σ in the range $339.0-352.5^\circ$.

3.4. Analysis of $X-H$ bond-length variation with temperature of structure determination

Although it is not possible to carry out librational corrections from CSD information, the database does record the

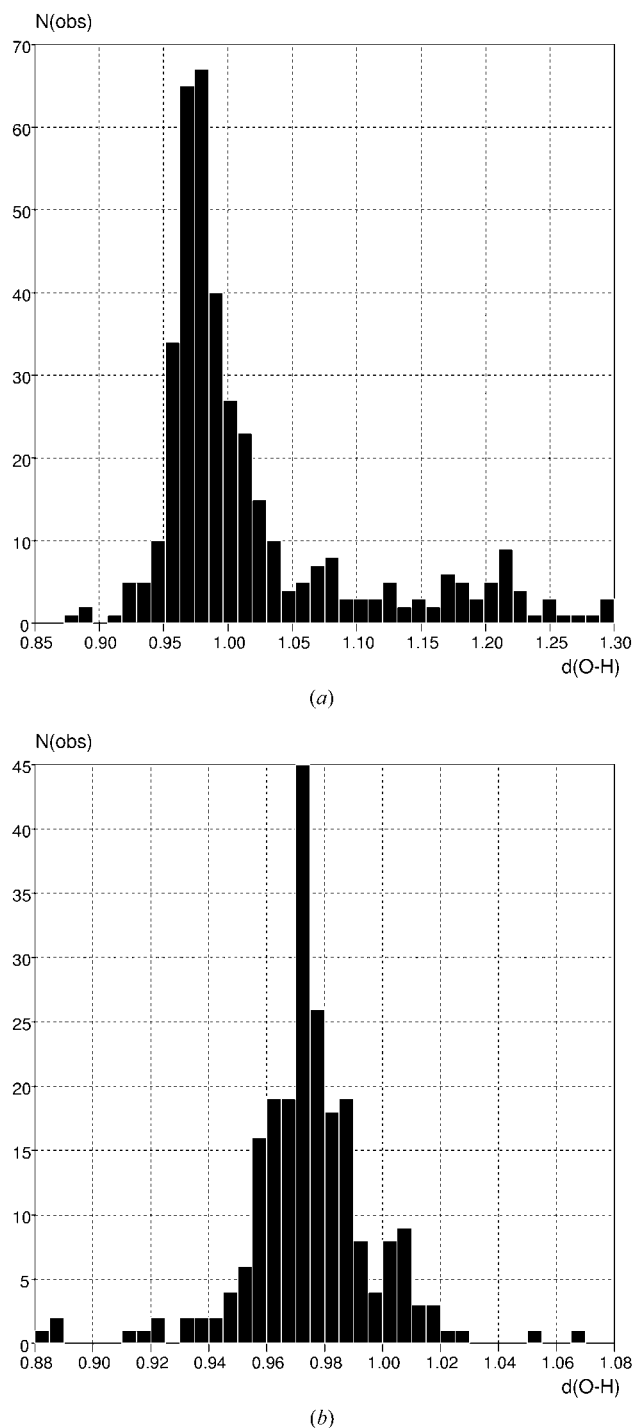


Figure 1
(a) Histogram of unfiltered $O-H$ bond lengths (Å) from neutron structures in the CSD; note the tail towards longer $O-H$ distances which arise from very short hydrogen bonds as discussed in the text. (b) Histogram of $O-H$ bond lengths (Å) from neutron structures in the CSD after removal of those $O-H$ bonds that are involved in hydrogen bonds $O-H \cdots A$ ($A = O, N$) having $H \cdots A$ distances ≤ 1.60 Å.

Table 4

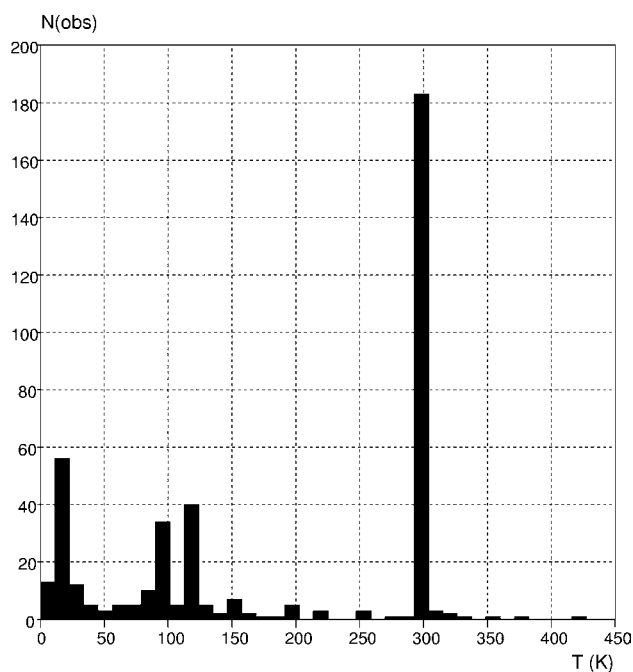
Mean $X-H$ distances (\AA) from single-crystal neutron diffraction studies of organic compounds for the three temperature ranges identified in Fig. 2 and Table 3.

Column headings are as described in §2. In the substructure column, Z is any element except H and C(ar) is an aromatic carbon; all σ_s values are multiplied by 10^3 .

Substructure	$T \leq 60$ K			$60 \leq T \leq 140$ K			$T \geq 240$ K		
	d	σ_s	n	d	σ_s	n	d	σ_s	n
Z_3-Csp^3-H	1.101	6	88	1.099	7	66	1.099	10	167
$Z_2-Csp^3-H_2$	1.097	10	154	1.097	6	136	1.087	16	371
$Z-Csp^3-H_3$	1.088	9	550	1.084	13	228	1.055	36	276
Csp^2 or C(ar)-H	1.085	7	333	1.085	9	184	1.083	12	901
C(ar)-H†	1.085	8	227	1.085	9	93	1.083	14	127
$Z-O-H‡§$	–	–	–	0.989	27	85	0.978	22	171
$Z-N-H¶$	1.020	10	63	1.019	13	53	1.011	20	110
$N^+-H§$	–	–	–	1.040	10	30	1.034	16	154

† C–H in phenyl rings only, data from polycyclic aromatic systems removed. ‡ O–H bonds averaged after removal of those instances where O–H is involved in symmetrical and very short intramolecular hydrogen bonds (see text). § Too few structures in one or both of the separate low-temperature ranges: low-temperature mean calculated from all structures having $T \leq 140$ K. ¶ N is three-coordinate, no formal charge, and with either one or two H substituents.

temperature of each structure determination (T in Kelvin). Hence, analysis of $X-H$ distances at different temperatures may indicate the extent of librational effects if sufficient numbers of low-temperature studies are available. A histogram of T for the 411 organic neutron structures that contain C–H, N–H or O–H bonds and pass the criteria in §2 is shown in Fig. 2. The T distribution can be divided into three major groupings having $T \leq 60$ K (94 structures, 22.9% of the total), $60 \text{ K} < T \leq 140$ K (100 structures, 24.3%) and $T \geq 240$ K (197 structures, 47.9%), with 20 structures determined at other temperatures (4.9%). Table 3 shows the numbers and


Figure 2

Distribution of temperature of structure determination (T in K) for 411 organic structures determined by neutron diffraction and containing $X-H$ bonds ($X = C, N, O$).

percentages of structures within these three temperature ranges for a variety of $X-H$ -containing substructures.

While the numbers of structures available at lower temperatures preclude the determination of mean $X-H$ bond lengths for the full range of chemical subdivisions presented in Table 2, it is possible to determine means for broader chemical environments and these data are presented in Table 4. The results show minimal variation of $X-H$ bond lengths with temperature for Z_3-Csp^3-H , Csp^2-H and C(ar)-H, even though data in the latter grouping is restricted to C–H in phenyl rings only. However, the $X-H$ bonds in $Z_2-Csp^3-H_2$, $Z-O-H$, $Z-N-H$ and N^+-H are consistently longer, by up to 0.01 \AA , at $T \leq 140$ K in comparison with the room-temperature values, but the most

pronounced temperature effect arises for C–H in methyl groups, where the bond-length difference between room temperature and $T \leq 60$ K structures is +0.03 \AA . The general message seems to be that libration corrections are essential to maximize the value of information derived from neutron studies. It is not possible to assess from the CSD how often such corrections are made and published, and such a highly detailed survey was not contemplated here.

3.5. Neutron-normalization values for $X-H$ for use in hydrogen-bond studies

The new data allow for improved ‘neutron normalization’ of $X-H$ distances for use in systematic and individual structure studies of hydrogen-bond geometry. In this context current CSD software, *ConQuest* and *Mercury*, both contain options for generating normalized H positions based on the default $X-H$ distances: C–H = 1.083, O–H = 0.983 and N–H = 1.009 \AA , which were derived from the compilation of Allen *et al.* (1987, 1992), either directly (N–H) or by taking a mean of means (C–H, O–H). Both programs allow these defaults to be edited, and normalization distances for other $X-H$ bond types may also be entered. This work indicates that small changes to these defaults are now appropriate, but how do we arrive at suitable overall values for a given $X-H$ from the data of Tables 2 and 4?

In line with the previous methodology, designed to avoid bias due to the domination of a particular $X-H$ subset by one or two specific chemical environments, we can derive a mean of means over similar chemical environments, where ‘similar’ can, of course, be seen as rather subjective. Within these caveats, the following would appear to be acceptable revisions. For C–H the default is taken as the average of the well determined means for Csp^3-H [Z_3-Csp^3-H , $Z_2-Csp^3-H_2$, but not C–H (methyl) for reasons noted in the discussion] and Csp^2-H [C(ar)-H, $C = Csp^2-H$] to give a mean default C–H distance of 1.089 \AA . The Csp^1-H value is not consid-

Table 5

Mean $X-H$ distances (\AA) from single-crystal neutron diffraction studies of metal-organic compounds.

Column headings are as described in §2. Data for bridging hydrides are for homometallic bridges, data from a very small subset of heterometallic bridges are not included.

Element	Terminal $M-H$				Homometallic $M-H-M$ bridges			
	d	σ_s	n	m	d	σ_s	n	m
Re—H	1.686	18	21	1.685	1.849	35	16	1.842
Os—H	1.649	14	15	1.648	1.819	24	50	1.823
W—H	1.739	23	13	1.737	1.916	18	3	1.920
Ir—H	1.593	21	7	1.593	1.821, 1.847	in CUSGAY01		
Fe—H	1.527	11	5	1.529	1.670	10	4	1.670
Ta—H \dagger	1.769, 1.774, 1.776 in TACPTH				1.977	36	7	1.976
Ru—H	1.626, 1.627 in NEBNEO				1.776	12	19	1.776
Pt—H	1.610 in CAKNEH01				1.656–2.049 in CAKNEH01			
Cr—H	—	—	—	—	1.723, 1.725 in KCPTCR01			
Zr—H	—	—	—	—	1.951, 1.975 in RIDJAP01			
Mn—H	1.573 in CABNIC01; 1.600 in FOKCEN02				—	—	—	—
Nb—H	1.817 in ZEYVAA02				—	—	—	—
Mo—H	1.684 in HCYPMO02; 1.712, 1.719 in KEWLUU02				1.816, 1.830 in CEHDAU01			
Rh—H	1.530 in SITKUB02; 1.536 in LAXPUV				—	—	—	—
	1.572 in EBUDGA02; 1.578, 1.583 in CONFEO01				—	—	—	—

\dagger CSD refcodes: CABNIC01 (Abramov *et al.*, 1998), CAKNEH01 (Chiang *et al.*, 1984), CEHDAU01 (Cotton *et al.*, 1984), CONFEO01 (Fernandez *et al.*, 1984), CUSGAY01 (Bau *et al.*, 1984), EBUDAG02 (Lam *et al.*, 2003), FOKCEN02 (La Placa *et al.*, 1969), HCYPMO02 (Schultz *et al.*, 1977), KCPTCR01 (Petersen *et al.*, 1981), KEWLUU02 (Baya *et al.*, 2007), LAXPUV (Hanke *et al.*, 1993), NEBNEO (Grellier *et al.*, 2005), RIDJAP01 (Basch *et al.*, 1999), SITKUB02 (Lam *et al.*, 2003), TACPTH (Wilson *et al.*, 1977), ZEYVAA02 (Bakhtmutov *et al.*, 2000).

ered due to the paucity of examples available. For O—H, the average of Csp^3-O-H , $O=Csp^2-O-H$ and $C(ar)-O-H$ gives a new default value of 0.993 \AA , while for N—H the mean value in Table 2 for $Z-N-H$ (all) at 1.015 \AA is appropriate. These suggested updated defaults are all longer than the current values, but only by 0.006 (C—H), 0.010 (O—H) and 0.006 \AA (N—H). However, these means are overall values taken across the full available temperature range, and take no account of the librational effects which are implicit in the results of Table 4. They are probably satisfactory for most routine work. Nevertheless, Table 4 reinforces the message of Table 2 that mean $X-H$ distances can now be determined that are dependent on both the hybridization state of X (for C and N) and on chemical environment. Thus, the lowest-temperature data of Table 4 indicate the following mean values (taking means of means where required): $Csp^3-H = 1.095 \text{\AA}$, $Csp^2-H = 1.085 \text{\AA}$, O—H (hydroxy) = 0.989 \AA , N—H = 1.020 \AA , and $N^+-H = 1.040 \text{\AA}$. Table 2 provides the only well defined mean value for O—H (carboxylic acid) of 1.018 \AA , and a rather poorly defined mean of 1.055 \AA for Csp^1-H . Any of these more specific mean values may be input by the user to override the default values in *ConQuest*, *Mercury* or other programs, depending on the nature of the search or analysis being undertaken.

3.6. Transition metal hydrides (Tr—H)

Table 1 shows that proportionally more metal-organic neutron studies have been carried out since 1985 by comparison with the situation for organic structures. Much of this activity has been directed at transition metal hydrides in order

to provide accurate H-atom positions and Tr—H geometries which can then be used in modelling H atoms in X-ray structure refinements. Thus, Orpen *et al.* (1989) used all the available data, both X-ray and neutron, and without differentiation due to the paucity of data available in the late 1980s. Table 5 shows that it is now possible to derive acceptable mean values for a significant number of Tr—H species, for both terminal and bridging ligands. Where comparison is possible, the earlier results are generally consistent with data in Table 3. We note that a small number of heterometallic bridges Tr_a-H-Tr_b ($Tr_a \neq Tr_b$) are also available from neutron studies in the CSD, but not in sufficient numbers for meaningful analysis here.

4. Conclusions

This study is reassuring in showing that mean $X-H$ bond lengths derived from limited data in the late 1980s are fully consistent, certainly within $2-3\sigma_m$, with nearly all of the overall mean values derived

here and presented in Table 2. However, the temperature-based mean values reported in Table 4 are indicative of the significant effects of thermal motion on $X-H$ distances. Now that the CSD has expanded by an order of magnitude, a similar study is in progress to re-examine some of the less well defined mean X-ray bond lengths involving non-H atoms in organic compounds presented by Allen *et al.* (1987, 1992). Certainly though, the increased amount of neutron data now available in the CSD does extend the range of chemical environments for which mean $X-H$ bond lengths can now be derived with acceptable statistical reliability. However, additional neutron data is required to generate reliable mean $X-H$ values in some relatively common chemical environments, *e.g.* acetylenic Csp^1-H , carboxylic acid O—H *etc.* Nevertheless, it is hoped that the current mean values will be of use in hydrogen-bond analyses, modelling experiments and particularly in density-deformation studies (see *e.g.* Hoser *et al.*, 2009).

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References

- Abramov, Y. A., Brammer, L., Klooster, W. T. & Bullock, R. M. (1998). *Inorg. Chem.* **37**, 6317–6328.
- Allen, F. H. (1980). *Acta Cryst.* **B36**, 81–96.
- Allen, F. H. (1986). *Acta Cryst.* **B42**, 515–522.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Doyle, M. J. & Taylor, R. (1991). *Acta Cryst.* **B47**, 29–40.

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* **2**, S1–S19.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1992). *International Tables for X-ray Crystallography*, Vol. C, pp. 685–706. Dordrecht, The Netherlands: Kluwer Academic Publishers.
- Bakhmutov, V. I., Howard, J. A. K., Keen, D. A., Kuzmina, L. G., Leech, M. A., Nikonov, G. I., Vorontsov, E. V. & Wilson, C. C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 1631–1635.
- Basch, H., Musaeov, D. G., Morokuma, K., Fryzuk, M. D., Love, J. B., Seidel, W. W., Albinati, A., Koetzle, T. F., Klooster, W. T., Mason, S. A. & Eckert, J. (1999). *J. Am. Chem. Soc.* **121**, 523–528.
- Bau, R., Chiang, M. Y., Wei, C. Y., Garlaschelli, L., Martinengo, S. & Koetzle, T. F. (1984). *Inorg. Chem.* **23**, 4758–4762.
- Baya, M., Houghton, J., Daran, J.-C., Poli, R., Male, L., Albinati, L. & Gutman, M. (2007). *Chem. Eur. J.* **13**, 5347–5359.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Cambridge Structural Database (1998). *Vista*. Cambridge Crystallographic Data Centre, Cambridge, England.
- Chiang, M. Y., Bau, R., Minghetti, G., Bandini, A. L., Banditelli, G. & Koetzle, T. F. (1984). *Inorg. Chem.* **23**, 122–124.
- Cotton, F. A., Leung, P. C. W., Roth, W. J., Schultz, A. J. & Williams, J. M. (1984). *J. Am. Chem. Soc.* **106**, 117–120.
- Fast, H. & Welsh, H. L. (1972). *J. Mol. Spectrosc.* **41**, 203–221.
- Fernandez, M. J., Bailey, P. M., Bentz, P. O., Ricci, J. S., Koetzle, T. F. & Maitlis, P. M. (1984). *J. Am. Chem. Soc.* **106**, 5458–5463.
- Fox, M. A., Goeta, A. E., Howard, J. A. K., Hughes, A. K., Johnson, A. L., Keen, D. A., Wade, K. & Wilson, C. C. (2001). *Inorg. Chem.* **40**, 173–175.
- Gaspar, P. P., Beatty, A. M., Chen, T., Haile, T., Lei, D., Winchester, W. R., Braddock-Wilking, J., Rath, N. P., Klooster, W. T., Koetzle, T. F., Mason, S. A. & Albinati, A. (1999). *Organometallics*, **18**, 3921–3932.
- Grellier, M., Vendier, L., Chaudret, B., Albinati, A., Rizzato, S., Mason, S. & Sabo-Etienne, S. (2005). *J. Am. Chem. Soc.* **127**, 17592–17593.
- Hanke, D., Wieghardt, K., Nuber, B., Lu, R. S., McMullan, R. K., Koetzle, T. F. & Bau, R. (1993). *Inorg. Chem.* **32**, 4300–4305.
- Hoser, A. A., Dominiak, P. M. & Woźniak, K. (2009). *Acta Cryst.* **A65**, 300–311.
- Khan, S. I., Chiang, M. Y., Bau, R., Koetzle, T. F., Shore, S. G. & Lawrence, S. H. (1986). *J. Chem. Soc. Dalton Trans.* pp. 1753–1757.
- La Placa, S. J., Hamilton, W. C., Ibers, J. A. & Davison, A. (1969). *Inorg. Chem.* **8**, 1928–1935.
- Lam, W. H., Shimada, S., Batsanov, A. S., Lin, Z., Marder, T. B., Cowan, J. A., Howard, J. A. K., Mason, S. A. & McIntyre, G. J. (2003). *Organometallics*, **22**, 4557–4568.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S83.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1992). *International Tables for X-ray Crystallography*, Vol. C, pp. 707–791. Dordrecht: Kluwer Academic Publishers.
- Petersen, J. L., Brown, R. K. & Williams, J. M. (1981). *Inorg. Chem.* **20**, 158–165.
- Schultz, A. J., Stearley, K. L., Williams, J. M., Mink, R. & Stucky, G. D. (1977). *Inorg. Chem.* **16**, 3303–3306.
- Taylor, R. & Allen, F. H. (1994). *Structure Correlation*, Vol. 1, edited by H.-B. Büergi & J. D. Dunitz, pp. 111–161. VCH: Weinheim, Germany.
- Takusagawa, F., Koetzle, T. F., Kou, W. W. H. & Parthasarathy, R. (1981). *Acta Cryst.* **B37**, 1591–1596.
- Vishweshwar, P., Babu, N. J., Nangia, A., Mason, S. A., Puschmann, H., Mondal, R. & Howard, J. A. K. (2004). *J. Phys. Chem. A*, **108**, 9406–9416.
- Wilson, C. C., Shankland, K. & Shankland, N. (2001). *Z. Kristallogr.* **316**, 303–306.
- Wilson, R. D., Koetzle, T. F., Hart, D. W., Kvik, A., Tipton, D. L. & Bau, R. (1977). *J. Am. Chem. Soc.* **99**, 1775–1781.