9. BASIC STRUCTURAL FEATURES

N, torsional constraints in conjugated systems; (c) any peculiarities of a particular bond-length distribution, e.g. sample dominated by $C^\equiv$=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, $C\equiv P$ 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 (Bergerhoff, 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 ‘ensemble 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.

APPENDIX 1

Notes to Table 9.5.1.1

(1) Sample dominated by $B=CH_2$. For longer bonds in $B'=CH_2$, see LITMEB1 [B(4) = $CH_3 = 1.621-1.644 \text{Å}$].
(2) $p(\pi)-p(\pi)$ bond with $Bsp^2$ and $Nsp^2$ 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. Retig & J. Trotter [Can. J. Chem. (1982), 60, 2957–2964].
(5) Structures 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 $Csp^3=Csp^2$ 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 (σ = 0.022) Å.
(11) Cyclopropanones and cyclobutanones excluded.
(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 $20–160^\circ$.
(18) Other conjugative substituents excluded.
(19) TCNO is tetracyanoquinodimethane (see diagrams).
(20) No difference detected between $C_2 \equiv C_3$ and $C_3 \equiv C_4$ bonds.
(21) Derived from neutron diffraction results only.
(22) Nsp$^1$: pyramidal; mean valence angle at N is in the range 108–114$^\circ$.
(23) Nsp$^2$: planar; mean valence angle at N is $\geq 117.5^\circ$.
(24) Cyclic and acyclic peptides.
(27) $n = 3$ or 4; i.e. tri- or tetrasubstituted amines.
(28) Overall value also includes structures with mean valence angle at N in the range 115–118$^\circ$.
(33) Sample dominated by P—CH$_3$ and P—CH$_2$—C.
(34) Sample dominated by $C^\equiv$ = methyl.
(36) Bimidodal distribution resolved into 22 ‘short’ bonds and 5 longer outliers.
(37) All 24 observations come from BUDETZ.
(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 the range 100–113.5$^\circ$; N planar has average angle $\geq 117.5^\circ$.
(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

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