

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

9.5. TYPICAL INTERATOMIC DISTANCES: ORGANIC COMPOUNDS

BAPPAJ	<i>Inorg. Chem.</i>	20	3071	1981	CMBIDZ	<i>J. Org. Chem.</i>	44	1447	1979
BARRIV	<i>Acta Chem. Scand. Ser. A</i>	35	433	1981	CODDEE	<i>Z. Naturforsch. Teil B</i>	39	1257	1984
BAWFUA	<i>Cryst. Struct. Commun.</i>	10	1345	1981	CODDII	<i>Z. Naturforsch. Teil B</i>	39	1257	1984
BAWGAH	<i>Cryst. Struct. Commun.</i>	10	1353	1981	COFVOI	<i>Z. Naturforsch. Teil B</i>	39	1027	1984
BECTAE	<i>J. Org. Chem.</i>	46	5048	1981	COJCUZ	<i>Chem. Ber.</i>	117	2686	1984
BELNIP	<i>Z. Naturforsch. Teil B</i>	37	299	1982	COSDIX	<i>Z. Naturforsch. Teil B</i>	39	1344	1984
BEMLIO	<i>Chem. Ber.</i>	115	1126	1982	COZPIQ	<i>Chem. Ber.</i>	117	2063	1984
BEPZEB	<i>Cryst. Struct. Commun.</i>	11	175	1982	COZVIW	<i>Z. Anorg. Allg. Chem.</i>	515	7	1984
BETJOZ	<i>J. Am. Chem. Soc.</i>	104	1683	1982	CTCNSE	<i>J. Am. Chem. Soc.</i>	102	5430	1980
BETUTE10	<i>Acta Chem. Scand. Ser. A</i>	30	719	1976	CUCPIZ	<i>J. Am. Chem. Soc.</i>	106	7529	1984
BIBLAZ	<i>Zh. Strukt. Khim.</i>	22	118-4	1981	CUDLOC	<i>J. Cryst. Spectrosc.</i>	15	53	1985
BICGEZ	<i>Z. Anorg. Allg. Chem.</i>	486	90	1982	CUDLUI	<i>J. Cryst. Spectrosc.</i>	15	53	1985
BIHXIZ	<i>J. Chem. Soc. Chem. Commun.</i>		982	1982	CUGBAH	<i>Acta Cryst. Sect. C</i>	41	476	1985
BIRGUE10	<i>Z. Naturforsch. Teil B</i>	38	20	1983	CXMSEO	<i>Acta Cryst. Sect. B</i>	29	595	1973
BIRHAL10	<i>Z. Naturforsch. Teil B</i>	37	1410	1982	DGLYSE	<i>Acta Cryst. Sect. B</i>	31	1785	1975
BIZJAV	<i>J. Organomet. Chem.</i>	238	C1	1982	DMESIP01	<i>Acta Cryst. Sect. C</i>	40	895	1984
BOGPAC	<i>Z. Naturforsch. Teil B</i>	37	1402	1982	DSEMOR10	<i>J. Chem. Soc. Dalton Trans.</i>		628	1980
BOGSUL	<i>Z. Naturforsch. Teil B</i>	37	1230	1982	DTHIBR10	<i>Inorg. Chem.</i>	10	697	1971
BOJLER	<i>Z. Anorg. Allg. Chem.</i>	493	53	1982	EPHTEA	<i>Inorg. Chem.</i>	19	2487	1980
BOJPUL	<i>Acta Chem. Scand. Ser. A</i>	36	829	1982	ESEARS	<i>J. Chem. Soc. C</i>		1511	1971
BOPFER	<i>Chem. Ber.</i>	116	146	1983	ETEARS	<i>J. Chem. Soc. C</i>		1511	1971
BOPFIV	<i>Chem. Ber.</i>	116	146	1983	FMESIB	<i>J. Organomet. Chem.</i>	197	275	1980
BOVMEE	<i>Acta Cryst. Sect. B</i>	38	1048	1982	FPHTEL	<i>J. Chem. Soc. Dalton Trans.</i>		2306	1980
BQUINI	<i>Acta Cryst. Sect. B</i>	35	1930	1979	FPSULF10	<i>J. Am. Chem. Soc.</i>	104	1683	1982
BTUPTE	<i>Acta Chem. Scand. Ser. A</i>	29	738	1975	HCLENE10	<i>Acta Cryst. Sect. B</i>	38	3139	1982
BUDTEZ	<i>Z. Naturforsch. Teil B</i>	38	454	1983	HMTITI	<i>Acta Cryst. Sect. B</i>	31	1505	1975
BUPSIB10	<i>Z. Anorg. Allg. Chem.</i>	474	31	1981	HMTNTI	<i>Z. Anorg. Allg. Chem.</i>	409	237	1974
BUSHAY	<i>Z. Naturforsch. Teil B</i>	38	692	1983	HXPASC	<i>J. Chem. Soc. Dalton Trans.</i>		1381	1975
BUTHAZ10	<i>Inorg. Chem.</i>	23	2582	1984	IBZDAC11	<i>J. Chem. Soc. Dalton Trans.</i>		854	1979
BUTSUE	<i>J. Chem. Soc. Chem. Commun.</i>		862	1983	IFORAM	<i>Monatsh. Chem.</i>	105	621	1974
BUWZUO	<i>Acta Chem. Scand. Ser. A</i>	37	219	1983	IODMAM	<i>Acta Cryst. Sect. B</i>	33	3209	1977
BZPRIB	<i>Z. Naturforsch. Teil B</i>	36	922	1981	IPMUDS	<i>Acta Cryst. Sect. B</i>	29	2128	1973
BZTPPI	<i>Inorg. Chem.</i>	17	894	1978	ISUREA10	<i>Acta Cryst. Sect. B</i>	28	643	1972
CAHJOK	<i>Inorg. Chem.</i>	22	1809	1983	LITMEB10	<i>J. Am. Chem. Soc.</i>	97	6401	1975
CAJMAB	<i>Chem. Z.</i>	107	169	1983	MESIAD	<i>Z. Naturforsch. Teil B</i>	35	789	1980
CANLUY	<i>Tetrahedron Lett.</i>	24	4337	1983	METAMM	<i>Acta Cryst.</i>	17	1336	1964
CASSAQ	<i>J. Struct. Chem.</i>	2	101-2	1983	MNPSIL	<i>J. Am. Chem. Soc.</i>	91	4134	1969
CASTOF10	<i>Acta Cryst. Sect. C</i>	40	1879	1984	MODIAZ	<i>J. Heterocycl. Chem.</i>	17	1217	1980
CASYOK	<i>J. Struct. Chem.</i>	2	107-2	1983	MOPHTE	<i>Acta Chem. Scand. Ser. A</i>	34	333	1980
CECHEX	<i>Z. Anorg. Allg. Chem.</i>	508	61	1984	MORTRS10	<i>J. Chem. Soc. Dalton Trans.</i>		628	1980
CECXEN	<i>J. Struct. Chem.</i>	2	207-3	1983	NAPSEZ10	<i>J. Am. Chem. Soc.</i>	102	5070	1980
CEDCUJ	<i>J. Org. Chem.</i>	48	5149	1983	NBBZAM	<i>Z. Naturforsch. Teil B</i>	32	1416	1977
CEHKAB	<i>Z. Naturforsch. Teil B</i>	39	139	1984	OPIMAS	<i>Aust. J. Chem.</i>	30	2417	1977
CELDOM	<i>Acta Cryst. Sect. C</i>	40	556	1984	OPNTEC10	<i>J. Chem. Soc. Dalton Trans.</i>		251	1982
CESSAU	<i>Acta Cryst. Sect. C</i>	40	653	1984	PHASCL	<i>Acta Cryst. Sect. B</i>	37	1357	1981
CETTAW	<i>Chem. Ber.</i>	117	1089	1984	PHASOC01	<i>Aust. J. Chem.</i>	28	15	1975
CETUTE	<i>Acta Chem. Scand. Ser. A</i>	29	763	1975	PNPOSI	<i>J. Am. Chem. Soc.</i>	90	5102	1968
CEYLUN	<i>Isv. Akad. Nauk SSR Ser. Khim.</i>		2744	1983	SEBZQI	<i>J. Chem. Soc. Chem. Commun.</i>		325	1977
CIFZUM	<i>Acta Chem. Scand. Ser. A</i>	38	289	1984	SPSEBU	<i>Acta Chem. Scand. Ser. A</i>	33	403	1979
CIHRAM	<i>Angew. Chem. Int. Ed. Engl.</i>	23	302	1984	TEACBR	<i>Cryst. Struct. Commun.</i>	3	753	1974
CILRUK	<i>J. Chem. Soc. Chem. Commun.</i>		1023	1984	THINBR	<i>J. Am. Chem. Soc.</i>	92	4002	1970
CILSAR	<i>J. Chem. Soc. Chem. Commun.</i>		1021	1984	TMPBTI	<i>Acta Cryst. Sect. B</i>	31	1116	1975
CIMHIP	<i>Acta Cryst. Sect. C</i>	40	1458	1984	TPASSN	<i>J. Chem. Soc. Dalton Trans.</i>		514	1977
CINTEY	<i>Dokl. Akad. Nauk SSSR</i>	274	615	1984	TPASTB	<i>Cryst. Struct. Commun.</i>	5	39	1976
CIPBUY	<i>J. Struct. Chem.</i>	2	281-4	1983	TPHOSI	<i>Z. Naturforsch. Teil B</i>	34	1064	1979
CISMUM	<i>Z. Naturforsch. Teil B</i>	39	485	1984	TTEBPZ	<i>Z. Naturforsch. Teil B</i>	34	256	1979
CISTED	<i>Z. Anorg. Allg. Chem.</i>	511	95	1984	ZCMXSP	<i>Cryst. Struct. Commun.</i>	6	93	1977
CIWYIQ	<i>Inorg. Chem.</i>	23	1946	1984					
CIYFOF	<i>Inorg. Chem.</i>	23	1790	1984					

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