

9.5. TYPICAL INTERATOMIC DISTANCES: ORGANIC COMPOUNDS

A combination of chemical name and linear formulation is often employed to increase the precision of the definition, *e.g.* $\text{NH}_2\text{—C=O}$ 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: $\text{Csp}^3\text{—Csp}^3$: in cyclobutane (any substituent); X—C—F_3 ($\text{X} = \text{C}, \text{H}, \text{N}, \text{O}$); $\text{C}_{\text{ar}}\text{—NH—Csp}^3$ (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 $\text{C}^\#$. C^* indicates

Csp^3 whose bonds, additional to those specified in the linear formulation, are to C or H atoms only. $\text{C}^*\text{—OH}$ would then represent the group of alcohols $\text{CH}_3\text{—OH}$, $\text{—C—CH}_2\text{—OH}$, $\text{—C}_2\text{—CH—OH}$ and $\text{—C}_3\text{—C—OH}$. 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 $\text{C}^\#$ 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

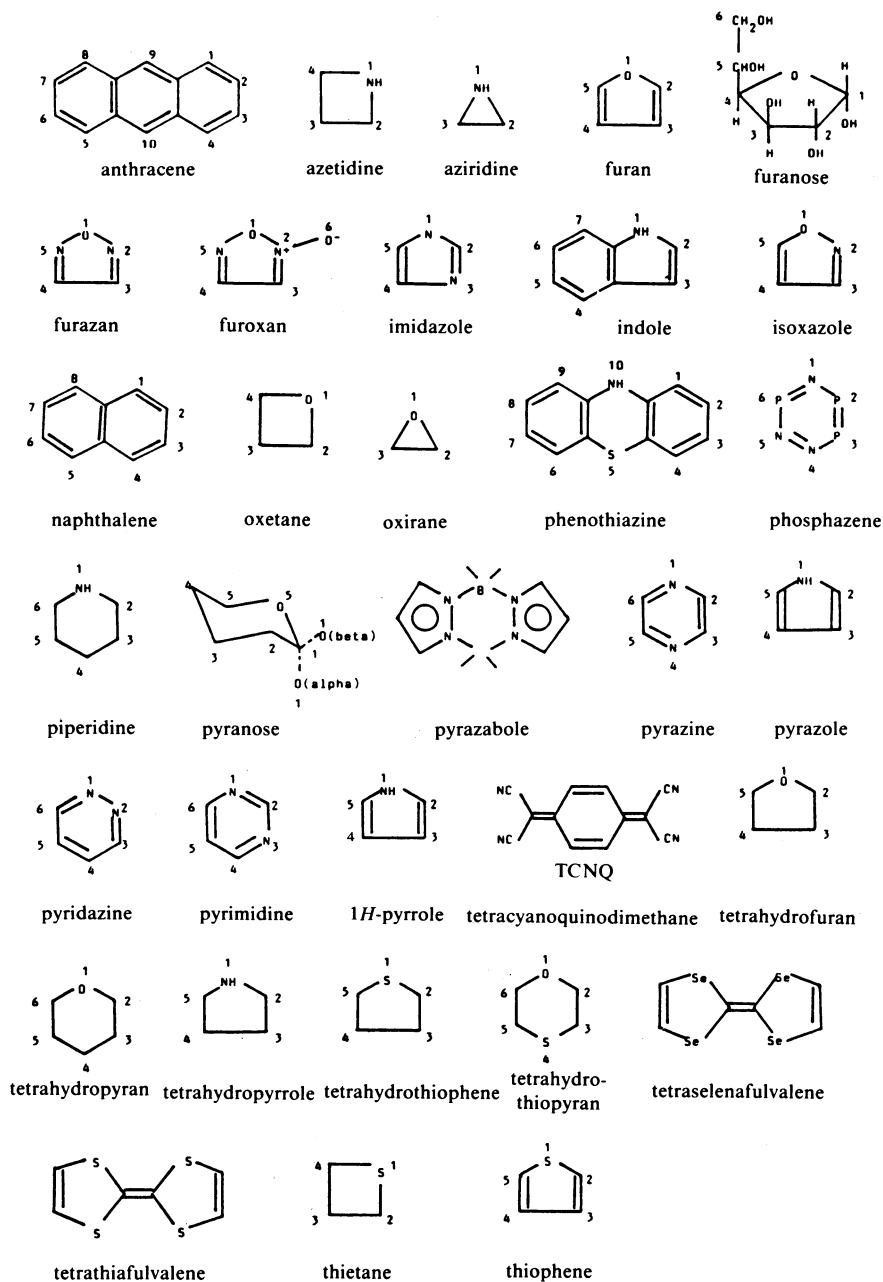


Fig. 9.5.3.2. Alphabetized index of ring systems referred to in the table; the numbering scheme used in assembling the bond-length data is given where necessary.

9. BASIC STRUCTURAL FEATURES

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 \equiv 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—CH₃. For longer bonds in B⁻—CH₃, see LITMEB10 [B(4)—CH₃ = 1.621–1.644 Å].
- (2) *p*(π)—*p*(π) bonding with B sp^2 and N sp^2 coplanar ($\tau_{BN} = 0 \pm 15^\circ$) 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, pseudo-halides 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 C sp^3 —C sp^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 $0 \pm 20^\circ$ (*cis*) or $180 \pm 20^\circ$ (*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 \equiv C3 and C3 \equiv C4 bonds.
- (21) Derived from neutron diffraction results only.
- (22) N sp^3 : pyramidal; mean valence angle at N is in the range 108–114°.
- (23) N sp^2 : planar; mean valence angle at N is $\geq 117.5^\circ$.
- (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—CH₃ and P—CH₂—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 $\geq 117.5^\circ$.
- (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	<i>J. Am. Chem. Soc.</i>	97	6729	1975
ACLTEP	<i>J. Organomet. Chem.</i>	184	417	1980
ASAZOC	<i>Dokl. Akad. Nauk SSSR</i>	249	120	1979
BALXOB	<i>J. Am. Chem. Soc.</i>	103	4587	1981