9.5. Typical interatomic distances: organic compounds

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9.5.1. Introduction

The determination of molecular geometry is of vital importance to our understanding of chemical structure and bonding. The majority of experimental data have come from X-ray and neutron diffraction, microwave spectroscopy, and electron diffraction. Over the years, compilations of results from these techniques have appeared sporadically. The first major compilation was Chemical Society Special Publication No. 11: *Tables of Interatomic Distances and Configuration in Molecules and Ions* (Sutton, 1958). This volume summarized results obtained by diffraction and spectroscopic methods prior to 1956; a supplementary volume (Sutton, 1965) extended this coverage to 1959. Summary tables of bond lengths between carbon and other elements were also published in Volume III of *International Tables for X-ray Crystallography* (Kennard, 1962). Some years later, the Cambridge Crystallographic Data Centre (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979) produced an atlas-style compendium of all organic, organometallic and metal-complex crystal structures published in the period 1960–1965 (Kennard, Watson, Allen, Isaacs, Motherwell, Pettersen & Town, 1972). More recently, a survey of geometries determined by spectroscopic methods (Harmony, Laurie, Kuczkowski, Schwendemann, Ramsay, Lovas, Lafferty & Maki, 1979) has extended coverage in this area to mid-1977.

The production of further comprehensive compendia of X-ray and neutron diffraction results has been precluded by the steep rise in the number of published crystal structures, as illustrated by Fig. 9.5.1.1. Printed compilations have been effectively superseded by computerized databases. In particular, the Cambridge Structural Database now (1991) contains bibliographic, chemical, and numerical results for some 86 000 organo-carbon crystal structures. This machine-readable file fulfils the function of a comprehensive structure-by-structure compendium of molecular geometries. However, the amount of data now held in the CSD is so large that there is also a need for concise, printed tabulations of average molecular dimensions.

The only tables of average geometry in general use are those contained in Sutton (1958, 1965) which list mean bond lengths for a variety of atom pairs and functional groups. Since these early tables were based on data obtained before 1960, we have used the CSD to prepare a new table of average bond lengths in organic compounds. Table 9.5.1.1 given here specifically lists average lengths for bonds involving the elements H, B, C, N, O, F, Si, P, S, Cl, As, Se, Br, Te, and I. Mean values are presented for 682 different bond types involving these elements.

9.5.2. Methodology

9.5.2.1. *Selection of crystallographic data*

All results given in Table 9.5.1.1 are based on X-ray and neutron diffraction results retrieved from the September 1985 version of the CSD. Neutron diffraction data only were used to derive mean bond lengths involving H atoms. This version of the CSD contained results for 49 854 single-crystal diffraction studies of organo-carbon compounds; 10 324 of these satisfied the acceptance criteria listed below and were used in the averaging procedures:

(i) Structure is 'organic', *i.e.* belongs to the CSD chemical classes 1–65 or 70 (*Cambridge Crystallographic Data Centre User Manual*, 1978).

(ii) Atomic coordinates for the structure have been published and are available in the CSD.

(iii) Structure was determined from diffractometer data.

(iv) Structure does not contain unresolved numeric data errors from the original publication (such errors are usually typographical and are normally resolved by consultation with the authors).

(v) Structure was not reported to be disordered.

(vi) Only structures of higher precision were included on the basis of *either* (*a*) the crystallographic *R* factor was ≤ 0.07 and the reported mean estimated standard deviation (e.s.d.) of the C—C bond lengths was ≤ 0.010 Å (corresponds to AS flag = 1 or 2 in the CSD), *or* (*b*) the crystallographic *R* factor ≤ 0.05 and the mean e.s.d. for C—C bonds was not available in the database (AS = 0 in the CSD).

(vii) Where the structure of a given compound had been determined more than once within the limits of (i)–(vi), then only the most precise determination was used.

9.5.2.2. *Program system*

All calculations were performed on the University of Cambridge IBM 3081 D using the programs *BIBSER*, *CONNSER*, *RETRIEVE*, *GEOM*78, and *PLUTO*78 (Allen *et al.*, 1979). A stand-alone program was written to implement the selection criteria, whilst a new program (*STATS*) was written to perform the statistical calculations described below. It was also necessary to modify *CONNSER* to improve the precision with which it locates chemical substructures. In particular, the program was altered to permit the location of atoms with specified coordination numbers. This was essential in the case of carbon so that atoms with coordination numbers 2, 3 and 4 (equivalent to formal hybridization states sp^1, sp^2, sp^3) could be distinguished easily and reliably. Considerable care was taken to ensure that the correct molecular fragment was located by *GEOM*78 in the generation of geometrical tabulations. This often involved the explicit specification of H atoms in fragments, and the extensive use of geometrical tests on valence and torsion angles. Considerable use was also made of chemical structural diagrams, which are available in the Cambridge in-house version
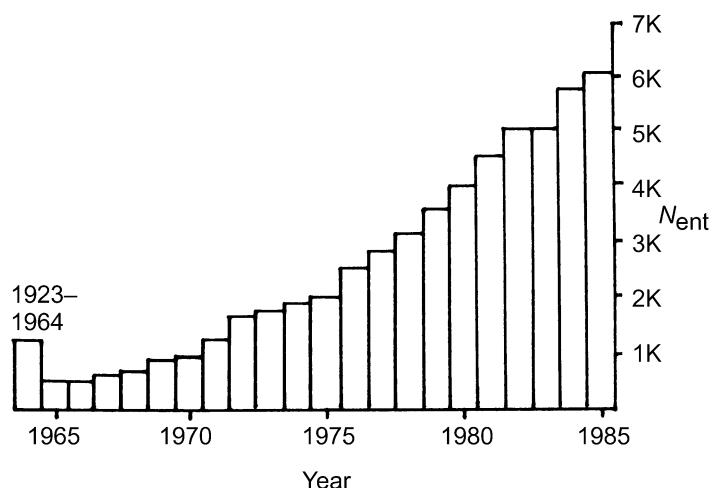

Fig. 9.5.1.1. Growth of the Cambridge Structural Database 1965–1985 as number of entries (N_{ent}) published in a given year.

of the CSD for some 81% of all entries. Chemical diagrams proved useful, for example, in identifying the various coordination environments commonly adopted by atoms such as As, B, P, *etc*.

9.5.2.3. *Classification of bonds*

The classification of bonds used in Table 9.5.1.1 is based on common functional groups, rings and ring systems, coordination spheres, *etc*. It is designed: (i) to appear logical, useful and reasonably self-explanatory to chemists, crystallographers, and others who may use the table; (ii) to permit a meaningful average value to be cited for each bond length. With reference to (ii), it was considered that a sample of bond lengths could be averaged meaningfully if: (*a*) the sample was unimodally distributed; (*b*) the sample standard deviation (σ) was reasonably small, ideally less than *ca* 0.02 Å; (*c*) there were no conspicuous outlying observations – those that occurred at $> 4\sigma$ from the mean were automatically eliminated from the sample by *STATS*, other outliers were inspected carefully; (*d*) there were no compelling chemical reasons for further subdivision of the sample.

9.5.2.4. *Statistics*

Where there are less than four independent observations of a given bond length, then each individual observation is given explicitly in the table. In all other cases, the following statistics were generated by the program *STATS*.

(i) The unweighted sample mean, d, where

$$d = \sum_{i=1}^{n} d_i/n$$

and d_i is the ith observation of the bond length in a total sample of n observations. Recent work (Taylor & Kennard, 1983, 1985, 1986) has shown that the unweighted mean is an acceptable (even preferable) alternative to the weighted mean, where the ith observation is assigned a weight equal to $1/\sigma^2(d_i)$. This is especially true (Taylor & Kennard, 1985) where structures have been pre-screened on the basis of precision.

(ii) The sample median, m. This has the property that half of the observations in the sample exceed m, and half fall short of it.

(iii) The sample standard deviation, denoted here as σ, where:

$$\sigma = \sum_{i=1}^{n} [(d_i - d)^2/(n - 1)]^{1/2}.$$

(iv) The lower quartile for the sample, q_l. This has the property that 25% of the observations are less than q_l and 75% exceed it.

(v) The upper quartile for the sample, q_u. This has the property that 25% of the observations exceed q_u, and 75% fall short of it.

(vi) The number (n) of observations in the sample.

The statistics given in the final table correspond to distributions for which the automatic 4σ cut-off (see above) had been applied, and any manual removal of additional outliers (an infrequent operation) has been performed. In practice, a very small percentage of observations was excluded by these methods. The major effect of removing outliers is to improve the sample standard deviation, as shown in Fig. 9.5.2.1 in which a single observation is deleted.

The statistics chosen for tabulation effectively describe the distribution of bond lengths in each case. For a symmetrical, normal distribution: the mean (d) will be approximately equal to the median (m); the lower and upper quartiles (q_l, q_u) will be approximately symmetric about the median: $m - q_l \simeq q_u - m$,

and 95% of the observations may be expected to lie within $\pm 2\sigma$ of the mean value. For a skewed distribution, d and m may differ appreciably and q_l and q_u will be asymmetric with respect to m. When a bond-length distribution is negatively skewed as in Fig. 9.5.2.2, *i.e.* very short values are more common than very long values, then it may be due to thermal-motion effects; the distances used to prepare the table were not corrected for thermal libration.

In a number of cases, the initial bond-length distribution was clearly bimodal, as in Fig. 9.5.2.3(*a*). All cases of bimodality were resolved on chemical grounds before inclusion in the table, on the basis of hybridization, conformation-dependent conjugation interactions, *etc*. For example, the histogram of Fig. 9.5.2.3(*a*) was resolved into the two discrete unimodal distributions of Figs. 9.5.2.3(*b*), (*c*), which correspond to planar N(sp^2), pyramidal N(sp^3), respectively. The mean valence angle at N was used as the discriminator, with a range of 108–114° for N(sp^3) and $\geq 117.5°$ for N(sp^2).

9.5.3. Content and arrangement of the table

The upper triangular matrix of Fig. 9.5.3.1(*a*) shows the 120 possible element-pair combinations that can be formed from the 15 elements As, B, Br, C, Cl, F, H, I, N, O, P, S, Se, Si, Te.
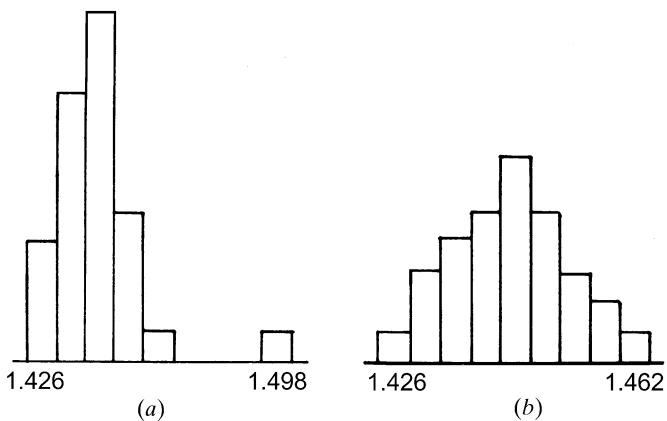
Fig. 9.5.2.1. Effect of the removal of outliers (contributors that are $> 4\sigma$ from the mean) for the C—C bond in C_{ar}—C$\equiv$N fragments. Relevant statistics (see text) are:

	d	m	σ	q_l	q_u	n
(*a*) before	1.445	1.444	0.012	1.436	1.448	32
(*b*) after	1.455	1.444	0.008	1.436	1.448	31.
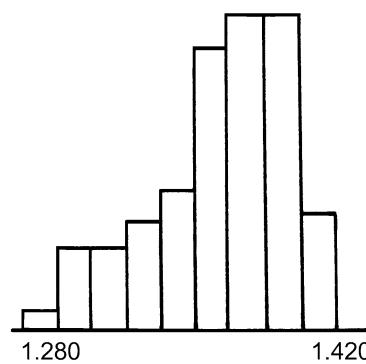
Fig. 9.5.2.2. Skewed distribution of B—F bond lengths in BF_4^- ions: $d = 1.365$, $m = 1.372$, $\sigma = 0.029$, $q_l = 1.352$, $q_u = 1.390$ for 84 observations. Note that $d \neq m$ and that q_l, q_u are asymmetrically disposed about the mean d.

Fig. 9.5.3.1(*a*) contains the number of discrete average bond lengths given in the table for each element pair. 682 average values are cited for 65 element pairs, of which 511 (75%) involve carbon. Bond-length values from individual structures are given for a further 30 element pairs indicated by an asterisk in Fig. 9.5.3.1(*a*). Individual structures are identified by their CSD reference code (*e.g.* BOGSUL), and short-form literature references, ordered alphabetically by reference code, are given in Appendix 2. For eight element pairs, the acceptance criterion (vi) was relaxed to include all available structures, irrespective of precision. These entries are denoted by a dagger in the table. No bonds were found for 25 element pairs within the subset of CSD used in this study.

Each entry in Table 9.5.1.1 contains nine columns, of which six record the statistics of the bond-length distribution described above. The content of the remaining three columns: 'Bond', 'Structure', 'Note', are now described.

9.5.3.1. *Ordering of entries: the 'Bond' column*

For an element pair $X-Y$, the primary ordering is alphabetic by element symbols according to the rows of Fig. 9.5.3.1(*a*); *i.e.* X changes slowest, Y fastest. The complete sequence runs from As—As to Te—Te with bonds involving carbon in the natural position: As—C...C—C...C—Te. Within a given $X-Y$ pair, a secondary ordering is based on the coordination numbers (j) of X and Y, and on the nature of the bond between them. The bond definition is of the form $X(j)-Y(j)$, with j decreasing fastest for Y, slowest for X, and with all single bonds preceding any multiple bonds. For carbon, the formal hybridization state replaces (but is equivalent to) the coordination number and it is for this element that the ordering rules are most clearly required. The ordering of the most populous C—C, C—N, C—O sections is illustrated in Fig. 9.5.3.1(*b*). The 13 possible C—C combinations follow the sequence Csp^3-Csp^3, Csp^3-Csp^2, Csp^3-C_{ar}, Csp^3-Csp^1, Csp^2-Csp^2, Csp^2-C_{ar}, Csp^2-Csp^1, $C_{ar}-C_{ar}$, $C_{ar}-Csp^1$, Csp^1-Csp^1, $Csp^2=Csp^2$, $C_{ar}\dddot{}C_{ar}$, $Csp^1\equiv Csp^1$. The symbol C_{ar} represents

aryl carbon in six-membered rings, which is treated separately from Csp^2 throughout the table. The symbol $\dddot{}$ is used to indicate a delocalized double or aromatic bond according to context.

9.5.3.2. *Definition of 'Substructure'*

The chemical environment of each bond is normally defined by a linear formulation of the substructure. The target bond is set in bold type, *e.g.* $C_{ar}-\mathbf{C}\equiv\mathbf{N}$ (aryl cyanides); $C-\mathbf{CH_2}-\mathbf{O}-C_{ar}$ (primary alkyl aryl ethers); $(C-O)_2-\mathbf{P}(\dddot{}\mathbf{O})_2$ (phosphate diesters). Occasionally, the chemical name of a functional group or ring system is used to define bond environment, *e.g.* in naphthalene, C2—C3; in imidazole, N1—C2. To avoid any possible ambiguity in these cases, we include numbered chemical diagrams in Fig. 9.5.3.2.

	As	B	Br	C	Cl	F	H	I	N	O	P	S	Se	Si	Te
As	1	*	*	6	1	1	0	*	2	2	+	2	+	+	+
B		2	2	5	2	2	0	*	4	2	1	4	0	0	0
Br			1	5	+	0	0	*	*	1	*	+	*	*	*
C				175	16	13	10	2	97	119	12	40	3	6	2
Cl					*	0	0	*	*	1	2	1	*	2	1
F						0	0	0	1	0	2	2	0	3	*
H							0	0	2	3	0	0	0	0	0
I								1	*	1	+	*	0	0	1
N									15	18	15	8	*	6	*
O										4	20	9	*	5	2
P											2	3	1	1	*
S												5	1	1	2
Se													1	0	+
Si														1	0
Te															*

(*a*)

(*a*)

(*b*)

(*c*)
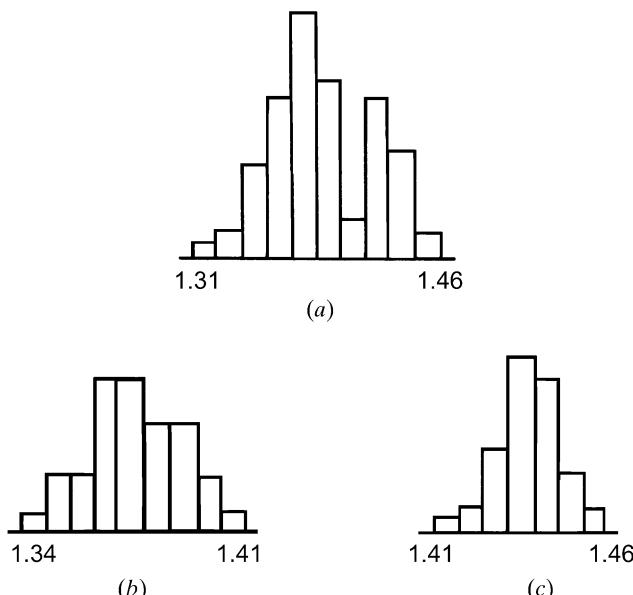
Fig. 9.5.2.3. Resolution of the bimodal distribution of C—N bond lengths in $C_{ar}-N(Csp^3)_2$ fragments: (*a*) complete distribution; (*b*) distribution for planar N, mean valence angle at $N > 117.6°$; (*c*) distribution for pyramidal N, mean valence angle at N in the range 108–114°.

	C—C							C—N				C—O	
	Csp^3	Csp^2	C_{ar}	Csp^1	Csp^2	C_{ar}	Csp^1	N(4)	N(3)	N(2)	N(1)	O(2)	O(1)
Csp^3-	27	30	6	4	-	-	-	5	22	2	-	60	-
Csp^2-		24	14	2	-	-	-	-	28	1	-	17	-
$C_{ar}-$			2	2	-	-	-	1	9	2	-	4	-
Csp^1-				1	-	-	-	-	-	-	-	-	-
$Csp^2=$					34	-	-	-	1	8	-	-	38
$C_{ar}\dddot{}$						24	-	-	3	9	-	-	-
$Csp^1\equiv$							5	-	-	1	5	-	-

(*b*)

Fig. 9.5.3.1. (*a*) Distribution of mean bond-length values reported in the table by element pair. An asterisk indicates a bonded pair represented by less than four contributors in the original data set. A '+' indicates bonded pairs located when restrictions on R factor and reported e.s.d. limits were lifted (see text). (*b*) Distribution of mean bond-length values reported in the table for C—C, C—O, C—N.

A combination of chemical name and linear formulation is often employed to increase the precision of the definition, *e.g.* NH_2—C=O in acyclic amides; C=C—$C(=O)$—C=O in benzoquinone. Finally, for very simple ions, the accepted conventional representation is deemed to be sufficient, *e.g.* in NO_3^-, SO_4^{2-}, *etc*.

The chemical definition of substructure may be followed by brief qualifying information, concerning substitution, conformational restrictions, *etc*. For example: Csp^3—Csp^3: in cyclobutane (any substituent); X—C—F_3 (X = C, H, N, O); C_{ar}—NH—Csp^3 (Nsp^3: pyramidal). Where the generic symbol X is unqualified, it denotes any element type, including hydrogen. If the qualifying information is too extensive, then it will be given as a table footnote (see below).

The 'Substructure' column is designed to convey as much unambiguous information as possible within a small space. For Csp^3, we have employed the short forms C* and C#. C* indicates Csp^3 whose bonds, additional to those specified in the linear formulation, are to C or H atoms only. C*—OH would then represent the group of alcohols CH_3—OH, —C—CH_2—OH, —C_2—CH—OH and —C_3—C—OH. C* is frequently used to restrict the secondary environment of a given bond to avoid the perturbing influence of, *e.g.*, electronegative substituents. The symbol C# is merely a space-saving device to indicate any Csp^3 atom and includes C* as a subset.

9.5.3.3. *Use of the 'Note' column*

The 'Note' column refers to the footnotes collected in Appendix 1. These record additional information as follows: (*a*) additional details concerning the chemical definition of substructures, *e.g.* the omission of three- and four-membered rings; (*b*) statements of geometrical constraints used in obtaining the cited average, *e.g.* definition of planarity or pyramidality at
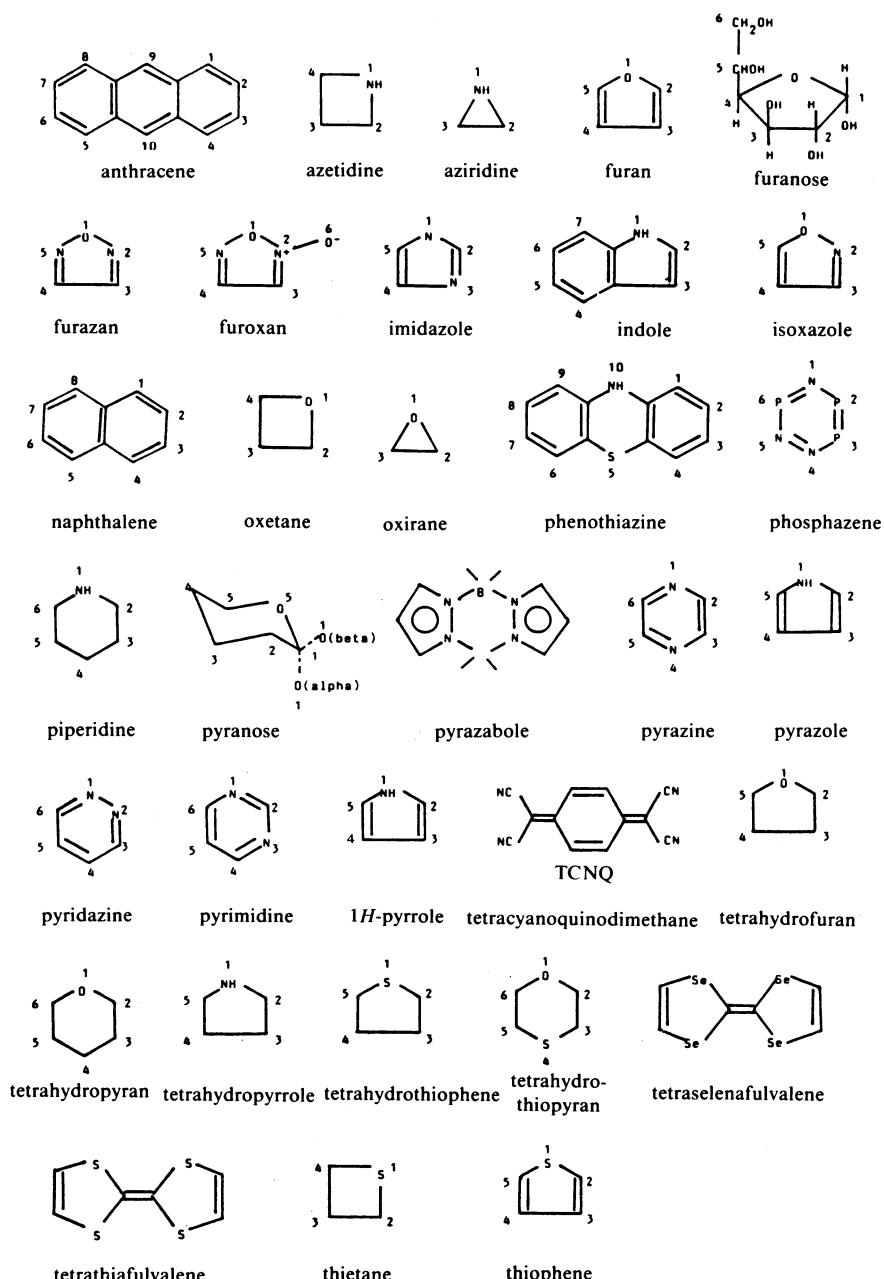

Fig. 9.5.3.2. Alphabetized index of ring systems referred to in the table; the numbering scheme used in assembling the bond-length data is given where necessary.

N, torsional constraints in conjugated systems; (c) any peculiarities of a particular bond-length distribution, e.g. sample dominated by $C* =$ methyl; (d) references to previously published surveys of crystallographic results relevant to the substructure in question. We do not claim that these references are in any way comprehensive and we would be grateful to authors for notification (to FHA) of any omissions. This will serve to improve the content of any future version of the table.

9.5.4. Discussion

It should be remembered that this table has been derived from the organic section of CSD. We are aware that a number of organic bond types which occur very frequently in organometallics and metal complexes (e.g. $C \cdots C$ in cyclopentadienyl, C—P in triphenylphosphine, etc.) are either absent or poorly represented in this work. These omissions are rectified in Chapter 9.6. We also note that certain bond types listed here (e.g. As—O, Si—O, Si—N, etc.) will occur with greater frequency in inorganic compounds. The interested reader is referred to the Inorganic Crystal Structure Database (Bergerhof, Hundt, Sievers & Brown, 1983) for a machine-readable compendium of more relevant structural data.

The tabulation given here represents the first stage in a major project designed to obtain the average geometries of function groups, rigid rings, and the low-energy conformations of flexible rings. Details of mean bond lengths, valence angles, and conformational preferences in a wide range of substructures will form the basis of a machine-readable 'fragment library' for use in molecular modelling and other areas of research. The systematic survey will be extended to derive information about distances, angles, directionality, and environmental dependence of hydrogen bonds and non-bonded interactions.

APPENDIX 1
Notes to Table 9.5.1.1

(1) Sample dominated by B—CH_3. For longer bonds in B^-—CH_3, see LITMEB10 [B(4)—CH_3 = 1.621–1.644 Å].

(2) $p(\pi)$—$p(\pi)$ bonding with Bsp^2 and Nsp^2 coplanar ($\tau BN = 0 \pm 15°$) predominates. See G. Schmidt, R. Boese & D. Bläser [Z. Naturforsch. Teil B (1982), **37**, 1230–1233].

(3) 84 observations range from 1.38 to 1.62 Å and individual values depend on substituents on B and O. For a discussion of borinic acid adducts, see S. J. Rettig & J. Trotter [Can. J. Chem. (1982), **60**, 2957–2964].

(4) See M. Kaftory (1983). [In The chemistry of functional groups. Supplement D: The chemistry of halides, pseudohalides and azides, Part 2, Chap. 24, edited by S. Patai & Z. Rappoport. New York: John Wiley.]

(5) Bonds that are endocyclic or exocyclic to any three- or four-membered rings have been omitted from all averages in this section.

(6) The overall average given here is for Csp^3—Csp^3 bonds which carry only C or H substituents. The value cited reflects the relative abundance of each 'substitution' group. The 'mean of means' for the nine subgroups is 1.538 ($\sigma = 0.022$) Å.

(7) See (a) F. H. Allen [Acta Cryst. (1980), **B36**, 81—96] and (b) F. H. Allen [Acta Cryst. (1981), **B37**, 890–900].

(8) See F. H. Allen [Acta Cryst. (1984), **B40**, 64–72].

(9) See F. H. Allen [Tetrahedron (1982), **38**, 2843–2853].

(10) See F. H. Allen [Tetrahedron (1982), **38**, 645–655].

(11) Cyclopropanones and cyclobutanones excluded.

(12) See W. B. Schweizer & J. D. Dunitz [Helv. Chim. Acta (1982), **65**, 1547–1554].

(13) See L. Norskov-Lauritsen, H.-B. Bürgi, P. Hoffmann & H. R. Schmidt [Helv. Chim. Acta (1985), **68**, 76–82].

(14) See P. Chakrabarti & J. D. Dunitz [Helv. Chim. Acta (1982), **65**, 1555–1562].

(15) See J. L. Hencher (1978). [In The chemistry of the $C \equiv C$ triple bond, Chap. 2, edited by S. Patai. New York: John Wiley.]

(16) Conjugated: torsion angles about central C—C single bond is $0 \pm 20°$ (cis) or $180 \pm 20°$ (trans).

(17) Unconjugated: torsion angle about central C—C single bond is 20–160°.

(18) Other conjugative substituents excluded.

(19) TCNQ is tetracyanoquinodimethane (see diagrams).

(20) No difference detected between $C2 \cdots C3$ and $C3 \cdots C4$ bonds.

(21) Derived from neutron diffraction results only.

(22) Nsp^3: pyramidal; mean valence angle at N is in the range 108–114°.

(23) Nsp^2: planar; mean valence angle at N is $\geq 117.5°$.

(24) Cyclic and acyclic peptides.

(25) See R. H. Blessing [J. Am. Chem. Soc. (1983), **105**, 2776–2783].

(26) See L. Lebioda [Acta Cryst. (1980), **B36**, 271–275].

(27) $n = 3$ or 4; i.e. tri- or tetrasubstituted ureas.

(28) Overall value also includes structures with mean valence angle at N in the range 115–118°.

(29) See F. H. Allen & A. J. Kirby [J. Am. Chem. Soc. (1984), **106**, 6197–6200].

(30) See A. J. Kirby (1983). [The anomeric effect and related stereoelectronic effects at oxygen. Berlin: Springer.]

(31) See B. Fuchs, L. Schleifer & E. Tartakovsky [Nouv. J. Chim. (1984), **8**, 275–278].

(32) See S. C. Nyburg & C. H. Faerman [J. Mol. Struct. (1986), **140**, 347–349].

(33) Sample dominated by P—CH_3 and P—CH_2—C.

(34) Sample dominated by $C* =$ methyl.

(35) See A. Kálmán, M. Czugler & G. Argay [Acta Cryst. (1981), **B37**, 868–877].

(36) Bimodal distribution resolved into 22 'short' bonds and 5 longer outliers.

(37) All 24 observations come from BUDTEZ.

(38) 'Long' O—H bonds in centrosymmetric $O \cdots H \cdots O$ H-bonded dimers are excluded.

(39) N—N bond length also dependent on torsion angle about N—N bond and on nature of substituent C atoms – these effects are ignored here.

(40) N pyramidal has average angle at N in the range 100–113.5°; N planar has average angle $\geq 117.5°$.

(41) See R. R. Holmes & J. A. Deiters [J. Am. Chem. Soc. (1977), **99**, 3318–3326].

(42) No detectable variation in S=O bond length with type of C substituent.

APPENDIX 2
Short-form references to individual CSD entries cited by reference code in Table 9.5.1.1

REFCODE	Journal	Vol.	Page	Year
ACBZPO01	J. Am. Chem. Soc.	97	6729	1975
ACLTEP	J. Organomet. Chem.	184	417	1980
ASAZOC	Dokl. Akad. Nauk SSSR	249	120	1979
BALXOB	J. Am. Chem. Soc.	103	4587	1981

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Code	Journal	Vol	Page	Year
BAPPAJ	Inorg. Chem.	20	3071	1981
BARRIV	Acta Chem. Scand. Ser. A	35	433	1981
BAWFUA	Cryst. Struct. Commun.	10	1345	1981
BAWGAH	Cryst. Struct. Commun.	10	1353	1981
BECTAE	J. Org. Chem.	46	5048	1981
BELNIP	Z. Naturforsch. Teil B	37	299	1982
BEMLIO	Chem. Ber.	115	1126	1982
BEPZEB	Cryst. Struct. Commun.	11	175	1982
BETJOZ	J. Am. Chem. Soc.	104	1683	1982
BETUTE10	Acta Chem. Scand. Ser. A	30	719	1976
BIBLAZ	Zh. Strukt. Khim.	22	118-4	1981
BICGEZ	Z. Anorg. Allg. Chem.	486	90	1982
BIHXIZ	J. Chem. Soc. Chem. Commun.		982	1982
BIRGUE10	Z. Naturforsch. Teil B	38	20	1983
BIRHAL10	Z. Naturforsch. Teil B	37	1410	1982
BIZJAV	J Organomet. Chem.	238	C1	1982
BOGPOC	Z. Naturforsch. Teil B	37	1402	1982
BOGSUL	Z. Naturforsch. Teil B	37	1230	1982
BOJLER	Z. Anorg. Allg. Chem.	493	53	1982
BOJPUL	Acta Chem. Scand. Ser. A	36	829	1982
BOPFER	Chem. Ber.	116	146	1983
BOPFIV	Chem. Ber.	116	146	1983
BOVMEE	Acta Cryst. Sect. B	38	1048	1982
BQUINI	Acta Cryst. Sect. B	35	1930	1979
BTUPTE	Acta Chem. Scand. Ser. A	29	738	1975
BUDTEZ	Z. Naturforsch. Teil B	38	454	1983
BUPSIB10	Z. Anorg. Allg. Chem.	474	31	1981
BUSHAY	Z. Naturforsch. Teil B	38	692	1983
BUTHAZ10	Inorg. Chem.	23	2582	1984
BUTSUE	J. Chem. Soc. Chem. Commun.		862	1983
BUWZUO	Acta Chem. Scand. Ser. A	37	219	1983
BZPRIB	Z. Naturforsch. Teil B	36	922	1981
BZTPPI	Inorg. Chem.	17	894	1978
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CETTAW	Chem. Ber.	117	1089	1984
CETUTE	Acta Chem. Scand. Ser. A	29	763	1975
CEYLUN	Isv. Akad. Nauk SSR Ser. Khim.		2744	1983
CIFZUM	Acta Chem. Scand. Ser. A	38	289	1984
CIHRAM	Angew. Chem. Int. Ed. Engl.	23	302	1984
CILRUK	J. Chem. Soc. Chem. Commun.		1023	1984
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CINTEY	Dokl. Acak. Nauk SSSR	274	615	1984
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CISMUM	Z. Naturforsch. Teil B	39	485	1984
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COJCUZ	Chem. Ber.	117	2686	1984
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COZPIQ	Chem. Ber.	117	2063	1984
COZVIW	Z. Anorg. Allg. Chem.	515	7	1984
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DSEMOR10	J. Chem. Soc. Dalton Trans.		628	1980
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HMTNTI	Z. Anorg. Allg. Chem.	409	237	1974
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IFORAM	Monatsh. Chem.	105	621	1974
IODMAM	Acta Cryst. Sect. B	33	3209	1977
IPMUDS	Acta Cryst. Sect. B	29	2128	1973
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MESIAD	Z. Naturforsch. Teil B	35	789	1980
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NBBZAM	Z. Naturforsch. Teil B	32	1416	1977
OPIMAS	Aust. J. Chem.	30	2417	1977
OPNTEC10	J. Chem. Soc. Dalton Trans.		251	1982
PHASCL	Acta Cryst. Sect. B	37	1357	1981
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PNPOSI	J. Am. Chem. Soc.	90	5102	1968
SEBZQI	J. Chem. Soc. Chem. Commun.		325	1977
SPSEBU	Acta Chem. Scand. Ser. A	33	403	1979
TEACBR	Cryst. Struct. Commun.	3	753	1974
THINBR	J. Am. Chem. Soc.	92	4002	1970
TMPBTI	Acta Cryst. Sect. B	31	1116	1975
TPASSN	J. Chem. Soc. Dalton Trans.		514	1977
TPASTB	Cryst. Struct. Commun.	5	39	1976
TPHOSI	Z. Naturforsch. Teil B	34	1064	1979
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ZCMXSP	Cryst. Struct. Commun.	6	93	1977

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Table 9.5.1.1. *Average lengths (Å) for bonds involving the elements H, B, C, N, O, F, Si, P, S, Cl, As, Se, Br, Te, and I*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
As(3)—As(3)	X_2—**As**—**As**—X_2	2.459	2.457	0.011	2.456	2.466	8	
As—B	see CUDLOC (2.065), CUDLUI (2.041)							
As—Br	see CODDEE, CODDII (2.346–3.203)							
As(4)—C	X_3—**As**—**CH**$_3$	1.903	1.907	0.016	1.893	1.916	12	
	$(X)_2$(C, O, S=)**As**—**C**sp^3	1.927	1.929	0.017	1.921	1.937	16	
	As—**C**$_{ar}$ in Ph$_4$As$^+$	1.905	1.909	0.012	1.897	1.912	108	
	$(X)_2$(C, O, S=)**As**—**C**$_{ar}$	1.922	1.927	0.016	1.908	1.934	36	
As(3)—C	X_2—**As**—**C**sp^3	1.963	1.965	0.017	1.948	1.978	6	
	X_2—**As**—**C**$_{ar}$	1.956	1.956	0.015	1.944	1.964	41	
As(3)—Cl	X_2—**As**—**Cl**	2.268	2.256	0.039	2.247	2.281	10	
As(6)—F	in **AsF**$_6^-$	1.678	1.676	0.020	1.659	1.695	36	
As(3)—I	see OPIMAS (2.579, 2.590)							
As(3)—N(3)	X_2—**As**—**N**—X_2	1.858	1.858	0.029	1.839	1.873	19	
As(4)=N(2)	see TPASSN (1.837)							
As(4)—O	$(X)_2$(O=)**As**—**OH**	1.710	1.712	0.017	1.695	1.726	6	
As(3)—O	see ASAZOC, PHASOC01 (1.787–1.845)							
As(4)=O	X_3—**As**=**O**	1.661	1.661	0.016	1.652	1.667	9	
As(3)—P(3)	see BELNIP (2.350, 2.362)							†
As(3)=P(3)	see BUTHAZ10 (2.124)							†
As(3)—S	X_2—**As**—**S**	2.275	2.266	0.032	2.247	2.298	14	
As(4)=S	X_3—**As**=**S**	2.083	2.082	0.004	2.080	2.086	9	
As(3)—Se(2)	see COSDIX, ESEARS (2.355–2.401)							†
As(3)—Si(4)	see BICGEZ, MESIAD (2.351–2.365)							†
As(3)—Te(2)	see ETEARS (2.571, 2.576)							†
B(n)—B(n)	n = 5–7 in boron cages	1.775	1.773	0.031	1.763	1.786	688	
B(4)—B(4)	see CETTAW (2.041)							
B(4)—B(3)	see COFVOI (1.698)							
B(3)—B(3)	X_2—**B**—**B**—X_2	1.701	1.700	0.014	1.691	1.712	8	
B(6)—Br		1.967	1.971	0.014	1.954	1.979	7	†
B(4)—Br		2.017	2.008	0.031	1.990	2.044	15	†
B(n)—C	n = 5–7: **B**—**C** in cages	1.716	1.717	0.020	1.707	1.728	96	
	n = 3–4: **B**—**C**sp^3 not cages	1.597	1.599	0.022	1.585	1.611	29	*1*
	n = 4: **B**—**C**$_{ar}$	1.606	1.607	0.012	1.596	1.615	41	
	B$^-$—**C**$_{ar}$ in Ph$_4$B$^-$	1.643	1.643	0.006	1.641	1.645	16	
	n = 3: **B**—**C**$_{ar}$	1.556	1.552	0.015	1.546	1.566	24	
B(n)—Cl	**B**(5)—**Cl** and **B**(3)—**Cl**	1.751	1.751	0.011	1.743	1.761	14	
	B(4)—**Cl**	1.833	1.833	0.013	1.821	1.843	22	
B(4)—F	**B**—**F** (B neutral)	1.366	1.368	0.017	1.356	1.375	25	
	B$^-$—**F** in BF$_4^-$	1.365	1.372	0.029	1.352	1.390	84	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
B(4)—I	see TMPBTI (2.220, 2.253)							
B(4)—N(3)	X_3—**B**—**N**(=C)(X)	1.611	1.617	0.013	1.601	1.625	8	
	in pyrazaboles	1.549	1.552	0.015	1.536	1.560	10	
B(3)—N(3)	X_2—**B**—**N**—C_2: all coplanar	1.404	1.404	0.014	1.389	1.408	40	2
	for τ(BN) > 30° see BOGSUL, BUSHAY,							
	CILRUK (1.434–1.530)							
	S_2—**B**—**N**—X_2	1.447	1.443	0.013	1.435	1.470	14	
B(4)—O	**B**—**O** in BO_4^-	1.468	1.468	0.022	1.453	1.479	24	
	for neutral **B**—**O** see Note 3							3
B(3)—O(2)	X_2—**B**—**O**—X	1.367	1.367	0.024	1.349	1.382	35	
B(n)—P	$n = 4$: **B**—**P**	1.922	1.927	0.027	1.900	1.954	10	
	$n = 3$: see BUPSIB10 (1.892, 1.893)							
B(4)—S	**B**(4)—**S**(3)	1.930	1.927	0.009	1.925	1.934	10	
	B(4)—**S**(2)	1.896	1.896	0.004	1.893	1.899	6	
B(3)—S	N—**B**—S_2	1.806	1.806	0.010	1.799	1.816	28	
	(=X—)(N—)**B**—**S**	1.851	1.854	0.013	1.842	1.859	10	
Br—Br	see BEPZEB, TPASTB	2.542	2.548	0.015	2.526	2.551	4	
Br—C	**Br**—**C***	1.966	1.967	0.029	1.951	1.983	100	4
	Br—**C**sp^3 (cyclopropane)	1.910	1.910	0.010	1.900	1.914	8	
	Br—**C**sp^2	1.883	1.881	0.015	1.874	1.894	31	4
	Br—**C**$_{ar}$ (mono-Br + m,p-Br$_2$)	1.899	1.899	0.012	1.892	1.906	119	4
	Br—**C**$_{ar}$ (o-Br$_2$)	1.875	1.872	0.011	1.864	1.884	8	4
$^-$Br(2)—Cl	see TEACBR (2.362–2.402)							†
Br—I	see DTHIBR10 (2.646), TPHOSI (2.695)							
Br—N	see NBBZAM (1.843)							
Br—O	see CIYFOF	1.581	1.581	0.007	1.574	1.587	4	
Br—P	see CISTED (2.366)							
Br—S(2)	see BEMLIO (2.206)							†
Br—S(3)	see CIWYIQ (2.435, 2.453)							†
Br—S(3)$^+$	see THINBR (2.321)							†
Br—Se	see CIFZUM (2.508, 2.619)							
Br—Si	see BIZJAV (2.284)							
Br—Te	In **Br**$_6$**Te**$^{2-}$ see CUGBAH (2.692–2.716)							
	Br—**Te**(4) see BETUTE10 (3.079, 3.015)							
	Br—**Te**(3) see BTUPTE (2.835)							
Csp^3—Csp^3	C$^\#$—**CH**$_2$—**CH**$_3$	1.513	1.514	0.014	1.507	1.523	192	
	(C$^\#$)$_2$—**CH**—**CH**$_3$	1.524	1.526	0.015	1.518	1.534	226	
	(C$^\#$)$_3$—**C**—**CH**$_3$	1.534	1.534	0.011	1.527	1.541	825	
	C$^\#$—**CH**$_2$—**CH**$_2$—C$^\#$	1.524	1.524	0.014	1.516	1.532	2459	
	(C$^\#$)$_2$—**CH**—**CH**$_2$—C$^\#$	1.531	1.531	0.012	1.524	1.538	1217	
	(C$^\#$)$_3$—**C**—**CH**$_2$—C$^\#$	1.538	1.539	0.010	1.533	1.544	330	
	(C$^\#$)$_2$—**CH**—**CH**—(C$^\#$)$_2$	1.542	1.542	0.011	1.536	1.549	321	
	(C$^\#$)$_3$—**C**—**CH**—(C$^\#$)$_2$	1.556	1.556	0.011	1.549	1.562	215	
	(C$^\#$)$_3$—**C**—**C**—(C$^\#$)$_3$	1.588	1.580	0.025	1.566	1.610	21	
	C*—**C*** (overall)	1.530	1.530	0.015	1.521	1.539	5777	5, 6

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
Csp^3—Csp^3 (cont.)	in cyclopropane (any substituent)	1.510	1.509	0.026	1.497	1.523	888	7
	in cyclobutane (any substituent)	1.554	1.553	0.021	1.540	1.567	679	8
	in cyclopentane (C,H substituents)	1.543	1.543	0.018	1.532	1.554	1641	
	in cyclohexane (C,H substituents)	1.535	1.535	0.016	1.525	1.545	2814	
	cyclopropyl—C* (exocyclic)	1.518	1.518	0.019	1.505	1.531	366	7
	cyclobutyl—C* (exocyclic)	1.529	1.529	0.016	1.519	1.539	376	8
	cyclopentyl—C* (exocyclic)	1.540	1.541	0.017	1.527	1.549	956	
	cyclohexyl—C* (exocyclic)	1.539	1.538	0.016	1.529	1.549	2682	
	in cyclobutene (any substituent)	1.573	1.574	0.017	1.566	1.586	25	8
	in cyclopentene (C,H substituents)	1.541	1.539	0.015	1.532	1.549	208	
	in cyclohexene (C,H substituents)	1.541	1.541	0.020	1.528	1.554	586	
	in oxirane (epoxide)	1.466	1.466	0.015	1.458	1.474	249	9
	in aziridine	1.480	1.481	0.021	1.465	1.496	67	9
	in oxetane	1.541	1.541	0.019	1.527	1.557	16	
	in azetidine	1.548	1.543	0.018	1.536	1.558	22	
	oxiranyl—C* (exocyclic)	1.509	1.507	0.018	1.497	1.519	333	9
	aziridinyl—C* (exocyclic)	1.512	1.512	0.018	1.496	1.526	13	9
Csp^3—Csp^2	**CH₃—C=C**	1.503	1.504	0.011	1.497	1.509	215	
	C#—CH₂—C=C	1.502	1.502	0.013	1.494	1.510	483	
	(C#)₂—CH—C=C	1.510	1.510	0.014	1.501	1.518	564	
	(C#)₃—C—C=C	1.522	1.522	0.016	1.511	1.533	193	
	C*—C=C (overall)	1.507	1.507	0.015	1.499	1.517	1456	5
	C*—C=C (endocylic):							
	in cyclopropene	1.509	1.508	0.016	1.500	1.516	20	10
	in cyclobutene	1.513	1.512	0.018	1.500	1.525	50	8
	in cyclopentene	1.512	1.512	0.014	1.502	1.521	208	
	in cyclohexene	1.506	1.505	0.016	1.495	1.516	391	
	in cyclopentadiene	1.502	1.503	0.019	1.490	1.515	18	
	in cyclohexa-1,3-diene	1.504	1.504	0.017	1.491	1.517	56	
	C*—C≡C (exocyclic):							
	cyclopropenyl—C*	1.478	1.475	0.012	1.470	1.485	7	10
	cyclobutenyl—C*	1.489	1.483	0.015	1.479	1.496	11	8
	cyclopentenyl—C*	1.504	1.506	0.012	1.495	1.512	115	
	cyclohexenyl—C*	1.511	1.511	0.013	1.502	1.519	292	
	C*—CH=O in aldehydes	1.510	1.510	0.008	1.501	1.518	7	
	(C*)₂—C=O in ketones	1.511	1.511	0.015	1.501	1.521	952	11
	in cyclobutanone	1.529	1.530	0.016	1.514	1.545	18	
	in cyclopentanone	1.514	1.514	0.016	1.505	1.523	312	
	acyclic and 6+ rings	1.509	1.509	0.016	1.499	1.519	626	
	C*—COOH in carboxylic acids	1.502	1.502	0.014	1.495	1.510	176	
	C*—COO⁻ in carboxylate anions	1.520	1.521	0.011	1.516	1.528	57	
	C*—C(=O)(—OC*) in acyclic esters	1.497	1.496	0.018	1.484	1.509	553	12
	in β-lactones	1.519	1.519	0.020	1.500	1.538	4	13
	in γ-lactones	1.512	1.512	0.015	1.501	1.521	110	12
	in δ-lactones	1.504	1.502	0.013	1.495	1.517	27	12
	cyclopropyl (**C**)—**C**=O in ketones, acids, and esters	1.486	1.485	0.018	1.474	1.497	105	7
	C*—C(=O)(—NH₂) in acyclic amides	1.514	1.512	0.016	1.506	1.526	32	14
	C*—C(=O)(—NHC*) in acyclic amides	1.506	1.505	0.012	1.498	1.515	78	14
	C*—C(=O)[—N(C*)₂] in acyclic amides	1.505	1.505	0.011	1.496	1.517	15	14
Csp^3—C_{ar}	**CH₃—C_ar**	1.506	1.507	0.011	1.501	1.513	454	
	C#—CH₂—C_ar	1.510	1.510	0.009	1.505	1.516	674	
	(C#)₂—C—C_ar	1.515	1.515	0.011	1.508	1.522	363	
	(C#)₃—C—C_ar	1.527	1.530	0.016	1.517	1.539	308	
	C*—C_ar (overall)	1.513	1.513	0.014	1.505	1.521	1813	
	cylopropyl (**C**)—**C_ar**	1.490	1.490	0.015	1.479	1.503	90	7

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
Csp^3—Csp^1	**C***—**C**≡**C**	1.466	1.465	0.010	1.460	1.469	21	*15*
	C#—**C**≡**C**	1.472	1.472	0.012	1.464	1.481	88	*15*
	C*—**C**≡**N**	1.470	1.469	0.013	1.463	1.479	106	*7(b)*
	cyclopropyl (**C**)—**C**≡**N**	1.444	1.447	0.010	1.436	1.451	38	*7*
Csp^2—Csp^2	**C**=**C**—**C**=**C** (conjugated)	1.455	1.455	0.011	1.447	1.463	30	*16, 18*
	(unconjugated)	1.478	1.476	0.012	1.470	1.479	8	*17, 18*
	(overall)	1.460	1.460	0.015	1.450	1.470	38	
	C=**C**—**C**=**C**—**C**=**C**	1.443	1.445	0.013	1.431	1.454	29	*18*
	C=**C**—**C**=**C** (endocyclic in TCNQ)	1.432	1.433	0.012	1.424	1.441	280	*19*
	C=**C**—**C**(=**O**)(—**C***) (conjugated)	1.464	1.462	0.018	1.453	1.476	211	*16, 18*
	(unconjugated)	1.484	1.486	0.017	1.475	1.497	14	*17, 18*
	(overall)	1.465	1.462	0.018	1.453	1.478	226	
	C=**C**—**C**(=**O**)—**C**=**C**:							
	in benzoquinone (C,H substituents only)	1.478	1.476	0.011	1.469	1.488	28	
	in benzoquinone (any substituent)	1.478	1.478	0.031	1.464	1.498	172	
	non-quinonoid	1.456	1.455	0.012	1.447	1.464	28	
	C—**C**—**COOH**	1.475	1.476	0.015	1.461	1.488	22	
	C=**C**—**COOC***	1.488	1.489	0.014	1.478	1.497	113	
	C=**C**—**COO**⁻	1.502	1.499	0.017	1.488	1.510	11	
	HOOC—**COOH**	1.538	1.537	0.007	1.535	1.541	9	
	HOOC—**COO**⁻	1.549	1.552	0.009	1.546	1.553	13	
	⁻**OOC**—**COO**⁻	1.564	1.559	0.022	1.554	1.568	9	
	formal Csp^2—Csp^2 single bond in selected, non-fused heterocycles:							
	in 1*H*-pyrrole (C3—C4)	1.412	1.410	0.016	1.401	1.427	29	
	in furan (C3—C4)	1.423	1.423	0.016	1.412	1.433	62	
	in thiophene (C3—C4)	1.424	1.425	0.015	1.415	1.433	40	
	in pyrazole (C3—C4)	1.410	1.412	0.016	1.400	1.418	20	
	in isoxazole (C3—C4)	1.425	1.425	0.016	1.413	1.438	9	
	in furazan (C3—C4)	1.428	1.427	0.007	1.422	1.435	6	
	in furoxan (C3—C4)	1.417	1.417	0.006	1.412	1.422	14	
Csp^2—C_{ar}	**C**=**C**—**C**$_{ar}$ (conjugated)	1.470	1.470	0.015	1.463	1.480	37	*16, 18*
	(unconjugated)	1.488	1.490	0.012	1.480	1.496	87	*17, 18*
	(overall)	1.483	1.483	0.015	1.472	1.494	124	
	cyclopropenyl (**C**=**C**)—**C**$_{ar}$	1.447	1.448	0.006	1.441	1.452	8	*10*
	C$_{ar}$—**C**(=**O**)—**C***	1.488	1.489	0.016	1.478	1.500	84	
	C$_{ar}$—**C**(=**O**)—**C**$_{ar}$	1.480	1.481	0.017	1.468	1.494	58	
	C$_{ar}$—**COOH**	1.484	1.485	0.014	1.474	1.491	75	
	C$_{ar}$—**C**(=**O**)(—**OC***)	1.487	1.487	0.012	1.480	1.494	218	
	C$_{ar}$—**COO**⁻	1.504	1.509	0.014	1.495	1.512	26	
	C$_{ar}$—**C**(=**O**)—**NH**$_2$	1.500	1.503	0.020	1.498	1.510	19	
	C$_{ar}$—**C**=**N**—**C**# (conjugated)	1.476	1.478	0.014	1.466	1.486	27	*16*
	(unconjugated)	1.491	1.490	0.008	1.485	1.496	48	*17*
	(overall)	1.485	1.487	0.013	1.481	1.493	75	
	in indole (C3—C3a)	1.434	1.434	0.011	1.428	1.439	40	
Csp^2—Csp^1	**C**=**C**—**C**≡**C**	1.431	1.427	0.014	1.425	1.441	11	*7(b)*
	C=**C**—**C**≡**N** in TCNQ	1.427	1.427	0.010	1.420	1.433	280	*19*
C_{ar}—C_{ar}	in biphenyls (*ortho* substituent all H)	1.487	1.488	0.007	1.484	1.493	30	
	(≥ 1 non-H *ortho* substituent)	1.490	1.491	0.010	1.486	1.495	212	
C_{ar}—Csp^1	**C**$_{ar}$—**C**≡**C**	1.434	1.436	0.006	1.430	1.437	37	
	C$_{ar}$—**C**≡**N**	1.443	1.444	0.008	1.436	1.448	31	
Csp^1—Csp^1	**C**≡**C**—**C**≡**C**	1.377	1.378	0.012	1.374	1.384	21	
Csp^2=Csp^2	**C***—**CH**=**CH**$_2$	1.299	1.300	0.027	1.280	1.311	42	
	(**C***)$_2$—**C**=**CH**$_2$	1.321	1.321	0.013	1.313	1.328	77	
	C*—**CH**=**CH**—**C*** (*cis*)	1.317	1.318	0.013	1.310	1.232	106	
	(*trans*)	1.312	1.311	0.011	1.304	1.320	19	
	(overall)	1.316	1.317	0.015	1.309	1.323	127	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
$Csp^2{=}Csp^2$ (cont.)	$(C^*)_2{-}\mathbf{C}{=}\mathbf{CH}{-}C^*$	1.326	1.328	0.011	1.319	1.334	168	
	$(C^*)_2{-}\mathbf{C}{=}\mathbf{C}{-}(C^*)_2$	1.331	1.330	0.009	1.326	1.334	89	
	$(C^*,H)_2{-}\mathbf{C}{=}\mathbf{C}{-}(C^*,H)_2$ (overall)	1.322	1.323	0.014	1.315	1.331	493	5
	in cyclopropene (any substituent)	1.294	1.288	0.017	1.284	1.302	10	10
	in cyclobutene (any substituent)	1.335	1.335	0.019	1.324	1.347	25	8
	in cyclopentene (C,H substituents)	1.323	1.324	0.013	1.314	1.331	104	
	in cyclohexene (C,H substituents)	1.326	1.325	0.012	1.318	1.334	196	
	$\mathbf{C}{=}\mathbf{C}{=}\mathbf{C}$ (allenes, any substituents)	1.307	1.307	0.005	1.303	1.310	18	
	$\mathbf{C}{=}\mathbf{C}{-}\mathbf{C}{=}\mathbf{C}$ (C,H substituents, conjugated)	1.330	1.330	0.014	1.322	1.338	76	16
	$\mathbf{C}{=}\mathbf{C}{-}\mathbf{C}{=}\mathbf{C}{-}\mathbf{C}{=}\mathbf{C}$ (C,H substituents, conjugated)	1.345	1.345	0.012	1.337	1.350	58	16
	$\mathbf{C}{=}\mathbf{C}{-}C_{ar}$ (C,H substituents, conjugated)	1.339	1.340	0.011	1.334	1.346	124	16
	$\mathbf{C}{=}\mathbf{C}$ in cyclopenta-1,3-diene (any substituent)	1.341	1.341	0.017	1.328	1.356	18	
	$\mathbf{C}{=}\mathbf{C}$ in cyclohexa-1,3-diene (any substituent)	1.332	1.332	0.013	1.323	1.341	56	
	in $\mathbf{C}{=}\mathbf{C}{-}\mathbf{C}{=}O$ (C,H substituent, conjugated)	1.340	1.340	0.013	1.332	1.348	211	16, 18
	(C,H substituent, unconjugated)	1.331	1.330	0.008	1.326	1.339	14	17, 18
	(C,H substituent, overall)	1.340	1.339	0.013	1.332	1.348	226	
	in cyclohexa-2,5-dien-1-ones	1.329	1.327	0.011	1.321	1.335	28	
	in p-benzoquinones (C*,H substituents)	1.333	1.337	0.011	1.325	1.338	14	
	(any substituent)	1.349	1.339	0.030	1.330	1.364	86	
	in TCNQ (endocyclic)	1.352	1.353	0.010	1.345	1.358	142	19
	(exocyclic)	1.392	1.391	0.017	1.379	1.405	139	19
	$\mathbf{C}{=}\mathbf{C}{-}OH$ in enol tautomers	1.362	1.360	0.020	1.349	1.370	54	
	in heterocycles (any substituent)							
	1*H*-pyrrole (C2—C3, C4—C5)	1.375	1.377	0.018	1.361	1.388	58	
	furan (C2—C3, C4—C5)	1.341	1.342	0.021	1.329	1.351	125	
	thiophene (C2—C3, C4—C5)	1.362	1.359	0.025	1.346	1.377	60	
	pyrazole (C4—C5)	1.369	1.372	0.019	1.362	1.383	20	
	imidazole (C4—C5)	1.360	1.361	0.014	1.352	1.367	44	
	isoxazole (C4—C5)	1.341	1.336	0.012	1.331	1.355	9	
	indole (C2—C3)	1.364	1.363	0.012	1.355	1.371	40	
$C_{ar}{\cdots}C_{ar}$	in phenyl rings with C*,H substituents only:							
	$H{-}\mathbf{C}{\cdots}\mathbf{C}{-}H$	1.380	1.381	0.013	1.372	1.388	2191	
	$C^*{-}\mathbf{C}{\cdots}\mathbf{C}{-}H$	1.387	1.388	0.010	1.382	1.393	891	
	$C^*{-}\mathbf{C}{\cdots}\mathbf{C}{-}C^*$	1.397	1.397	0.009	1.392	1.403	182	
	$\mathbf{C}{\cdots}\mathbf{C}$ (overall)	1.384	1.384	0.013	1.375	1.391	3264	
	$F{-}\mathbf{C}{\cdots}\mathbf{C}{-}F$	1.372	1.374	0.011	1.366	1.380	84	4
	$Cl{-}\mathbf{C}{\cdots}\mathbf{C}{-}Cl$	1.388	1.389	0.014	1.380	1.398	152	4
	in napthalene (D_{2h}) C1—C2	1.364	1.364	0.014	1.356	1.373	440	
	(any substituent) C2—C3	1.406	1.406	0.014	1.397	1.415	218	
	C1—C8a	1.420	1.419	0.012	1.412	1.426	440	
	C4a—C8a	1.422	1.424	0.011	1.417	1.429	109	
	in anthracene (D_{2h}) C1—C2	1.356	1.356	0.009	1.350	1.360	56	
	(any substituent) C2—C3	1.410	1.410	0.010	1.401	1.416	34	
	C1—C9a	1.430	1.430	0.006	1.426	1.434	56	
	C4a—C9a	1.435	1.436	0.007	1.429	1.440	34	
	C9—C9a	1.400	1.402	0.009	1.395	1.406	68	
	in pyridine (C,H substituent)	1.379	1.381	0.012	1.371	1.387	276	20
	(any substituents)	1.380	1.380	0.015	1.371	1.389	537	20
	in pyridinium cation:							
	($N^+{-}H$; C,H substituents on C) C2—C3	1.373	1.375	0.012	1.368	1.380	30	
	C3—C4	1.379	1.380	0.011	1.371	1.388	30	
	($N^+{-}X$; C,H substituents on C) C2—C3	1.373	1.372	0.019	1.362	1.382	151	
	C3—C4	1.383	1.385	0.019	1.372	1.394	151	
	in pyrazine (H substituent on C)	1.379	1.377	0.010	1.370	1.388	10	
	(any substituent on C)	1.405	1.405	0.024	1.388	1.420	60	
	in pyrimidine (C,H substituents on C)	1.387	1.389	0.018	1.379	1.400	28	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
$Csp^1\equiv Csp^1$	X—C≡C—X	1.183	1.183	0.014	1.174	1.193	119	*15*
	C,H—C≡C—C,H	1.181	1.181	0.014	1.173	1.192	104	*15*
	in C≡C—C(sp^2, ar)	1.189	1.193	0.010	1.181	1.195	38	*15*
	in C≡C—C≡C	1.192	1.192	0.010	1.187	1.197	42	*15*
	in CH≡C—C$^{\#}$	1.174	1.174	0.011	1.167	1.180	42	*15*
Csp^3—Cl	Omitting 1,2-dichlorides:							
	C—CH$_2$—Cl	1.790	1.790	0.007	1.783	1.795	13	*4*
	C$_2$—CH—Cl	1.803	1.802	0.003	1.800	1.807	8	*4*
	C$_3$—C—Cl	1.849	1.856	0.011	1.837	1.858	5	*4*
	X—CH$_2$—Cl (X = C,H,N,O)	1.790	1.791	0.011	1.783	1.797	37	*4*
	X_2—CH—Cl (X = C,H,N,O)	1.805	1.803	0.014	1.800	1.812	26	*4*
	X_3—C—Cl (X = C,H,N,O)	1.843	1.838	0.014	1.835	1.858	7	*4*
	X_2—C—Cl$_2$ (X = C,H,N,O)	1.779	1.776	0.015	1.769	1.790	18	*4*
	X—C—Cl$_3$ (X = C,H,N,O)	1.768	1.765	0.011	1.761	1.776	33	*4*
	Cl—CH(—C)—CH(—C)—Cl	1.793	1.793	0.013	1.786	1.800	66	*4*
	Cl—C(—C$_2$)—C(—C$_2$)—Cl	1.762	1.760	0.010	1.757	1.765	54	*4*
	cyclopropyl—Cl	1.755	1.756	0.011	1.749	1.763	64	
Csp^2—Cl	C=C—Cl (C,H,N,O substituents on C)	1.734	1.729	0.019	1.719	1.748	63	*4*
	C=C—Cl$_2$ (C,H,N,O substituents on C)	1.720	1.716	0.013	1.708	1.729	20	*4*
	Cl—C=C—Cl	1.713	1.711	0.011	1.705	1.720	80	*4*
C_{ar}—Cl	C_{ar}—Cl (mono-Cl + m,p-Cl$_2$)	1.739	1.741	0.010	1.734	1.745	340	*4*
	C_{ar}—Cl (o-Cl$_2$)	1.720	1.720	0.010	1.713	1.717	364	*4*
Csp^1—Cl	see HCLENE10 (1.634, 1.646)							
Csp^3—F	Omitting 1,2-difluorides:							
	C—CH$_2$—F and C$_2$—CH—F	1.399	1.399	0.017	1.389	1.408	25	*4*
	C$_3$—C—F	1.428	1.431	0.009	1.421	1.435	11	*4*
	(C*,H)$_2$—C—F$_2$	1.349	1.347	0.012	1.342	1.356	58	*4*
	C*—C—F$_3$	1.336	1.334	0.007	1.330	1.344	12	*4*
	F—C*—C*—F	1.371	1.374	0.007	1.362	1.375	26	*4*
	X_3—C—F (X = C,H,N,O)	1.386	1.389	0.033	1.373	1.408	70	*4*
	X_2—C—F$_2$ (X = C,H,N,O)	1.351	1.349	0.013	1.342	1.356	58	*4*
	X—C—F$_3$ (X = C,H,N,O)	1.322	1.323	0.015	1.314	1.332	309	*4*
	F—C(—X)$_2$—C(—X)$_2$—F (X = C,H,N,O)	1.373	1.374	0.009	1.362	1.377	30	*4*
	F—C(—X)$_2$—NO$_2$ (X = any substituent)	1.320	1.319	0.009	1.312	1.327	18	
Csp^2—F	C=C—F (C,H,N,O substituents on C)	1.340	1.340	0.013	1.334	1.346	34	*4*
C_{ar}—F	C_{ar}—F (mono-F + m,p-F$_2$)	1.363	1.362	0.008	1.357	1.368	38	*4*
	C_{ar}—F (o-F$_2$)	1.340	1.340	0.009	1.336	1.344	167	*4*
Csp^3—H	C—C—H$_3$ (methyl)	1.059	1.061	0.030	1.039	1.083	83	*21*
	C$_2$—C—H$_2$ (primary)	1.092	1.095	0.013	1.088	1.099	100	*21*
	C$_3$—C—H (secondary)	1.099	1.097	0.004	1.095	1.103	14	*21*
	C$_{2,3}$—C—H (primary and secondary)	1.093	1.095	0.012	1.089	1.100	118	*21*
	X—C—H$_3$ (methyl)	1.066	1.074	0.028	1.049	1.087	160	*21*
	X_2—C—H$_2$ (primary)	1.092	1.095	0.012	1.088	1.099	230	*21*
	X_3—C—H (secondary)	1.099	1.099	0.007	1.095	1.103	117	*21*
	$X_{2,3}$—C—H (primary and secondary)	1.094	1.096	0.011	1.091	1.100	348	*21*
Csp^2—H	C—C=C—H	1.077	1.079	0.012	1.074	1.085	14	*21*
C_{ar}—H	C_{ar}—H	1.083	1.083	0.011	1.080	1.087	218	*21*
Csp^3—I	C*—I	2.162	2.159	0.015	2.149	2.179	15	*4*
C_{ar}—I	C_{ar}—I	2.095	2.095	0.015	2.089	2.104	51	*4*
Csp^3—N(4)	C*—NH$_3^+$	1.488	1.488	0.013	1.482	1.495	298	
	(C*)$_2$—NH$_2^+$	1.494	1.493	0.016	1.484	1.503	249	
	(C*)$_3$—NH$^+$	1.502	1.502	0.015	1.491	1.512	509	
	(C*)$_4$—N$^+$	1.510	1.509	0.020	1.496	1.523	319	
	C*—N$^+$ (overall)	1.499	1.498	0.018	1.488	1.510	1370	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
Csp^3—N(3)	**C***—**N**$^+$ in N-substituted pyridinium	1.485	1.484	0.009	1.477	1.490	32	
	C*—**NH$_2$** (Nsp^3: pyramidal)	1.469	1.470	0.010	1.462	1.474	19	22
	(C*)$_2$—**NH** (Nsp^3: pyramidal)	1.469	1.467	0.012	1.461	1.477	152	5, 22
	(C*)$_3$—**N** (Nsp^3: pyramidal)	1.469	1.468	0.014	1.460	1.476	1042	5, 22
	C*—**N**sp^3 (overall)	1.469	1.468	0.014	1.460	1.476	1201	
	Csp^3—Nsp^3 in aziridine	1.472	1.471	0.016	1.464	1.482	134	
	in azetidine	1.484	1.481	0.018	1.472	1.495	21	
	in tetrahydropyrrole	1.475	1.473	0.016	1.464	1.483	66	
	in piperidine	1.473	1.473	0.013	1.460	1.479	240	
	Csp^3—Nsp^2 (N planar) in:							23
	acyclic amides **C***—**NH**—**C**=**O**	1.454	1.451	0.011	1.446	1.461	78	14
	β-lactams **C***—**N**(—X)—**C**=**O** (endo)	1.464	1.465	0.012	1.458	1.475	23	13
	γ-lactams **C***—**NH**—**C**=**O** (endo)	1.457	1.458	0.011	1.449	1.465	20	13
	C*—**N**(—**C***)—**C**=**O** (endo)	1.462	1.461	0.010	1.453	1.466	15	13
	C*—**N**(—**C***)—**C**=**O** (exo)	1.458	1.456	0.014	1.448	1.465	15	13
	δ-lactams **C***—**NH**—**C**=**O** (endo)	1.478	1.472	0.016	1.467	1.491	6	14
	C*—**N**(—**C***)—**C**=**O** (endo)	1.479	1.476	0.007	1.475	1.482	15	14
	C*—**N**(—**C***)—**C**=**O** (exo)	1.468	1.471	0.009	1.462	1.477	15	14
	nitro compounds (1,2-dinitro omitted):							
	C—**CH$_2$**—**NO$_2$**	1.485	1.483	0.020	1.478	1.502	8	
	C$_2$—**CH**—**NO$_2$**	1.509	1.509	0.011	1.502	1.511	12	
	C$_3$—**C**—**NO$_2$**	1.533	1.533	0.013	1.530	1.539	17	
	C$_2$—**C**—**(NO$_2$)$_2$**	1.537	1.536	0.016	1.525	1.550	19	
	1,2-dinitro: **NO$_2$**—**C***—**C***—**NO$_2$**	1.552	1.550	0.023	1.536	1.572	32	
Csp^3—N(2)	**C**$^\#$—**N**=**N**	1.493	1.493	0.020	1.477	1.506	54	
	C*—**N**=**C**—**C**$_{ar}$	1.465	1.468	0.011	1.461	1.472	75	
Csp^2—N(3)	**C**=**C**—**NH$_2$** Nsp^2 planar	1.336	1.344	0.017	1.317	1.348	10	23
	C=**C**—**NH**—**C**$^\#$ Nsp^2 planar	1.339	1.340	0.016	1.327	1.351	17	23
	C=**C**—**N**—**(C**$^\#$)$_2$ Nsp^2 planar	1.355	1.358	0.014	1.341	1.363	22	23
	Nsp^3 pyramidal	1.416	1.418	0.018	1.397	1.432	18	22
	Csp^2—Nsp^2 (N planar) in:							23
	acyclic amides **NH$_2$**—**C**=**O**	1.325	1.323	0.009	1.318	1.331	32	14
	acyclic amides **C***—**NH**—**C**=**O**	1.334	1.333	0.011	1.326	1.343	78	14
	acyclic amides **(C*)$_2$**—**N**—**C**=**O**	1.346	1.342	0.011	1.339	1.356	5	14
	β-lactams **C***—**NH**—**C**=**O**	1.385	1.388	0.019	1.374	1.396	23	13
	γ-lactams **C***—**NH**—**C**=**O**	1.331	1.331	0.011	1.326	1.337	20	13
	γ-lactams **C***—**N**(—**C***)—**C**=**O**	1.347	1.344	0.014	1.335	1.359	15	13
	δ-lactams **C***—**NH**—**C**=**O**	1.334	1.334	0.006	1.330	1.339	6	14
	δ-lactams **C***—**N**(—**C***)—**C**=**O**	1.352	1.353	0.010	1.344	1.356	15	14
	peptides **C**$^\#$—**N**(—X)—**C**(—**C**$^\#$)(=**O**)	1.333	1.334	0.013	1.326	1.340	380	24
	ureas **(NH$_2$)$_2$**—**C**=**O**	1.334	1.334	0.008	1.329	1.339	48	25, 26
	ureas **(C**$^\#$—**NH)$_2$**—**C**=**O**	1.347	1.345	0.010	1.341	1.354	26	25
	ureas **[(C**$^\#$)$_n$—**N]$_2$**—**C**=**O**	1.363	1.359	0.014	1.354	1.370	40	25, 27
	thioureas **(X_2N)$_2$**—**C**=**S**	1.346	1.343	0.023	1.328	1.361	192	
	imides **[C**$^\#$—**C**(=**O**)]$_2$—**NH**	1.376	1.377	0.012	1.369	1.383	64	
	[C$^\#$—**C**(=**O**)]$_2$—**N**—**C**$^\#$	1.389	1.383	0.017	1.376	1.404	38	
	[Csp^2—**C**(=**O**)]$_2$—**N**—**C**$^\#$	1.396	1.396	0.010	1.389	1.403	46	
	[Csp^2—**C**(=**O**)]$_2$—**N**—**C**sp^2	1.409	1.406	0.020	1.391	1.419	28	
	guanidinium **[C**—**(NH$_2$)$_3$]**$^+$ (unsubstituted)	1.321	1.320	0.008	1.314	1.327	39	
	(any substituent)	1.328	1.325	0.015	1.317	1.333	140	
	in heterocyclic systems (any substituent):							
	1H-pyrrole (N1—C2, N1—C5)	1.372	1.374	0.016	1.363	1.384	58	
	indole (N1—C2)	1.370	1.370	0.012	1.364	1.377	40	
	pyrazole (N1—C5)	1.357	1.359	0.012	1.347	1.365	20	
	imidazole (N1—C2)	1.349	1.349	0.018	1.338	1.358	44	
	imidazole (N1—C5)	1.370	1.370	0.010	1.365	1.377	44	
Csp^2—N(2)	in imidazole (N3—C4)	1.376	1.377	0.011	1.369	1.384	44	
C_{ar}—N(4)	**C**$_{ar}$—**N**$^+$(**C,H**)$_3$	1.465	1.466	0.007	1.461	1.470	23	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
C_{ar}—N(3)	C_{ar}—NH_2 (Nsp^2: planar)	1.355	1.360	0.020	1.340	1.372	33	*23*
	(Nsp^3: pyramidal)	1.394	1.396	0.011	1.385	1.403	25	*22*
	(overall)	1.375	1.377	0.025	1.363	1.394	98	*28*
	C_{ar}—NH—$C^\#$ (Nsp^2: planar)	1.353	1.353	0.007	1.347	1.359	16	*23*
	(Nsp^3: pyramidal)	1.419	1.423	0.017	1.412	1.432	8	*22*
	(overall)	1.380	1.364	0.032	1.353	1.412	31	*28*
	C_{ar}—N—$(C^\#)_2$ (Nsp^2: planar)	1.371	1.370	0.016	1.363	1.382	41	*23*
	(Nsp^3: pyramidal)	1.426	1.425	0.011	1.421	1.431	22	*22*
	(overall)	1.390	1.385	0.030	1.366	1.420	69	*28*
	in indole (N1—C7a)	1.372	1.372	0.007	1.367	1.376	40	
	C_{ar}—NO_2	1.468	1.469	0.014	1.460	1.476	556	
C_{ar}—N(2)	C_{ar}—N=N	1.431	1.435	0.020	1.422	1.442	26	
Csp^2=N(3)	in furoxan ($^+$N2=C3)	1.316	1.316	0.009	1.311	1.324	14	
Csp^2=N(2)	C_{ar}—C=N—$C^\#$	1.279	1.279	0.008	1.275	1.285	75	
	$(C,H)_2$—C=N—OH in oximes	1.281	1.280	0.013	1.273	1.288	67	
	S—C=N—X	1.302	1.302	0.021	1.285	1.319	36	
	in pyrazole (N2=C3)	1.329	1.331	0.014	1.315	1.339	20	
	in imidazole (C2=N3)	1.313	1.314	0.011	1.307	1.319	44	
	in isoxazole (N2=C3)	1.314	1.315	0.009	1.305	1.320	9	
	in furazan (N2=C3, C4=N5)	1.298	1.299	0.006	1.294	1.303	12	
	in furoxan (C4=N5)	1.304	1.306	0.008	1.300	1.308	14	
$C_{ar} \cdots$ N(3)	$C\cdots N^+$—H (pyrimidinium)	1.335	1.334	0.015	1.325	1.342	30	
	$C\cdots N^+$—C^* (pyrimidinium)	1.346	1.346	0.010	1.340	1.352	64	
	$C\cdots N^+$—O^- (pyrimidinium)	1.362	1.359	0.013	1.353	1.369	56	
$C_{ar} \cdots$ N(2)	$C\cdots N$ (pyridine)	1.337	1.338	0.012	1.300	1.344	269	
	$C\cdots N$ (pyrazine)	1.336	1.335	0.022	1.319	1.347	120	
	$C\cdots N\cdots C$ (pyrimidine)	1.339	1.338	0.015	1.333	1.342	28	
	$N\cdots C\cdots N$ (pyrimidine)	1.333	1.335	0.013	1.326	1.337	28	
	$C\cdots N$ (pyrimidine) (overall)	1.336	1.337	0.014	1.331	1.339	56	
	in any six-membered N-containing aromatic ring:							
	H—$C\cdots N\cdots C$—H	1.334	1.334	0.014	1.327	1.341	146	
	H—$C\cdots N\cdots C$—C^*	1.339	1.341	0.013	1.336	1.345	38	
	C^*—$C\cdots N\cdots C$—C^*	1.345	1.345	0.008	1.342	1.348	24	
	$C\cdots N\cdots C$ (overall)	1.336	1.337	0.014	1.329	1.344	204	
Csp^1≡N(2)	X—N^+≡C^- (isocyanide)	1.144	1.147	0.006	1.140	1.148	6	
Csp^1≡N(1)	C^*—C≡N	1.136	1.137	0.010	1.131	1.142	140	
	C=C—C≡N in TCNQ	1.144	1.144	0.008	1.139	1.149	284	*19*
	C_{ar}—C≡N	1.138	1.138	0.007	1.133	1.143	31	
	X—S—C≡N	1.144	1.141	0.012	1.138	1.151	10	
	$(S$—C≡N$)^-$	1.155	1.156	0.012	1.147	1.165	14	
Csp^3—O(2)	in alcohols:							
	CH_3—OH	1.413	1.414	0.018	1.395	1.425	17	
	C—CH_2—OH	1.426	1.426	0.011	1.420	1.431	75	
	C_2—CH—OH	1.432	1.431	0.011	1.425	1.439	266	
	C_3—C—OH	1.440	1.440	0.012	1.432	1.449	106	
	C^*—OH (overall)	1.432	1.431	0.013	1.424	1.441	464	
	in dialkyl ethers:							*29*
	CH_3—O—C^*	1.416	1.418	0.016	1.405	1.426	110	
	C—CH_2—O—C^*	1.426	1.424	0.011	1.418	1.435	34	
	C_2—CH—O—C^*	1.429	1.430	0.010	1.420	1.437	53	
	C_3—C—O—C^*	1.452	1.450	0.011	1.445	1.458	39	
	C^*—O—C^* (overall)	1.426	1.425	0.019	1.414	1.437	236	*5*
	in aryl alkyl ethers:							*29*
	CH_3—O—C_{ar}	1.424	1.424	0.012	1.417	1.431	616	
	C—CH_2—O—C_{ar}	1.431	1.430	0.013	1.422	1.438	188	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
Csp^2—O(2) (cont.)	in aryl alkyl ethers (cont.)							
	C_2—CH—**O**—C_{ar}	1.447	1.446	0.020	1.435	1.466	58	
	C_3—C—**O**—C_{ar}	1.470	1.469	0.018	1.456	1.483	55	
	C*—**O**—C_{ar} (overall)	1.429	1.427	0.018	1.419	1.436	917	
	in alkyl esters of carboxylic acids:							*12, 29*
	CH_3—**O**—C(=O)—C*	1.448	1.449	0.010	1.442	1.455	200	
	C—CH_2—**O**—C(=O)—C*	1.452	1.453	0.009	1.445	1.458	32	
	C_2—CH—**O**—C(=O)—C*	1.460	1.460	0.010	1.454	1.465	78	
	C_3—C—**O**—C(=O)—C*	1.477	1.475	0.008	1.472	1.484	6	
	C*—**O**—C(=O)—C* (overall)	1.450	1.451	0.014	1.442	1.459	314	
	in alkyl esters of α, β-unsaturated acids:							
	C*—**O**—C(=O)—C=C (overall)	1.453	1.452	0.013	1.444	1.459	112	
	in alkyl esters of benzoic acid							
	C*—**O**—C(=O)—C(phenyl) (overall)	1.454	1.454	0.012	1.446	1.463	219	
	in ring systems:							
	oxirane (epoxide) (any substituent)	1.446	1.446	0.014	1.438	1.456	498	*9*
	oxetane (any substituent)	1.463	1.460	0.015	1.451	1.474	16	
	tetrahydrofuran (C,H substituents)	1.442	1.441	0.017	1.430	1.451	154	
	tetrahydropyran (C,H substituents)	1.441	1.442	0.015	1.431	1.451	22	
	β-lactones: **C***—**O**—C(=O)	1.492	1.494	0.010	1.481	1.501	4	*16*
	γ-lactones: **C***—**O**—C(=O)	1.464	1.464	0.012	1.455	1.473	110	*12*
	δ-lactones: **C***—**O**—C(=O)	1.461	1.464	0.017	1.452	1.473	27	*12*
	O—C—O systems in *gem*-diols, and pyranose and furanose sugars:							*30, 31*
	HO—**C***—**OH**	1.397	1.401	0.012	1.388	1.405	18	
	C_5—O_5—C_1—O_1H in pyranoses:							
	O_1 axial (α): $\quad$ C_5—O_5	1.439	1.440	0.008	1.432	1.445	29	
	$\quad\quad\quad\quad\quad$ O_5—C_1	1.427	1.426	0.012	1.421	1.432	29	
	$\quad\quad\quad\quad\quad$ C_1—O_1	1.403	1.400	0.012	1.391	1.412	29	
	O_1 equatorial (β): C_5—O_5	1.435	1.436	0.008	1.429	1.440	17	
	$\quad\quad\quad\quad\quad$ O_5—C_1	1.430	1.431	0.010	1.424	1.436	17	
	$\quad\quad\quad\quad\quad$ C_1—O_1	1.393	1.393	0.007	1.386	1.399	17	
	$\alpha + \beta$ (overall): $\quad$ C_5—O_5	1.439	1.440	0.008	1.432	1.446	60	
	$\quad\quad\quad\quad\quad$ O_5—C_1	1.430	1.429	0.012	1.421	1.436	60	
	$\quad\quad\quad\quad\quad$ C_1—O_1	1.401	1.399	0.011	1.392	1.407	60	
	C_4—O_4—C_1—O_1H in furanoses:							
	(overall values) C_4—O_4	1.442	1.446	0.012	1.436	1.449	18	
	(overall values) O_4—C_1	1.432	1.432	0.012	1.421	1.443	18	
	(overall values) C_1—O_1	1.404	1.405	0.013	1.397	1.409	18	
	C_5—O_5—C_1—O_1—C* in pyranoses:							
	O_1 axial (α): $\quad$ C_5—O_5	1.439	1.438	0.010	1.433	1.446	67	
	$\quad\quad\quad\quad\quad$ O_5—C_1	1.417	1.417	0.009	1.410	1.424	67	
	$\quad\quad\quad\quad\quad$ C_1—O_1	1.409	1.409	0.014	1.401	1.417	67	
	$\quad\quad\quad\quad\quad$ O_1—C*	1.435	1.435	0.013	1.427	1.443	67	
	O_1 equatorial (β): C_5—O_5	1.434	1.435	0.006	1.429	1.439	39	
	$\quad\quad\quad\quad\quad$ O_5—C_1	1.424	1.424	0.008	1.418	1.431	39	
	$\quad\quad\quad\quad\quad$ C_1—O_1	1.390	1.390	0.011	1.381	1.400	39	
	$\quad\quad\quad\quad\quad$ O_1—C*	1.437	1.438	0.013	1.428	1.445	39	
	$\alpha + \beta$ (overall): $\quad$ C_5—O_5	1.436	1.436	0.009	1.431	1.442	126	
	$\quad\quad\quad\quad\quad$ O_5—C_1	1.419	1.419	0.011	1.412	1.426	126	
	$\quad\quad\quad\quad\quad$ C_1—O_1	1.402	1.403	0.016	1.391	1.413	126	
	$\quad\quad\quad\quad\quad$ O_1—C*	1.436	1.436	0.013	1.428	1.445	126	
	C_4—O_4—C_1—O_1—C* in furanoses:							
	(overall values) C_4—O_4	1.443	1.445	0.013	1.429	1.453	23	
	(overall values) O_4—C_1	1.421	1.418	0.012	1.413	1.431	23	
	(overall values) C_1—O_1	1.410	1.409	0.014	1.401	1.420	23	
	(overall values) O_1—C*	1.439	1.437	0.014	1.429	1.449	23	
	Miscellaneous:							
	$C^{\#}$—**O**—SiX_3	1.416	1.416	0.017	1.405	1.428	29	
	C*—**O**—SO_2—C	1.465	1.461	0.014	1.454	1.475	33	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
Csp^2—O(2) (cont.)	in enols: C=C—OH	1.333	1.331	0.017	1.324	1.342	53	
	in enol esters: C=C—O—C*	1.354	1.353	0.016	1.341	1.363	40	
	in acids: C*—C(=O)—OH	1.308	1.311	0.019	1.298	1.320	174	
	C=C—C(=O)—OH	1.293	1.295	0.019	1.279	1.307	22	
	C_{ar}—C(=O)—OH	1.305	1.311	0.020	1.291	1.317	75	
	in esters: C*—C(=O)—O—C*	1.336	1.337	0.014	1.328	1.346	551	12, 29
	C=C—C(=O)—O—C*	1.332	1.331	0.011	1.324	1.339	112	
	C_{ar}—C(=O)—O—C*	1.337	1.335	0.013	1.329	1.344	219	12
	C*—C(=O)—O—C=C	1.362	1.359	0.018	1.351	1.374	26	
	C*—C(=O)—O—C=C	1.407	1.405	0.017	1.394	1.420	26	
	C*—C(=O)—O—C_{ar}	1.360	1.359	0.011	1.355	1.367	40	12
	in anhydrides: O=C—O—C=O	1.386	1.386	0.011	1.379	1.393	70	
	in ring systems:							
	furan (O1—C2, O1—C5)	1.368	1.369	0.015	1.359	1.377	125	
	isoxazole (O1—C5)	1.354	1.354	0.010	1.345	1.360	9	
	β-lactones: C*—C(=O)—O—C*	1.359	1.359	0.013	1.348	1.371	4	13
	γ-lactones: C*—C(=O)—O—C*	1.350	1.349	0.012	1.342	1.359	110	12
	δ-lactones: C*—C(=O)—O—C*	1.339	1.339	0.016	1.332	1.347	27	12
C_{ar}—O(2)	in phenols: C_{ar}—OH	1.362	1.364	0.015	1.353	1.373	511	
	in aryl alkyl ethers: C_{ar}—O—C*	1.370	1.370	0.011	1.363	1.377	920	29, 32
	in diaryl ethers: C_{ar}—O—C_{ar}	1.384	1.381	0.014	1.375	1.391	132	
	in esters: C_{ar}—O—C(=O)—C*	1.401	1.401	0.010	1.394	1.408	40	12
Csp^2=O(1)	in aldehydes and ketones:							
	C*—CH=O	1.192	1.912	0.005	1.188	1.197	7	5
	(C*)$_2$—C=O	1.210	1.210	0.008	1.206	1.215	474	
	(C$^\#$)$_2$—C=O in cyclobutanones	1.198	1.198	0.007	1.194	1.204	12	
	in cyclopentanones	1.208	1.208	0.007	1.203	1.212	155	
	in cyclohexanones	1.211	1.211	0.009	1.207	1.216	312	
	C=C—C=O	1.222	1.222	0.010	1.216	1.229	225	
	(C=C)$_2$—C=O	1.233	1.229	0.010	1.226	1.242	28	
	C_{ar}—C=O	1.221	1.218	0.014	1.212	1.229	85	
	(C_{ar})$_2$—C=O	1.230	1.226	0.015	1.220	1.238	66	
	C=O in benzoquinones	1.222	1.220	0.013	1.211	1.231	86	
	delocalized double bonds in carboxylate anions:							
	H—C⋯O_2^- (formate)	1.242	1.243	0.012	1.234	1.252	24	
	C*—C⋯O_2^-	1.254	1.253	0.010	1.247	1.261	114	
	C=C—C⋯O_2^-	1.250	1.248	0.017	1.238	1.261	52	
	C_{ar}—C⋯O_2^-	1.255	1.253	0.010	1.249	1.262	22	
	HOOC—C⋯O_2^- (hydrogen oxalate)	1.243	1.247	0.015	1.232	1.256	26	
	$^-O_2$⋯C—C⋯O_2^- (oxalate)	1.251	1.251	0.007	1.248	1.254	18	
	in carboxylic acids (X—COOH):							
	C*—C(=O)—OH	1.214	1.214	0.019	1.203	1.224	175	
	C=C—C(=O)—OH	1.229	1.226	0.017	1.218	1.237	22	
	C_{ar}—C(=O)—OH	1.226	1.223	0.020	1.211	1.241	75	
	in esters:							
	C*—C(=O)—O—C*	1.196	1.196	0.010	1.190	1.202	551	12
	C=C—C(=O)—O—C*	1.199	1.198	0.009	1.193	1.203	113	
	C_{ar}—C(=O)—O—C*	1.202	1.201	0.009	1.196	1.207	218	12
	C*—C(=O)—O—C=C	1.190	1.190	0.014	1.184	1.198	26	
	C*—C(=O)—O—C_{ar}	1.187	1.188	0.011	1.181	1.195	40	12
	in anhydrides: O=C—O—C=O	1.187	1.187	0.010	1.184	1.193	70	
	in β-lactones: C*—C(=O)—O—C*	1.193	1.193	0.006	1.187	1.198	4	13
	γ-lactones: C*—C(=O)—O—C*	1.201	1.202	0.009	1.196	1.206	109	12
	δ-lactones: C*—C(=O)—O—C*	1.205	1.207	0.008	1.201	1.209	27	12
	in amides:							
	NH_2—C(—C*)=O	1.234	1.233	0.012	1.225	1.243	32	14
	(C*—)(C*,H—)N—C(—C*)=O	1.231	1.231	0.012	1.224	1.238	378	14
	β-lactams: C*—NH—C=O	1.198	1.200	0.012	1.193	1.204	23	13

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
$Csp^2{=}O(1)$ (cont.)	in amides (cont.)							
	γ-lactams: $C^*{-}NH{-}C{=}O$	1.235	1.235	0.008	1.232	1.240	20	13
	γ-lactams: $C^*{-}N({-}C^*){-}C{=}O$	1.225	1.226	0.011	1.217	1.233	15	13
	δ-lactams: $C^*{-}NH{-}C{=}O$	1.240	1.241	0.003	1.237	1.243	6	14
	δ-lactams: $O^*{-}N({-}C^*){-}C{=}O$	1.233	1.233	0.007	1.229	1.239	15	14
	in ureas:							
	$(NH_2)_2{-}C{=}O$	1.256	1.256	0.007	1.249	1.261	24	25, 26
	$(C^\#{-}NH)_2{-}C{=}O$	1.241	1.237	0.011	1.235	1.245	13	25
	$[(C^\#)_n{-}N]_2{-}C{=}O$	1.230	1.230	0.007	1.224	1.234	20	25, 27
$Csp^3{-}P(4)$	$C_3{-}P^+{-}C^*$	1.800	1.802	0.015	1.790	1.812	35	33
	$C_2{-}P({=}O){-}CH_3$	1.791	1.790	0.006	1786	1.795	10	
	$C_2{-}P({=}O){-}CH_2{-}C$	1.806	1.806	0.009	1.801	1.813	45	
	$C_2{-}P({=}O){-}CH{-}C_2$	1.821	1.821	0.009	1.815	1.828	15	
	$C_2{-}P({=}O){-}C{-}C_3$	1.841	1.842	0.008	1.835	1.847	14	
	$C_2{-}P({=}O){-}C^*$ (overall)	1.813	1.811	0.017	1.800	1.822	84	
$Csp^3{-}P(3)$	$C_2{-}P{-}C^*$	1.855	1.857	0.019	1.840	1.870	23	
$C_{ar}{-}P(4)$	$C_3{-}P^+{-}C_{ar}$	1.793	1.792	0.011	1.786	1.800	276	
	$C_2{-}P({=}O){-}C_{ar}$	1.801	1.802	0.011	1.796	1.807	98	
	$Ph_3{-}P{=}N^+{=}P{-}Ph_3$	1.795	1.795	0.008	1.789	1.800	197	
$C_{ar}{-}P(3)$	$C_2{-}P{-}C_{ar}$	1.836	1.837	0.010	1.830	1.844	102	
	$(N{\cdots})_2P{-}C_{ar}$ ($P{\cdots}N$ aromatic)	1.795	1.793	0.011	1.788	1.803	43	
$Csp^3{-}S(4)$	$C^*{-}SO_2{-}C$ ($C^* = CH_3$ excluded)	1.786	1.782	0.018	1.774	1.797	75	
	$C^*{-}SO_2{-}C$ (overall)	1.779	1.778	0.020	1.764	1.790	94	
	$C^*{-}SO_2{-}O{-}X$	1.745	1.744	0.009	1.738	1.754	7	34
	$C^*{-}SO_2{-}N{-}X_2$	1.758	1.736	0.018	1.746	1.773	17	34
$Csp^3{-}S(3)$	$C^*{-}S({=}O){-}C$ ($C^* = CH_3$ excluded)	1.818	1.814	0.024	1.802	1.829	69	
	$C^*{-}S({=}O){-}C$ (overall)	1.809	1.806	0.025	1.793	1.820	88	
	$CH_3{-}S^+{-}X_2$	1.786	1.787	0.007	1.779	1.792	21	
	$C^*{-}S^+{-}X_2$ ($C^* = CH_3$ excluded)	1.823	1.820	0.016	1.812	1.834	18	
	$C^*{-}S^+{-}C_2$ (overall)	1.804	1.794	0.025	1.788	1.820	41	
$Csp^3{-}S(2)$	$C^*{-}SH$	1.808	1.805	0.010	1.800	1.819	6	
	$CH_3{-}S{-}C^*$	1.789	1.787	0.008	1.784	1.794	9	
	$C{-}CH_2{-}S{-}C^*$	1.817	1.816	0.013	1.808	1.824	92	
	$C_2{-}CH{-}S{-}C^*$	1.819	1.819	0.011	1.811	1.825	32	
	$C_3{-}C{-}S{-}C^*$	1.856	1.860	0.011	1.854	1.863	26	
	$C^*{-}S{-}C^*$ (overall)	1.819	1.817	0.019	1.809	1.827	242	
	in thiirane	1.834	1.835	0.025	1.810	1.858	4	9
	in thietane: see ZCMXSP (1.817, 1.844)							
	in tetrahydrothiophene	1.827	1.826	0.018	1.811	1.837	20	
	in tetrahydrothiopyran	1.823	1.821	0.014	1.812	1.832	24	
	$C{-}CH_2{-}S{-}S{-}X$	1.823	1.820	0.014	1.813	1.832	41	
	$C_3{-}C{-}S{-}S{-}X$	1.863	1.865	0.015	1.848	1.878	11	
	$C^*{-}S{-}S{-}X$ (overall)	1.833	1.828	0.022	1.818	1.848	59	
$Csp^2{-}S(2)$	$C{=}C{-}S{-}C^*$	1.751	1.755	0.017	1.740	1.764	61	
	$C{=}C{-}S{-}C{=}C$ (in tetrathiafulvalene)	1.741	1.741	0.011	1.733	1.750	88	
	$C{=}C{-}S{-}C{=}C$ (in thiophene)	1.712	1.712	0.013	1.703	1.722	60	
	$O{=}C{-}S{-}C^\#$	1.762	1.759	0.018	1.747	1.778	20	
$C_{ar}{-}S(4)$	$C_{ar}{-}SO_2{-}C$	1.763	1.764	0.009	1.756	1.769	96	
	$C_{ar}{-}SO_2{-}O{-}X$	1.752	1.750	0.008	1.749	1.756	27	
	$C_{ar}{-}SO_2{-}N{-}X_2$	1.758	1.759	0.013	1.749	1.765	106	35
$C_{ar}{-}S(3)$	$C_{ar}{-}S({=}O){-}C$	1.790	1.790	0.010	1.783	1.798	41	
	$C_{ar}{-}S^+{-}X_2$	1.778	1.779	0.010	1.771	1.787	10	
$C_{ar}{-}S(2)$	$C_{ar}{-}S{-}C^*$	1.773	1.774	0.009	1.765	1.779	44	
	$C_{ar}{-}S{-}C_{ar}$	1.768	1.767	0.010	1.762	1.774	158	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
C_{ar}—S(2) (*cont.*)	C_{ar}—**S**—C_{ar} (in phenothiazine) C_{ar}—**S**—**S**—X	1.764 1.777	1.764 1.777	0.008 0.012	1.760 1.767	1.769 1.785	48 47	
Csp^1—S(2)	N≡**C**—**S**—X	1.679	1.683	0.026	1.645	1.698	10	
Csp^1—S(1)	(N≡**C**—**S**)$^-$	1.630	1.630	0.014	1.619	1.641	14	
Csp^2=S(1)	(C*)$_2$—**C**=**S**: see IPMUDS (1.599) (C_{ar})$_2$—**C**=**S**: see CELDOM (1.611) (X)$_2$—**C**=**S** (X = C,N,O,S) X_2N—**C**(=**S**)—**S**—X (X_2N)$_2$—**C**=**S** (thioureas) N—**C**($\cdots$**S**)$_2$	 1.671 1.660 1.681 1.720	 1.675 1.660 1.684 1.721	 0.024 0.016 0.020 0.012	 1.656 1.648 1.669 1.709	 1.689 1.674 1.693 1.731	 245 38 96 20	
Csp^3—Se	**C**$^\#$—**Se**	1.970	1.967	0.032	1.948	1.998	21	
Csp^2—Se(2)	C=C—**Se**—C=C (in tetraselenafulvalene)	1.893	1.895	0.013	1.882	1.902	32	
C_{ar}—Se(3)	**Ph**$_3$—**Se**$^+$	1.930	1.929	0.006	1.924	1.936	13	
Csp^3—Si(5)	**C**$^\#$—**Si**$^-$—X_4	1.874	1.876	0.015	1.859	1.884	9	
Csp^3—Si(4)	**CH$_3$**—**Si**—X_3 **C***—**Si**—X_3 (C* = CH$_3$ excluded) **C***—**Si**—X_2 (overall)	1.857 1.888 1.863	1.857 1.887 1.861	0.018 0.023 0.024	1.848 1.872 1.850	1.869 1.905 1.875	552 124 681	
C_{ar}—Si(4)	C_{ar}—**Si**—X_3	1.868	1.868	0.014	1.857	1.878	178	
Csp^1—Si(4)	C≡**C**—**Si**—X_3	1.837	1.840	0.012	1.824	1.849	8	
Csp^3—Te	**C**$^\#$—**Te**	2.158	2.159	0.030	2.128	2.177	13	
C_{ar}—Te	C_{ar}—**Te**	2.116	2.115	0.020	2.104	2.130	72	
Csp^2=Te	see CEDCUJ (2.044)							
Cl—Cl	see PHASCL (2.306, 2.227)							
Cl—I	see CMBIDZ (2.563), HXPASC (2.541, 2.513), METAMM (2.552), BQUINI (2.416, 2.718)							
Cl—N	see BECTAE (1.743–1.757), BOGPOC (1.705)							
Cl—O(1)	in ClO$_4^-$	1.414	1.419	0.026	1.403	1.431	252	
Cl—P	(N$\cdots$)$_2$**P**—**Cl** (N$\cdots$P aromatic) **Cl**—**P** (overall)	1.997 2.008	1.994 2.001	0.015 0.035	1.989 1.986	2.004 2.028	46 111	
Cl—S	**Cl**—**S** (overall) see also longer bonds in CILSAR (2.283), BIHXIZ (2.357), CANLUY (2.749)	2.072	1.079	0.023	2.047	2.091	6	
Cl—Se	See BIRGUE10, BIRHAL10, CTCNSE (2.234–2.851)							
Cl—Si(4)	**Cl**—**Si**—X_3 (monochloro) **Cl$_2$**—**Si**—X_2 and **Cl$_3$**—**Si**—X	2.072 2.020	2.075 2.012	0.009 0.015	2.066 2.007	2.078 2.036	5 5	
Cl—Te	Cl—Te in range 2.34–2.60 see also longer bonds in BARRIV, BOJPUL, CETUTE, EPHTEA, OPNTEC10 (2.73–2.94)	2.520	2.515	0.034	2.493	2.537	22	*36*
F—N(3)	**F**—**N**—C$_2$ and **F$_2$**—**N**—C	1.406	1.404	0.016	1.395	1.416	9	
F—P(6)	in hexafluorophosphate, PF$_6^-$	1.579	1.587	0.025	1.563	1.598	72	
P—P(3)	(N$\cdots$)$_2$**P**—**F** (N$\cdots$P aromatic)	1.495	1.497	0.016	1.481	1.510	10	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
F—S	43 observations in range 1.409–1.770 in a wide variety of environments							
	F—**S**(6) in $\mathbf{F_2}$—$\mathbf{SO_2}$—$\mathbf{C_2}$ (see FPSULF10, BETJOZ)	1.640	1.646	0.011	1.626	1.649	6	
	F—**S**(4) in $\mathbf{F_2}$—**S**(=O)—N (see BUDTEZ)	1.527	1.528	0.004	1.524	1.530	24	*37*
F—Si(6)	in SiF_6^{2-}	1.694	1.701	0.013	1.677	1.703	6	
F—Si(5)	**F**—**Si**$^-$—X_4	1.636	1.639	0.035	1.602	1.657	10	
F—Si(4)	**F**—**Si**—X_3	1.588	1.587	0.014	1.581	1.599	24	
F—Te	see CUCPIZ [F—Te(6) = 1.942, 1.937], FPHTEL [F—Te(4) = 2.006]							
H—N(4)	X_3—$\mathbf{N^+}$—**H**	1.033	1.036	0.022	1.026	1.045	87	*21*
H—N(3)	X_2—**N**—**H**	1.009	1.010	0.019	0.997	1.023	95	*21*
H—O(2)	in alcohols C*—**O**—**H**	0.967	0.969	0.010	0.959	0.974	63	*21*
	C#—**O**—**H**	0.967	0.970	0.010	0.959	0.974	73	*21*
	in acids O=C—**O**—**H**	1.015	1.017	0.017	1.001	1.031	16	*21, 38*
I—I	in I_3^-	2.917	2.918	0.011	2.907	2.927	6	
I—N	see BZPRIB, CMBIDZ, HMTITI, HMTNTI, IFORAM, IODMAM (2.042–2.475)							
I—O	X—**I**—**O** (see BZPRIB, CAJMAB, IBZDAC11) for IO_6^- see BOVMEE (1.829–1.912)	2.144	2.144	0.028	2.127	2.164	6	
I—P(3)	see CEHKAB (2.490–2.493)							†
I—S	see DTHIBR10 (2.687), ISUREA10 (2.629), BZTPPI (3.251)							
I—Te(4)	**I**—**Te**—X_3	2.926	2.928	0.026	2.902	2.944	8	
N(4)—N(3)	X_3—$\mathbf{N^+}$—$\mathbf{N^0}$—X_2 (N^0 planar)	1.414	1.414	0.005	1.412	1.418	13	
N(3)—N(3)	(C)(C,H)—$\mathbf{N}_a$—$\mathbf{N}_b$—(C)(C,H)							*5, 39*
	N_a, N_b pyramidal	1.454	1.452	0.021	1.444	1.457	44	*40*
	N_a pyramidal, N_b planar	1.420	1.420	0.015	1.407	1.433	68	*40*
	N_a, N_b planar	1.401	1.401	0.018	1.384	1.418	40	*40*
	overall	1.425	1.425	0.027	1.407	1.443	139	
N(3)—N(2)	in pyrazole (N1—N2)	1.366	1.366	0.019	1.350	1.375	20	
	in pyridazinium (N1$^+$⋯N2)	1.350	1.349	0.010	1.345	1.361	7	
N(2)⋯N(2)	**N**⋯**N** (aromatic) in pyridine							
	with C,H as *ortho* substituents	1.304	1.300	0.019	1.287	1.326	6	
	with N,Cl as *ortho* substituents	1.368	1.373	0.011	1.362	1.375	9	
N(2)=N(2)	C#—**N**=**N**—C# (*cis*)	1.245	1.244	0.009	1.239	1.252	21	
	(*trans*)	1.222	1.222	0.006	1.218	1.227	6	
	(overall)	1.240	1.241	0.012	1.230	1.251	27	
	C_{ar}—**N**=**N**—C_{ar}	1.255	1.253	0.016	1.247	1.262	13	
	X—**N**=**N**=N (azides)	1.216	1.226	0.028	1.202	1.237	19	
N(2)=N(1)	X—N=**N**=**N** (azides)	1.124	1.128	0.015	1.114	1.137	19	
N(3)—O(2)	(C,H)$_2$—**N**—**OH** (Nsp^2: planar)	1.396	1.394	0.012	1.390	1.401	28	
	C_2—**N**—**O**—C (Nsp^3: pyramidal)	1.463	1.465	0.012	1.457	1.468	22	
	C_2—**N**—**O**—C (Nsp^2: planar)	1.397	1.394	0.011	1.388	1.409	12	
	in furoxan (N2—O1)	1.438	1.436	0.009	1.430	1.447	14	
N(3)—O(1)	(C⋯)$_2$$\mathbf{N^+}$—$\mathbf{O^-}$ in pyridine *N*-oxides	1.304	1.299	0.015	1.291	1.316	11	
	in furoxan ($^+$N2—O6$^-$)	1.234	1.234	0.008	1.228	1.240	14	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
N(2)—O(2)	in oximes:							
	$(C^{\#})_2$—C$=$N—OH	1.416	1.418	0.006	1.416	1.420	7	
	$(H)(Csp^2)$—C$=$N—OH	1.390	1.390	0.011	1.380	1.401	20	
	$(C^{\#})(Csp^2)$—C$=$N—OH	1.402	1.403	0.010	1.393	1.410	18	
	$(Csp^2)_2$—C$=$N—OH	1.378	1.377	0.017	1.365	1.393	16	
	$(C,H)_2$—C$=$N—OH (overall)	1.394	1.395	0.018	1.379	1.408	67	
	in furazan (O1—N2, O1—N5)	1.385	1.383	0.013	1.378	1.392	12	
	in furoxan (O1—N5)	1.380	1.380	0.011	1.370	1.388	14	
	in isoxazole (O1—N2)	1.425	1.425	0.010	1.417	1.434	9	
N(3)$=$O(1)	in nitrate ions NO_3^-	1.239	1.240	0.020	1.227	1.251	105	
	in nitro groups:							
	C*—NO_2	1.212	1.214	0.012	1.206	1.221	84	
	$C^{\#}$—NO_2	1.210	1.210	0.011	1.203	1.218	251	
	C_{ar}—NO_2	1.217	1.218	0.011	1.211	1.215	1116	
	C—NO_2 (overall)	1.218	1.219	0.013	1.210	1.226	1733	
N(3)—P(4)	X_2—P($=$X)—NX_2 Nsp^2: planar	1.652	1.651	0.024	1.634	1.670	205	
	Nsp^3: pyramidal	1.683	1.683	0.005	1.680	1.686	6	
	(overall)	1.662	1.662	0.029	1.639	1.682	358	
	subsets of this group are:							
	O_2—P($=$S)—NX_2	1.628	1.624	0.015	1.615	1.634	9	
	C—P($=$S)—$(NX_2)_2$	1.691	1.694	0.018	1.678	1.703	28	
	O—P($=$S)—$(NX_2)_2$	1.652	1.654	0.014	1.642	1.664	28	
	P($=$O)—$(NX_2)_3$	1.663	1.668	0.026	1.640	1.679	78	
N(3)—P(3)	—NX—P(—X)—NX—P(—X)— (P_2N_2 ring)	1.730	1.721	0.017	1.716	1.748	20	
	—NX—P($=$S)—NX—P($=$S)— (P_2N_2 ring)	1.697	1.697	0.015	1.690	1.703	44	
	in P-substituted phosphazenes:							
	$(N\vdots)_2$P—N (amino)	1.637	1.638	0.014	1.625	1.651	16	
	(aziridinyl)	1.672	1.674	0.010	1.665	1.676	15	
N(2)$=$P(4)	Ph_3—P$=$N$^+$$=$P—$Ph_3$	1.571	1.573	0.013	1.563	1.580	66	
	Ph_3—P$=$N—C,S	1.599	1.597	0.018	1.580	1.615	7	
N(2)$\vdots$P(3)	N$\vdots$P aromatic in phosphazenes	1.582	1.582	0.019	1.571	1.594	126	
	in P$\vdots$N$\vdots$S	1.604	1.606	0.009	1.594	1.612	36	
N(3)—S(4)	C—SO_2—NH_2	1.600	1.601	0.012	1.591	1.610	14	*35*
	C—SO_2—NH—$C^{\#}$	1.633	1.633	0.019	1.615	1.652	47	*35*
	C—SO_2—N—$(C^{\#})_2$	1.642	1.641	0.024	1.623	1.659	38	*35*
N(3)—S(2)	C—S—NX_2 Nsp^2: planar	1.710	1.707	0.019	1.698	1.722	22	*23*
	(for Nsp^3 pyramidal see MODIAZ: 1.765)							
	X—S—NX_2 Nsp^2: planar	1.707	1.705	0.012	1.699	1.715	30	*23*
N(2)—S(2)	C$=$N—S—X	1.656	1.663	0.027	1.632	1.677	36	
N(2)$\vdots$S(2)	N$\vdots$S aromatic in P$\vdots$N$\vdots$S	1.560	1.558	0.011	1.554	1.563	37	
N(2)$=$S(2)	N$=$S in N$=$S$=$N and N$=$S$=$S	1.541	1.546	0.022	1.521	1.558	37	
N(3)—Se	see COJCUZ (1.830), DSEMOR10 (1.846, 1.852), MORTRS10 (1.841)							
N(2)—Se	see SEBZQI (1.805), NAPSEZ10 (1.809, 1.820)							
N(2)$=$Se	see CISMUM (1.790, 1.791)							
N(3)—Si(5)	see DMESIP01, BOJLER, CASSAQ, CASYOK, CECXEN, CINTEY, CIPBUY, FMESIB, MNPSIL, PNPOSI (1.973–2.344)							
N(3)—Si(4)	X_3—Si—NX_2 (overall)	1.748	1.746	0.022	1.735	1.757	170	
	subsets of this group are:							
	X_3—Si—NHX	1.714	1.719	0.014	1.702	1.727	16	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
N(3)—Si(4) (*cont.*)	X_3—**Si**—NX—**Si**—X_3 acyclic	1.743	1.744	0.016	1.731	1.755	45	
	N—**Si**—**N** in four-membered rings	1.742	1.742	0.009	1.735	1.748	53	
	N—**Si**—**N** in five-membered rings	1.741	1.742	0.019	1.726	1.749	33	
N(2)—Si(4)	X_3—**Si**—**N**$^-$—**Si**—X_3	1.711	1.712	0.019	1.693	1.729	15	
N—Te	see ACLTEP (2.402), BIBLAZ (1.980), CESSAU (2.023)							
O(2)—O(2)	C*—**O**—**O**—C*,H τ(OO) = 70–85°	1.464	1.464	0.009	1.458	1.472	12	
	τ(OO) approx. 180°	1.482	1.480	0.005	1.478	1.486	5	
	(overall)	1.469	1.471	0.012	1.461	1.478	17	
	O=C—**O**—**O**—C=O see ACBZPO01 (1.446), CEYLUN (1.452), CIMHIP (1.454)							
	Si—**O**—**O**—Si	1.496	1.499	0.005	1.490	1.499	10	
O(2)—P(5)	X—**P**—(**O**X)$_4$							*41*
	trigonal bipyramidal: axial	1.689	1.685	0.024	1.675	1.712	20	
	equatorial	1.619	1.622	0.024	1.604	1.628	20	
	square pyramidal	1.662	1.661	0.020	1.649	1.673	28	
O(2)—P(4)	C—**O**—**P**(⋯**O**)$_3^{2-}$	1.621	1.622	0.007	1.615	1.628	12	
	(H—**O**)$_2$—**P**(⋯**O**)$_2^-$	1.560	1.561	0.009	1.555	1.566	16	
	(C—**O**)$_2$—**P**(⋯**O**)$_2^-$	1.608	1.607	0.013	1.599	1.615	16	
	(C$^\#$—**O**)$_3$—**P**=**O**	1.558	1.554	0.011	1.550	1.564	30	
	(C$_{ar}$—**O**)$_3$—**P**=**O**	1.587	1.588	0.014	1.572	1.599	19	
	X—**O**—**P**(=**O**)—(C,N)$_2$	1.590	1.585	0.016	1.577	1.601	33	
	(X—**O**)$_2$—**P**(=**O**)—(C,N)	1.571	1.572	0.013	1.563	1.579	70	
O(2)—P(3)	(N⋯)$_2$**P**—**O**—C (N⋯P aromatic)	1.573	1.573	0.011	1.563	1.584	16	
O(1)=P(4)	C—O—**P**(⋯**O**)$_3^{2-}$ (delocalized)	1.513	1.512	0.008	1.508	1.518	42	
	(H—O)$_2$—**P**(⋯**O**)$_2^-$ (delocalized)	1.503	1.503	0.005	1.499	1.508	16	
	(C—O)$_2$—**P**(⋯**O**)$_2^-$ (delocalized)	1.483	1.485	0.008	1.474	1.490	16	
	(C—O)$_3$—**P**=**O**	1.449	1.448	0.007	1.446	1.452	18	
	C$_3$—**P**=**O**	1.489	1.486	0.010	1.481	1.496	72	
	N$_3$—**P**=**O**	1.461	1.462	0.014	1.449	1.470	26	
	(C)$_2$(N)—**P**=**O**	1.487	1.489	0.007	1.479	1.493	5	
	(C,N)$_2$(O)—**P**=**O**	1.467	1.465	0.007	1.462	1.472	33	
	(C,N)(O)$_2$—**P**=**O**	1.457	1.458	0.009	1.454	1.462	35	
O(2)—S(4)	C—**O**—**SO**$_2$—C	1.577	1.576	0.015	1.566	1.584	41	
	C—**O**—**SO**$_2$—CH$_3$	1.569	1.569	0.013	1.556	1.582	7	
	C—**O**—**SO**$_2$—C$_{ar}$	1.580	1.578	0.015	1.571	1.588	27	
O(1)=S(4)	C—**SO**$_2$—C	1.436	1.437	0.010	1.431	1.442	316	*42*
	X—**SO**$_2$—NX_2	1.428	1.428	0.010	1.422	1.434	326	
	C—**SO**$_2$—N—(C,H)$_2$	1.430	1.430	0.009	1.425	1.435	206	
	C—**SO**$_2$—O—C	1.423	1.423	0.008	1.418	1.428	82	
	in **SO**$_4^{2-}$	1.472	1.473	0.013	1.463	1.481	104	
O(1)=S(3)	C—**S**(=**O**)—C	1.497	1.498	0.013	1.489	1.505	90	*5*
O—Se	see BAPPAJ, BIRGUE10, BIRHAL10, CXMSEO, DGLYSE, SPSEBU (1.597 for O=Se to 1.974 for O—Se)							
O(2)—Si(5)	(X—**O**)$_3$—**Si**—(N)(C)	1.663	1.658	0.023	1.650	1.665	21	
O(2)—Si(4)	X_3—**Si**—**O**—X (overall)	1.631	1.630	0.022	1.617	1.646	191	
	subsets of this group are:							
	X_3—**Si**—**O**—C$^\#$	1.645	1.647	0.012	1.634	1.652	29	
	X_3—**Si**—**O**—Si—X_3	1.622	1.625	0.014	1.614	1.631	70	
	X_3—**Si**—**O**—**O**—Si—X_3	1.680	1.676	0.008	1.673	1.688	10	
O(2)—Te(6)	(X—**O**)$_6$—**Te**	1.927	1.927	0.020	1.908	1.942	16	
O(2)—Te(4)	(X—**O**)$_2$—**Te**—X_2	2.133	2.136	0.054	2.078	2.177	12	

Table 9.5.1.1. *Average lengths (cont.)*

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
P(4)—P(4)	X_3—**P**—**P**—X_3	2.256	2.259	0.025	2.243	2.277	6	
P(4)—P(3)	see CECHEX (2.197), COZPIQ (2.249)							
P(3)—P(3)	X_2—**P**—**P**—X_2	2.214	2.210	0.022	2.200	2.224	41	
P(4)=P(4)	see BUTSUE (2.054)							
P(3)=P(3)	see BALXOB (2.034)							
P(4)=S(1)	C_3—**P**=**S**	1.954	1.952	0.005	1.950	1.957	13	
	$(N,O)_2(C)$—**P**=**S**	1.922	1.924	0.014	1.913	1.927	26	
	$(N,O)_3$—**P**=**S**	1.913	1.914	0.014	1.906	1.921	50	
P(4)=Se(1)	X_3—**P**=**Se**	2.093	2.099	0.019	2.075	2.108	12	
P(3)—Si(4)	X_2—**P**—**Si**—X_3: 3- and 4-rings excluded (see BOPFER, BOPFIV, CASTOF10, COZVIW: 2.201–2.317)	2.264	2.260	0.019	2.249	2.283	22	
P(4)=Te(1)	see MOPHTE (2.356), TTEBPZ (2.327)							
S(2)—S(2)	C—**S**—**S**—C τ (SS) = 75–105°	2.031	2.029	0.015	2.021	2.038	46	
	τ (SS) = 0–20°	2.070	2.068	0.022	2.057	2.077	28	
	(overall)	2.048	2.045	0.026	2.028	2.068	99	
	in polysulfide chain —**S**—**S**—**S**—	2.051	2.050	0.022	2.037	2.065	126	
S(2)—S(1)	X—**N**=**S**—**S**	1.897	1.896	0.012	1.887	1.908	5	
S—Se(4)	see BUWZUO (2.264, 2.269)							
S—Se(2)	X—**Se**—**S** (any)	2.193	2.195	0.015	2.174	2.207	9	
S(2)—Si(4)	X_3—**Si**—**S**—X	2.145	2.138	0.020	2.130	2.158	19	
S(2)—Te	X—**S**—**Te** (any)	2.405	2.406	0.022	2.383	2.424	10	
	X=**S**—**Te** (any)	2.682	2.686	0.035	2.673	2.694	28	
Se(2)—Se(2)	X—**Se**—**Se**—X	2.340	2.340	0.024	2.315	2.361	15	
Se(2)—Te(2)	see BAWFUA, BAWGAH (2.524–2.561)							†
Si(4)—Si(4)	X_3—**Si**—**Si**—X_3 three-membered rings excluded: see CIHRAM (2.511)	2.359	2.359	0.012	2.349	2.366	42	
Te—Te	see CAHJOK (2.751, 2.704)							

† See opening paragraph of Section 9.5.3. For numbered footnotes, see Appendix 1.

9.2.2 (cont.)

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