Tables of Bond Lengths determined by *X*-Ray and Neutron Diffraction. Part 1. Bond Lengths in Organic Compounds

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The average lengths of bonds involving the elements H, B, C, N, O, F, Si, P, S, Cl, As, Se, Br, Te, and I in organic compounds are reported.

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'.[1] This volume summarized results obtained by diffraction and spectroscopic methods prior to 1956; a supplementary volume[2] 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'.[3] Some years later the Cambridge Crystallographic Data Centre[4] produced an atlas-style compendium[5] of all organic, organometallic, and metal complex crystal structures published in the period 1960—1965. More recently a survey of geometries determined by spectroscopic methods[6] 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 Figure 1. Printed compilations have been effectively superseded by computerized databases. In particular the Cambridge Structural Database (CSD) now contains bibliographic, chemical and numerical results for *ca.* 55 000 organocarbon 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 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 the Chemical Society Special Publications[1,2] of 1958 and 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 CSD to prepare a new table of average bond lengths in organic compounds. The Table given here specificially 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. Average bond lengths in organometallic compounds and metal complexes will be presented in a later paper.

Methodology

Selection of Crystallographic Data.—All results given in the Table are based on *X*-ray and neutron diffraction results retrieved from the September 1985 version of CSD. Neutron diffraction data only were used to derive mean bond lengths involving hydrogen atoms. This version of CSD contained results for 49 854 single-crystals diffraction studies of organocarbon compounds 10 324 of these satisfied the acceptance criteria listed below and were used in the averaging procedures.

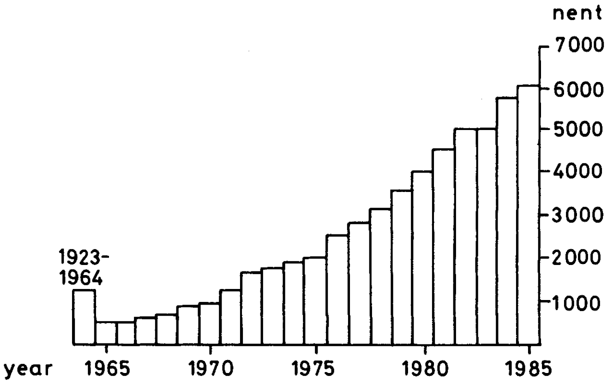

Figure 1. Growth of the Cambridge Structural Database 1965—1985 as no. of entries (nent) published in a given year

(i) Structure is 'organic', *i.e.* belongs to CSD classes 1—65 or 70.[7]

(ii) Atomic co-ordinates for the structure have been published and are available in 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 high precision were included on the basis of *either* (a) crystallographic *R* factor was $\leqslant 0.07$ and the reported mean estimated standard deviation (e.s.d.) for the C–C bond lengths was $\leqslant 0.010$ Å (corresponds to AS flag = 1 or 2 in CSD), *or* (b) crystallographic *R* factor $\leqslant 0.05$ and the mean e.s.d. for C–C bonds are not available in the database (AS = 0 in 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.

Program System.—All calculations were performed on the University of Cambridge IBM 3081D computer using the programs BIBSER, CONNSER, RETRIEVE, GEOM78, and PLUTO78.[4] A stand-alone program was written to implement the selection criteria, whilst a new program (STATS) was used for 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 co-ordination numbers. This was essential in the case of carbon so that atoms with co-ordination 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 GEOM78 in the generation of geometrical tabulations. This often involved the explicit specification of hydrogen 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 of CSD for *ca.* 65% of all entries. Chemical diagrams proved useful, for example, in identifying the various co-ordination environments commonly adopted by atoms such as As, B, P, *etc.*

Classification of Bonds.—The classification of bonds used in the Table is based on common functional groups, rings and ring systems, co-ordination spheres, *etc.* It is designed to: (i) 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 $<$ *ca.* 0.02 Å; (c) there were no conspicuous outlying observations (those which 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.

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 equation (1) holds

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

and d_i is the ith observation of the bond length in a total sample of n observations. Recent work[8–10] 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 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 equation (2) holds.

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

(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.

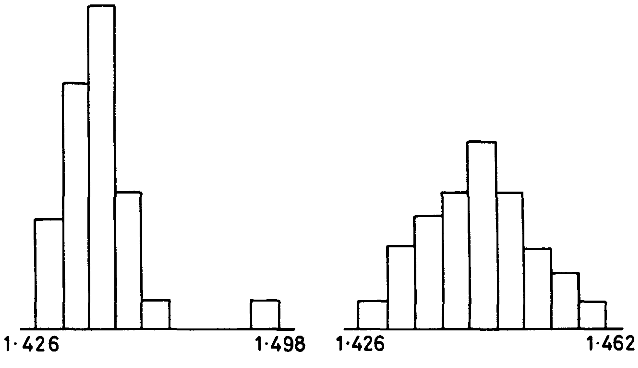

Figure 2. Effect of the removal of outliers (contributors which are $>4\sigma$ from the mean) for the C–C bond in C*ar*–C≡N fragments. Relevant statistics (see text) are:

	d	m	σ	q_l	q_u	n
(a) before:	1.445	1.444	0.012	1.436	1.448	32
(b) after:	1.445	1.444	0.008	1.436	1.448	31

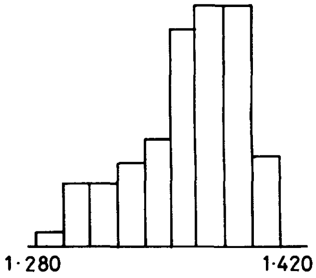

Figure 3. Skewed distribution of B–F bond lengths in BF_4^- ions: $d = 1.365, m = 1.372, \sigma = 0.029, q_l = 1.352, q_u = 1.390$ for 84 observations. Note that $d \neq m$ and that q_l q_u are asymmetrically disposed about the mean d

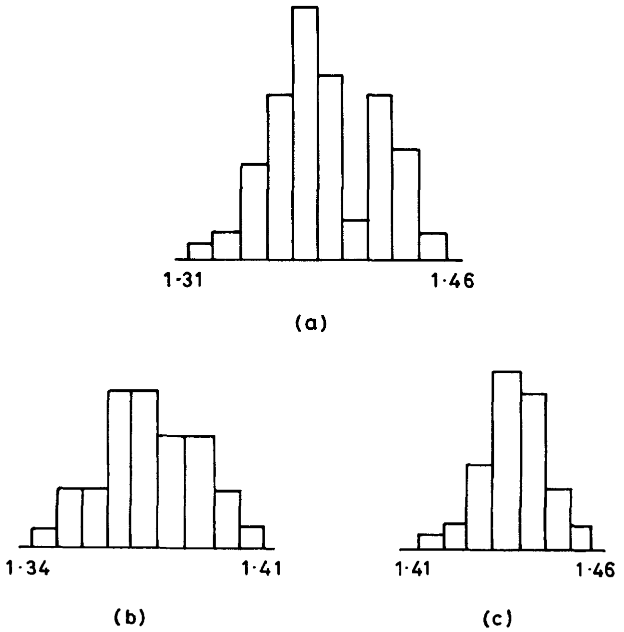

Figure 4. Resolution of the bimodal distribution of C–N bond lengths in C*ar*–N(C*sp*^{3})$_2$ fragments: (a) complete distribution, (b) distribution for planar N, mean valence angle at N > 117.5°, (c) distribution for pyramidal N, mean valence angle at N in the range 108—114°

(a)

	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															*

(b)

	C—C							C—N				C—O	
	C*sp*^{3}	C*sp*^{2}	C*ar*	C*sp*^{1}	C*sp*^{2}	C*ar*	C*sp*^{1}	N(4)	N(3)	N(2)	N(1)	O(2)	O(1)
C*sp*^{3}—	27	30	6	4				5	22	2		60	
C*sp*^{2}—		24	14	2					28	1		17	
C*ar*—			2	2				1	9	2		4	
C*sp*^{1}—				1									
C*sp*^{2}=					34				1	8			38
C*ar*≃						24			3	9			
C*sp*^{1}≡							5			1	5		

Figure 5. (a) Distribution of mean bond length values reported in the Table by element pair. An * 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, and C–N

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) had been performed. In practice a very small percentage of observations were excluded by these methods. The major effect of removing outliers is to improve the sample standard deviation, as shown in Figure 2 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_1, q_u) will be approximately symmetric about the median: $m-q_1 \simeq q_u-m$, 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_1 and q_u will be asymmetric with respect to *m*. When a bond-length distribution is negatively skewed as in Figure 3, *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 Figure 4a. All cases of biomodality were resolved on chemical grounds before inclusion in the Table, on the basis of hybridization, conformation-dependent conjugative interactions, *etc.* For example the histogram of Figure 4a was resolved into the two discrete unimodal distributions of Figures 4b,c which correspond to planar N(sp^2) and 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 ≥117.5° for N(sp^2).

Content and Arrangement of the Table

The upper triangular matrix of Figure 5a shows the 120 possible element pair combinations which can be formed from the 15 elements: As, B, Br, C, Cl, F, H, I, N, O, P. S, Se, Si, Te. Figure 5a contains the number of discrete average bond lengths given in the Table for each element pair. A total of 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 * in Figure 5a. 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. A full bibliographic listing is available as Supplementary Publication No SUP 56701 (12 pp.).* For 8 element pairs the acceptance criterion (vi) was relaxed to include all available structures, irrespective of precision. These entries are denoted by † in the Table. No bonds were found for 25 element pairs within the subset of CSD used in this study.

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

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 Figure 5a, *i.e.* X changes slowest, Y fastest. The complete sequence runs from As–As to Te–Te with bonds involving carbon in their natural position: As–C . . . C–C . . . C–Te. Within a given X–Y pair a secondary ordering is based on the co-ordination 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 co-ordination 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 Figure 5b. The 13 possible C–C combinations

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* For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1987, Issue 1.

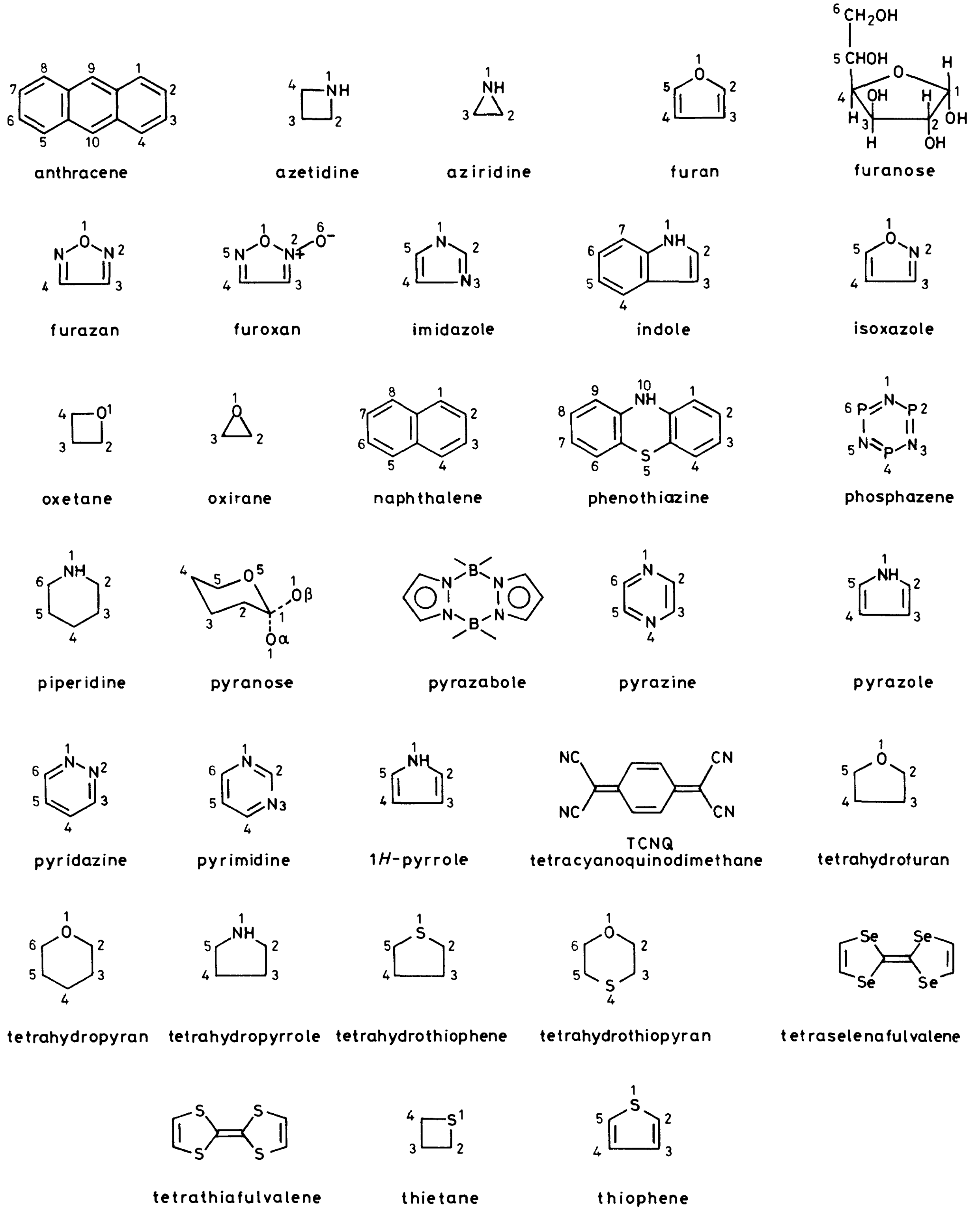

Figure 6. Alphabeticized index of ring systems referred to in the Table; the numbering scheme used in assembling the bond length data is given where necessary

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* ≃ C*ar*, Csp^1≡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 ≃ is used to indicate a delocalized double or aromatic bond according to context.

Definition of 'Substructures'.—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*–**C≡N** (aryl cyanides); C-CH$_2$–**O**–C*ar* (primary-alkyl aryl ethers); (C–O)$_2$–**P**(≃**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 Figure 6. 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 acylic 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^- in SO_4^-, *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 influences 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.

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 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 F. H. A.) of any omissions. This will serve to improve the content of any future version of the Table.

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 organometallic compounds and metal complexes (*e.g.* C$\simeq$C in cyclopentadienyl, C–P in triphenylphosphine, *etc.*) are either absent or poorly represented in this work. These omissions will be rectified in Part 2 which is in preparation. 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[11] 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 functional 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 modeling 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.

Table.

Bond	Substructure	*d*	*m*	σ	q_1	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–C**H_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–Car in Ph_4As^+	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–O**H	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	

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_l	q_u	*n*	Note
	n = 4: **B–C***ar* in Ph_4B^-	1.643	1.643	0.006	1.641	1.645	16	
B(*n*)–C	*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	
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)							
C*sp*^{3}–C*sp*^{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$_2$**	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	2 459	
	(C#)$_2$–**CH–CH$_2$**–C#	1.531	1.531	0.012	1.524	1.538	1 217	
	(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	5 777	5,6
	in cyclopropane (any subst.)	1.510	1.509	0.026	1.497	1.523	888	7
	in cyclobutane (any subst.)	1.554	1.553	0.021	1.540	1.567	679	8
	in cyclopentane (C,H-subst.)	1.543	1.543	0.018	1.532	1.554	1 641	
	in cyclohexane (**C**,H-subst.)	1.535	1.535	0.016	1.525	1.545	2 814	
	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	2 682	
	in cyclobutene (any subst.)	1.573	1.574	0.017	1.566	1.586	25	8
	in cyclopentene (C,H-subst.)	1.541	1.539	0.015	1.532	1.549	208	
	in cyclohexene (C,H-subst.)	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
C*sp*^{3}–C*sp*^{2}	**CH$_3$–C**=C	1.503	1.504	0.011	1.497	1.509	215	
	C#–**CH$_2$–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	

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_l	q_u	*n*	Note
Csp^3–Csp^2	C*–C=C (overall)	1.507	1.507	0.015	1.499	1.517	1 456	5
	C*–C=C (endocyclic)							
	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)(–NH$_2$) 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*	CH$_3$–C*ar*	1.506	1.507	0.011	1.501	1.513	454	
	C#–CH$_2$–C*ar*	1.510	1.510	0.009	1.505	1.516	674	
	(C#)$_2$–CH–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	1 813	
	cyclopropyl (C)–C*ar*	1.490	1.490	0.015	1.479	1.503	90	7
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	7b
	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-subst. only)	1.478	1.476	0.011	1.469	1.488	28	
	in benzoquinone (any subst.)	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

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_l	q_u	*n*	Note
Csp^2–Car		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*–**C**OOH	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*–**C**OO$^-$	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	7b
	C=**C**–**C**≡N in TCNQ	1.427	1.427	0.010	1.420	1.433	280	19
Car–Car	in biphenyls (*ortho* subst. all H)	1.487	1.488	0.007	1.484	1.493	30	
	(⩾1 non-H *ortho*-subst.)	1.490	1.491	0.010	1.486	1.495	212	
Car–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*–**C**H=**C**H$_2$	1.299	1.300	0.027	1.280	1.311	42	
	(C*)$_2$–**C**=**C**H$_2$	1.321	1.321	0.013	1.313	1.328	77	
	C*–**C**H=**C**H–C*							
	(*cis*)	1.317	1.318	0.013	1.310	1.323	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	
	(C*)$_2$–**C**=**C**H–C*	1.326	1.328	0.011	1.319	1.334	168	
	(C*)$_2$–**C**=**C**–(C*)$_2$	1.331	1.330	0.009	1.326	1.334	89	
	(C*,H)$_2$–**C**=**C**–(C*,H)$_2$ (overall)	1.322	1.323	0.014	1.315	1.331	493	5
	in cyclopropene (any subst.)	1.294	1.288	0.017	1.284	1.302	10	10
	in cyclobutene (any subst.)	1.335	1.335	0.019	1.324	1.347	25	8
	in cyclopentene (C,H-subst.)	1.323	1.324	0.013	1.314	1.331	104	
	in cyclohexene (C,H-subst.)	1.326	1.325	0.012	1.318	1.334	196	
	C=**C**=**C** (allenes, any subst.)	1.307	1.307	0.005	1.303	1.310	18	
	C=**C**–**C**=**C** (C,H subst., conjugated)	1.330	1.330	0.014	1.322	1.338	76	16
	C=**C**–**C**=**C**–**C**=**C** (C,H subst., conjugated)	1.345	1.345	0.012	1.337	1.350	58	16
	C=**C**-C*ar* (C,H subst., conjugated)	1.339	1.340	0.011	1.334	1.346	124	16
	C=**C** in cyclopenta-1,3-diene (any subst.)	1.341	1.341	0.017	1.328	1.356	18	
	C=**C** in cyclohexa-1,3-diene (any subst.)	1.332	1.332	0.013	1.323	1.341	56	
	in **C**=**C**–C=O							
	(C,H subst., conjugated)	1.340	1.340	0.013	1.332	1.348	211	16,18
	(C,H subst., unconjugated)	1.331	1.330	0.008	1.326	1.339	14	17,18
	(C,H subst., 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 subst.)	1.333	1.337	0.011	1.325	1.338	14	
	(any subst.)	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
	C=**C**–OH in enol tautomers	1.362	1.360	0.020	1.349	1.370	54	
	in heterocycles (any subst.):							
	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	
$Car \simeq Car$	in phenyl rings with C*,H subst. only							
	H–**C**≃**C**–H	1.380	1.381	0.013	1.372	1.388	2 191	
	C*–**C**≃**C**–H	1.387	1.388	0.010	1.382	1.393	891	
	C*–**C**≃**C**–C*	1.397	1.397	0.009	1.392	1.403	182	
	C≃**C** (overall)	1.384	1.384	0.013	1.375	1.391	3 264	
	F–**C**≃**C**–F	1.372	1.374	0.011	1.366	1.380	84	4
	Cl–**C**≃**C**–Cl	1.388	1.389	0.014	1.380	1.398	152	4
	in naphthalene (D_{2h}, any subst.)							
	C1–C2	1.364	1.364	0.014	1.356	1.373	440	
	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	

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_l	q_u	*n*	Note
C*ar*≃C*ar*	in anthracene (D_{2h}, any subst.)							
	C1–C2	1.356	1.356	0.009	1.350	1.360	56	
	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 subst.)	1.379	1.381	0.012	1.371	1.387	276	20
	(any subst.)	1.380	1.380	0.015	1.371	1.389	537	20
	in pyridinium cation							
	(N^+–H; C,H subst. 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 subst. 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 subst. on C)	1.379	1.377	0.010	1.370	1.388	10	
	(any subst. on C)	1.405	1.405	0.024	1.388	1.420	60	
	in pyrimidine (C,H subst. on C)	1.387	1.389	0.018	1.379	1.400	28	
C*sp*^{1}≡C*sp*^{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
C*sp*^{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	
C*sp*^{2}–Cl	C=**C**–**Cl** (C,H,N,O subst. on C)	1.734	1.729	0.019	1.719	1.748	63	4
	C=**C**–**Cl**$_2$ (C,H,N,O subst. 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
C*sp*^{1}–Cl	see HCLENE10 (1.634, 1.646)							
C*sp*^{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 subst.)	1.320	1.319	0.009	1.312	1.327	18	
C*sp*^{2}–F	C=**C**–**F** (C,H,N,O subst. 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
	Car–**F** (*o*-F$_2$)	1.340	1.340	0.009	1.336	1.344	167	4
C*sp*^{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
C*sp*^{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
C*sp*^{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
C*sp*^{3}–N(4)	**C***–**N**H_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	1 370	

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_1	q_u	*n*	Note
Csp^3–N(3)	C*–N^+ in N-subst. 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	1 042	5,22
	C*–Nsp^3 (overall)	1.469	1.468	0.014	1.460	1.476	1 201	
	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
	C*–NH–C=O	1.334	1.333	0.011	1.326	1.343	78	14
	$(C*)_2$–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
	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
	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
	(C#–NH)$_2$–C=O	1.347	1.345	0.010	1.341	1.354	26	25
	[(C#)$_n$–N]$_2$–C=O	1.363	1.359	0.014	1.354	1.370	40	25,27
	thioureas	1.346	1.343	0.023	1.328	1.361	192	
	$(X_2N)_2$–C=S							
	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–Csp^2	1.409	1.406	0.020	1.391	1.419	28	
	guanidinium $[C–(NH_2)_3]^+$ (unsubst.)	1.321	1.320	0.008	1.314	1.327	39	
	(any subst.)	1.328	1.325	0.015	1.317	1.333	140	
	in heterocyclic systems (any subst.)							
	1*H*-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	
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

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_1	q_u	*n*	Note
C*ar*–N(3)	C*ar*–NH–C#							
	(N*sp*^{2}: planar)	1.353	1.353	0.007	1.347	1.359	16	23
	(N*sp*^{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#)$_2$							
	(N*sp*^{2}: planar)	1.371	1.370	0.016	1.363	1.382	41	23
	(N*sp*^{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	
C*sp*^{2}=N(3)	in furoxan ($^+$N2=C3)	1.316	1.316	0.009	1.311	1.324	14	
C*sp*^{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*≃N(3)	C≃N$^+$–H (pyrimidinium)	1.335	1.334	0.015	1.325	1.342	30	
	C≃N$^+$–C* (pyrimidinium)	1.346	1.346	0.010	1.340	1.352	64	
	C≃N$^+$–O$^-$ (pyrimidinium)	1.362	1.359	0.013	1.353	1.369	56	
C*ar*≃N(2)	C≃N (pyridine)	1.337	1.338	0.012	1.330	1.344	269	
	C≃N (pyrazine)	1.336	1.335	0.022	1.319	1.347	120	
	C≃N≃C (pyrimidine)	1.339	1.338	0.015	1.333	1.342	28	
	N≃C≃N (pyrimidine)	1.333	1.335	0.013	1.326	1.337	28	
	C≃N (pyrimidine) (overall)	1.336	1.337	0.014	1.331	1.339	56	
	in any 6-membered N-containing aromatic ring:							
	H–C≃N≃C–H	1.334	1.334	0.014	1.327	1.341	146	
	H–C≃N≃C–C*	1.339	1.341	0.013	1.336	1.345	38	
	C*–C≃N≃C–C*	1.345	1.345	0.008	1.342	1.348	24	
	C≃N≃C (overall)	1.336	1.337	0.014	1.329	1.344	204	
C*sp*^{1}≡N(2)	X–S–C≡C$^-$ (isocyanide)	1.144	1.147	0.006	1.140	1.148	6	
C*sp*^{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–N$^+$≡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	
C*sp*^{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	
	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 (epoxides) (any subst.)	1.446	1.446	0.014	1.438	1.456	498	9
	oxetane (any subst.)	1.463	1.460	0.015	1.451	1.474	16	
	tetrahydrofuran (C,H subst.)	1.442	1.441	0.017	1.430	1.451	154	

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_l	q_u	*n*	Note
C*sp*^{3}–O(2)	tetrahydropyran (C,H subst.)	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 system 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):							
	C_5–O_5	1.439	1.440	0.008	1.432	1.445	29	
	O_5–C_1	1.427	1.426	0.012	1.421	1.432	29	
	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	
	O_5–C_1	1.430	1.431	0.010	1.424	1.436	17	
	C_1–O_1	1.393	1.393	0.007	1.386	1.399	17	
	α + β (overall):							
	C_5–O_5	1.439	1.440	0.008	1.432	1.446	60	
	O_5–C_1	1.430	1.429	0.012	1.421	1.436	60	
	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	
	O_4–C_1	1.432	1.432	0.012	1.421	1.443	18	
	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):							
	C_5–O_5	1.439	1.438	0.010	1.433	1.446	67	
	O_5–C_1	1.417	1.417	0.009	1.410	1.424	67	
	C_1–O_1	1.409	1.409	0.014	1.401	1.417	67	
	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	
	O_5–C_1	1.424	1.424	0.008	1.418	1.431	39	
	C_1–O_1	1.390	1.390	0.011	1.381	1.400	39	
	O_1–C*	1.437	1.438	0.013	1.428	1.445	39	
	α + β (overall):							
	C_5–O_5	1.436	1.436	0.009	1.431	1.442	126	
	O_5–C_1	1.419	1.419	0.011	1.412	1.426	126	
	C_1–O_1	1.402	1.403	0.016	1.391	1.413	126	
	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	
	O_4–C_1	1.421	1.418	0.012	1.413	1.431	23	
	C_1–O_1	1.410	1.409	0.014	1.401	1.420	23	
	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	
C*sp*^{2}–O(2)	in enols: C=**C**–**O**H	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)–**O**H	1.308	1.311	0.019	1.298	1.320	174	
	C=C–**C**(=O)–**O**H	1.293	1.295	0.019	1.279	1.307	22	
	C*ar*-**C**(=O)–**O**H	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*–**O**H	1.362	1.364	0.015	1.353	1.373	551	
	in aryl alkyl ethers: **C***ar*–**O**–**C***	1.370	1.370	0.011	1.363	1.377	920	29,32

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_l	q_u	*n*	Note
Car–O(2)	in diaryl ethers: Car–O–Car	1.384	1.381	0.014	1.375	1.391	132	
	in esters: Car–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	1.192	0.005	1.188	1.197	7	
	(C*)$_2$–C=O	1.210	1.210	0.008	1.206	1.215	474	5
	(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	
	Car–C=O	1.221	1.218	0.014	1.212	1.229	85	
	(Car)$_2$–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	
	Car–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	
	Car–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	
	Car–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–Car	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
	γ-lactams:							
	C*–NH–C=O	1.235	1.235	0.008	1.232	1.240	20	13
	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
	C*–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	1.786	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	
Car–P(4)	C$_3$–P$^+$–Car	1.793	1.792	0.011	1.786	1.800	276	
	C$_2$–P(=O)–Car	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	
Car–P(3)	C$_2$–P–Car	1.836	1.837	0.010	1.830	1.844	102	
	(N≃)$_2$P–Car (P≃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	1.756	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$^+$–X$_2$ (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	

Table (*continued*)

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
Csp^3–S(2)	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	
	C*ar*–S–C*ar* (in phenothiazine)	1.764	1.764	0.008	1.760	1.769	48	
	C*ar*–S–S–X	1.777	1.777	0.012	1.767	1.785	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)	1.671	1.675	0.024	1.656	1.689	245	
	X$_2$N–C(=S)–S–X	1.660	1.660	0.016	1.648	1.674	38	
	(X$_2$N)$_2$–C=S (thioureas)	1.681	1.684	0.020	1.669	1.693	96	
	N–C($\simeq$S)$_2$	1.720	1.721	0.012	1.709	1.731	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$_3$	1.857	1.857	0.018	1.848	1.869	552	
	C*–Si–X$_3$ (C* = CH$_3$ excluded)	1.888	1.887	0.023	1.872	1.905	124	
	C*–Si–X$_3$ (overall)	1.863	1.861	0.024	1.850	1.875	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$\simeq$)$_2$P–Cl (N$\simeq$P aromatic)	1.997	1.994	0.015	1.989	2.004	46	
	Cl–P (overall)	2.008	2.001	0.035	1.986	2.028	111	
Cl–S	Cl–S (overall)	2.072	2.079	0.023	2.047	2.091	6	
	see also longer bonds in CILSAR (2.283), BIHXIZ (2.357), CANLUY (2.749)							
Cl–Se	see BIRGUE10, BIRHAL10, CTCNSE (2.234—2.851)							
Cl–Si(4)	Cl–Si–X$_3$ (monochloro)	2.072	2.075	0.009	2.066	2.078	5	
	Cl$_2$–Si–X$_2$ and Cl$_3$–Si–X	2.020	2.012	0.015	2.007	2.036	5	
Cl–Te	Cl–Te in range 2.34—2.60	2.520	2.515	0.034	2.493	2.537	22	36
	see also longer bonds in BARRIV, BOJPUL, CETUTE, EPHTEA, OPNTEC10 (2.73—2.94)							
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	
F–P(3)	(N$\simeq$)$_2$P–F (N$\simeq$P aromatic)	1.495	1.497	0.016	1.481	1.510	10	
F–S	43 observations in range 1.409—1.770 in a wide variety of environments; F–S(6) in F$_2$–SO$_2$–C$_2$ (see FPSULF10, BETJOZ)	1.640	1.646	0.011	1.626	1.649	6	
	F–S(4) in 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	

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_1	q_u	*n*	Note
F–Te	see CUCPIZ (F–Te(6) = 1.942, 1.937), FPHTEL (F–Te(4) = 2.006)							
H–N(4)	X_3–**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)	2.144	2.144	0.028	2.127	2.164	6	
	for IO_6^- see BOVMEE (1.829—1.912)							
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–**N**$^+$–**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)–N_a–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 pyridazine							
	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** (N*sp*^{2}: planar)	1.396	1.394	0.012	1.390	1.401	28	
	C_2–**N–O**–C							
	(N*sp*^{3}: pyramidal)	1.463	1.465	0.012	1.457	1.468	22	
	(N*sp*^{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 ≃)$_2$**N**$^+$–**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	
N(2)–O(2)	in oximes							
	(C#)$_2$–C=**N–OH**	1.416	1.418	0.006	1.416	1.420	7	
	(H)(C*sp*^{2})–C=**N–OH**	1.390	1.390	0.011	1.380	1.401	20	
	(C#)(C*sp*^{2})–C=**N–OH**	1.402	1.403	0.010	1.393	1.410	18	
	(C*sp*^{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 $\mathbf{NO_3}^-$	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	1 116	
	C–NO$_2$ (overall)	1.218	1.219	0.013	1.210	1.226	1 733	
N(3)–P(4)	X_2–**P**(=X)–**N**X_2							
	N*sp*^{2}: planar	1.652	1.651	0.024	1.634	1.670	205	
	N*sp*^{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)–**N**X_2	1.628	1.624	0.015	1.615	1.634	9	
	C–**P**(=S)–(**N**X_2)$_2$	1.691	1.694	0.018	1.678	1.703	28	
	O–**P**(=S)–(**N**X_2)$_2$	1.652	1.654	0.014	1.642	1.664	28	
	P(=O)–(**N**X_2)$_3$	1.663	1.668	0.026	1.640	1.679	78	
N(3)–P(3)	–**N**X–**P**(–X)–**N**X–**P**(–X)– (P_2N_2 ring)	1.730	1.721	0.017	1.716	1.748	20	
	–**N**X–**P**(=S)–**N**X–**P**(=S)– (P_2N_2 ring)	1.697	1.697	0.015	1.690	1.703	44	
	in *P*-substituted phosphazenes:							
	(N ≃)$_2$**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	

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_1	q_u	*n*	Note
N(2)=*P(3)*	Ph$_3$–**P**=**N**–C,S	1.599	1.597	0.018	1.580	1.615	7	
N(2)≃P(3)	**N**≃**P** aromatic							
	in phosphazenes	1.582	1.582	0.019	1.571	1.594	126	
	in P≃N≃S	1.604	1.606	0.009	1.594	1.612	36	
N(3)–S(4)	C–**S**O$_2$–**N**H$_2$	1.600	1.601	0.012	1.591	1.610	14	35
	C–**S**O$_2$–**N**H–C#	1.633	1.633	0.019	1.615	1.652	47	35
	C–*S*O$_2$–**N**–C(#)$_2$	1.642	1.641	0.024	1.623	1.659	38	35
N(3)–S(2)	C–**S**–**N**X$_2$ Nsp^2: planar (for Nsp^3 pyramidal see MODIAZ: 1.765)	1.710	1.707	0.019	1.698	1.722	22	23
	X–**S**–**N**X$_2$ 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)≃S(2)	**N**≃**S** aromatic in P≃**N**≃**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**–**N**X$_2$ (overall)	1.748	1.746	0.022	1.735	1.757	170	
	subsets of this group are:							
	X$_3$–**Si**–**N**HX	1.714	1.719	0.014	1.702	1.727	16	
	X$_3$–**Si**–**N**X–Si–X$_3$ acyclic	1.743	1.744	0.016	1.731	1.755	45	
	N–**Si**–**N** in 4-membered rings	1.742	1.742	0.009	1.735	1.748	53	
	N–**Si**–**N** in 5-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) *ca.* 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**)$_3^{2-}$ (declocalized)	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**–**S**O$_2$–C	1.577	1.576	0.015	1.566	1.584	41	
	C–**O**–**S**O$_2$–CH$_3$	1.569	1.569	0.013	1.556	1.582	7	
	C–**O**–**S**O$_2$–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	

Table (*continued*)

Bond	Substructure	*d*	*m*	σ	q_1	q_u	*n*	Note
O(2)–Si(4)	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	0.614	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	
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 polysulphide 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)–Se(4)	X_3–**Si**–**Si**–X_3 3-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)							

Appendix 1. **(Footnotes to Table)**

1. Sample dominated by B–CH_3. For longer bonds in B^-–CH_3 see LITMEB10 [B(4)–CH_3 = 1.621—1.644Å].
2. *p*(π)–*p*(π) Bonding with Bsp^2 and Nsp^2 coplanar (τBN = 0 ± 15°) predominates. See G. Schmidt, R. Boese, and D. Bläser, *Z. Naturforsch.*, 1982, **37b**, 1230.
3. 84 observations range from 1.38 to 1.61 Å and individual values depend on substituents on B and O. For a discussion of borinic acid adducts see S. J. Rettig and J. Trotter, *Can. J. Chem.*, 1982, **60**, 2957.
4. See M. Kaftory in 'The Chemistry of Functional Groups. Supplement D: The Chemistry of Halides, Pseudohalides, and Azides' eds. S. Patai and Z. Rappoport, Wiley: New York, 1983, Part 2, ch. 24.
5. Bonds which are endocyclic or exocyclic to any 3- or 4-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 9 subgroups is 1.538 (σ = 0.022) Å.
7. See F. H. Allen, (*a*) *Acta Crystallogr.*, 1980, **B36**, 81; (*b*) 1981, **B37**, 890.
8. See F. H. Allen, *Acta Crystallogr.*, 1984, **B40**, 64.
9. See F. H. Allen, *Tetrahedron*, 1982, **38**, 2843.
10. See F. H. Allen, *Tetrahedron*, 1982, **38**, 645.
11. Cyclopropanones and cyclobutanones excluded.
12. See W. B. Schweizer and J. D. Dunitz, *Helv. Chim. Acta*, 1982, **65**, 1547.
13. See L. Norskov-Lauritsen, H.-B. Bürgi, P. Hoffmann, and H. R. Schmidt, *Helv. Chim. Acta*, 1985, **68**, 76.
14. See P. Chakrabarti and J. D. Dunitz, *Helv. Chim. Acta*, 1982, **65**, 1555.
15. See J. L. Hencher in 'The Chemistry of the C≡C Triple Bond,' ed. S. Patai, Wiley, New York, 1978, ch. 2.
16. Conjugated: torsion angle about central C–C single bond is 0 ± 20° (*cis*) or 180 ± 20° (*trans*).
17. Unconjugated: torsion angle about central C–C single bond is 20—160°.
18. Other conjugative substituents excluded.
19. TCNQ is tetracyanoquinodimethane.
20. No difference detected between C2$\simeq$C3 and C3$\simeq$C4 bonds.
21. Derived from neutron diffraction results only.
22. Nsp^3: pyramidal; mean valence angle at N is in range 108—114°.
23. Nsp^2: planar; mean valence angle at N is $\geqslant$117.5°.
24. Cyclic and acyclic peptides.
25. See R. H. Blessing, *J. Am. Chem. Soc.*, 1983, **105**, 2776.
26. See L. Lebioda, *Acta Crystallogr.*, 1980, **B36**, 271.
27. *n* = 3 or 4, *i.e.* tri- or tetra-substituted ureas.
28. Overall value also includes structures with mean valence angle at N in the range 115—118°.
29. See F. H. Allen and A. J. Kirby, *J. Am. Chem. Soc.*, 1984, **106**, 6197.
30. See A. J. Kirby, 'The Anomeric Effect and Related Stereoelectronic Effects at Oxygen,' Springer, Berlin, 1983.
31. See B. Fuchs, L. Schleifer, and E. Tartakovsky, *Nouv. J. Chim.*, 1984, **8**, 275.

32. See S. C. Nyburg and C. H. Faerman, *J. Mol. Struct.*, 1986, **140**, 347.
33. Sample dominated by P–CH_3 and P–CH_2–C.
34. Sample dominated by C* = methyl.
35. See A. Kalman, M. Czugler, and G. Argay, *Acta Crystallogr.*, 1981, **B37**, 868.
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 - - - H - - - 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 range 100—113.5°; N planar has average angle of ≥117.5°.
41. See R. R. Holmes and J. A. Deiters, *J. Amer. Chem. Soc.*, 1977, **99**, 3318.
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 the Table. A full list of CSD bibliographic entries is given in SUP 56701.

ACBZPO01	*J. Am. Chem. Soc.*, 1975, **97**, 6729.
ACLTEP	*J. Organomet. Chem.*, 1980, **184**, 417.
ASAZOC	*Dokl. Akad. Nauk SSSR*, 1979, **249**, 120.
BALXOB	*J. Am. Chem. Soc.*, 1981, **103**, 4587.
BAPPAJ	*Inorg. Chem.*, 1981, **20**, 3071.
BARRIV	*Acta Chem. Scand., Ser. A*, 1981, **35**, 443.
BAWFUA	*Cryst. Struct. Commun.*, 1981, **10**, 1345.
BAWGAH	*Cryst. Struct. Commun.*, 1981, **10**, 1353.
BECTAE	*J. Org. Chem.*, 1981, **46**, 5048, 1981.
BELNIP	*Z. Naturforsch., Teil B*, 1982, **37**, 299.
BEMLIO	*Chem. Ber.*, 1982, **115**, 1126.
BEPZEB	*Cryst. Struct. Commun.*, 1982, 11, 175.
BETJOZ	*J. Am. Chem. Soc.*, 1982, **104**, 1683.
BETUTE10	*Acta Chem. Scand., Ser. A*, 1976, **30**, 719.
BIBLAZ	*Zh. Strukt. Khim.*, 1981, **22**, 118.
BICGEZ	*Z. Anorg. Allg. Chem.*, 1982, **486**, 90.
BIHXIZ	*J. Chem. Soc., Chem. Commun.*, 1982, 982.
BIRGUE10	*Z. Naturforsch., Teil B*, 1983, **38**, 20.
BIRHAL10	*Z. Naturforsch., Teil B*, 1982, **37**, 1410.
BIZJAV	*J. Organomet. Chem.*, 1982, **238**, C1.
BOGPOC	*Z. Naturforsch., Teil B*, 1982, **37**, 1402.
BOGSUL	*Z. Naturforsch., Teil* B, 1982, **37**, 1230.
BOJLER	*Z. Anorg. Allg. Chem.*, 1982, **493**, 53.
BOJPUL	*Acta Chem. Scand., Ser. A*, 1982, **36**, 829.
BOPFER	*Chem. Ber.*, 1983, 116, 146.
BOPFIV	*Chem. Ber.*, 1983, 116, 146.
BOVMEE	*Acta Crystallogr., Sect. B*, 1982, **38**, 1048.
BQUINI	*Acta Crystallogr., Sect. B*, 1979, **35**, 1930.
BTUPTE	*Acta Chem. Scand., Ser. A*, 1975, **29**, 738.
BUDTEZ	*Z. Naturforsch., Teil B*, 1983, **38**, 454.
BUPSIB10	*Z. Anorg. Allg. Chem.*, 1981, **474**, 31.
BUSHAY	*Z. Naturforsch., Teil. B*, 1983, **38**, 692.
BUTHAZ10	*Inorg. Chem.*, 1984, **23**, 2582.
BUTSUE	*J. Chem. Soc., Chem. Commun.*, 1983, 862.
BUWZUO	*Acta Chem. Scand., Ser A*, 1983, **37**, 219.
BZPRIB	*Z. Naturforsch., Teil B*, 1981, **36**, 922.
BZTPPI	*Inorg. Chem.*, 1978, 17, 894.
CAHJOK	*Inorg. Chem.*, 1983, **22**, 1809.
CAJMAB	*Chem. Z*, 1983, **107**, 169.
CANLUY	*Tetrahedron Lett.*, 1983, **24**, 4337.
CASSAQ	*J. Struct. Chem.*, 1983, **2**, 101.
CASTOF10	*Acta Crystallogr., Sect. C*, 1984, **40**, 1879.
CASYOK	*J. Struct. Chem.*, 1983, **2**, 107.
CECHEX	*Z. Anorg. Allg. Chem.*, 1984, **508**, 61.
CECXEN	*J. Struct. Chem.*, 1983, **2**, 207.
CEDCUJ	*J. Org. Chem.*, 1983, **48**, 5149.
CEHKAB	*Z. Naturforsch., Teil B*, 1984, **39**, 139.
CELDOM	*Acta Crystallogr., Sect. C*, 1984, **40**, 556.
CESSAU	*Acta Crystallogr., Sect. C*, 1984, **40**, 653.
CETTAW	*Chem. Ber.*, 1984, 117, 1089.
CETUTE	*Acta Chem. Scand., Ser A*, 1975, **29**, 763.
CEYLUN	*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2744.
CIFZUM	*Acta Chem. Scand., Ser A*, 1984, **38**, 289.
CIHRAM	*Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 302.
CILRUK	*J. Chem. Soc., Chem. Commun.*, 1984, 1023.
CILSAR	*J. Chem. Soc., Chem. Commun.*, 1984, 1021.
CIMHIP	*Acta Crystallogr., C*, 1984, **40**, 1458.
CINTEY	*Dokl. Akad. Nauk SSSR*, 1984, **274**, 615.
CIPBUY	*J. Struct. Chem.*, 1983, **2**, 281.
CISMUM	*Z. Naturforsch., Teil B*, 1984, **39**, 485.
CISTED	*Z. Anorg. Allg. Chem.*, 1984, **511**, 95.
CIWYIQ	*Inorg. Chem.*, 1984, **23**, 1946.
CIYFOF	*Inorg. Chem.*, 1984, **23**, 1790.
CMBIDZ	*J. Org. Chem.*, 1979, **44**, 1447.
CODDEE	*Z. Naturforsch., Teil B*, 1984, **39**, 1257.
CODDII	*Z. Naturforsch., Teil B*, 1984, **39**, 1257.
COFVOI	*Z. Naturforsch., Teil B*, 1984, **39**, 1027.
COJCUZ	*Chem. Ber.*, 1984, 117, 2686.
COSDIX	*Z. Naturforsch., Teil B*, 1984, **39**, 1344.
COZPIQ	*Chem. Ber.*, 1984, 117, 2063.
COZVIW	*Z. Anorg. Allg. Chem.*, 1984, **515**, 7.
CTCNSE	*J. Am. Chem. Soc.*, 1980, **102**, 5430.
CUCPIZ	*J. Am. Chem. Soc.*, 1984, **106**, 7529.
CUDLOC	*J. Cryst. Spectrosc.*, 1985, **15**, 53.
CUDLUI	*J. Cryst. Spectrosc.*, 1985, **15**, 53.
CUGBAH	*Acta Crystallogr., Sect. C*, 1985, **41**, 476.
CXMSEO	*Acta Crystallogr., Sect. B*, 1973, **29**, 595.
DGLYSE	*Acta Crystallogr., Sect. B*, 1975, **31**, 1785.
DMESIP01	*Acta Crystallogr., Sect. C*, 1984, **40**, 895.
DSEMOR10	*J. Chem. Soc., Dalton Trans.*, 1980, 628.
DTHIBR10	*Inorg. Chem.*, 1971, **10**, 697.
EPHTEA	*Inorg. Chem.*, 1980, **19**, 2487.
ESEARS	*J. Chem. Soc. C*, 1971, 1511.
ETEARS	*J. Chem. Soc. C*, 1971, 1511.
FMESIB	*J. Organomet. Chem.*, 1980, **197**, 275.
FPHTEL	*J. Chem. Soc., Dalton Trans.*, 1980, 2306.
FPSULF10	*J. Am. Chem. Soc.*, 1982, **104**, 1683.
HCLENE10	*Acta Crystallogr., Sect. B*, 1982, **38**, 3139.
HMTITI	*Acta Crystallogr., Sect. B*, 1975, **31**, 1505.
HMTNTI	*Z. Anorg. Allg. Chem.*, 1974, **409**, 237.
HXPASC	*J. Chem. Soc., Dalton Trans.*, 1975, 1381.
IBZDAC11	*J. Chem. Soc., Dalton Trans.*, 1979, 854.
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