BOND LENGTHS IN CRYSTALLINE ORGANIC COMPOUNDS

The following table gives average interatomic distances for bonds between the elements H, B, C, N, O, F, Si, P, S, Cl, As, Se, Br, Te, and I as determined from X-ray and neutron diffraction measurements on organic crystals. The table has been derived from an analysis of high-precision structure data on about 10,000 crystals contained in the 1985 version of the Cambridge Structural Database, which is maintained by the Cambridge Crystallographic Data Center. The explanation of the columns is:

Column 1: Specification of elements in the bond, with coordination number given in parentheses, and bond type (single, double, etc.). For carbon, the hybridization state is given.
Column 2: Substructure in which the bond is found. The target bond is set in boldface. Where X is not specified, it denotes any element type. C# indicates any sp^3 carbon atom, and C* denotes an sp^3 carbon whose bonds, in addition to those specified in the linear formulation, are to C and H atoms only.
Column 3: d is the unweighted mean in Å units of all the values for that bond length found in the sample.
Column 4: m is the median in Å units of all values.
Column 5: σ is the standard deviation in the sample.
Column 6: q_1 is the lower quartile for the sample (i.e., 25% of values are less than q_1 and 75% exceed it).
Column 7: q_2 is the upper quartile for the sample.
Column 8: n is number of observations in the sample.
Column 9: Notes refer to the footnotes in Appendix 1.

References to special cases are given in a shorthand form and listed in Appendix 2. Further information on the method of analysis of the data may be found in the reference cited below.

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REFERENCE

Frank H. Allen, Olga Kennard, David G. Watson, Lee Brammer, A. Guy Orpen, and Robin Taylor, *J. Chem. Soc. Perkin Trans. II*, S1—S19, 1987.

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–CH_3**	1.903	1.907	0.016	1.893	1.916	12	
	$(X)_2$(C,O,S=)As–C*sp*^{3}	1.927	1.929	0.017	1.921	1.937	16	
	As–C*ar* in Ph_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–OH**	1.710	1.712	0.017	1.695	1.726	6	
As(3)–O	see ASAZOC, PHASOC01 (1.787—1.845)							
As(4)=O	**X_3–As=O**	1.661	1.661	0.016	1.652	1.667	9	
As(3)=P(3)	see BELNIP (2.350, 2.362)							†
As(3)–P(3)	see BUTHAZ10 (2.124)							†
As(3)–S	**X_2–As–S**	2.275	2.266	0.032	2.247	2.298	14	
As(4)=S	**X_3–As=S**	2.083	2.082	0.004	2.080	2.086	9	
As(3)–Se(2)	see COSDIX, ESEARS (2.355—2.401)							†
As(3)–Si(4)	see BICGEZ, MESIAD (2.351—2.365)							†
As(3)–Te(2)	see ETEARS (2.571, 2.576)							†
B(n)–B(n)	*n* = 5—7 in boron cages	1.775	1.773	0.031	1.763	1.786	688	
B(4)–B(4)	see CETTAW (2.041)							
B(4)–B(3)	see COFVOI (1.698)							
B(3)–B(3)	**X_2–B–B–X_2**	1.701	1.700	0.014	1.691	1.712	8	
B(6)–Br		1.967	1.971	0.014	1.954	1.979	7	†
B(4)–Br		2.017	2.008	0.031	1.990	2.044	15	†
B(*n*)–C	*n* = 5—7: **B–C** in cages	1.716	1.717	0.020	1.707	1.728	96	
	n = 3—4: **B–C*sp*^{3}** not cages	1.597	1.599	0.022	1.585	1.611	29	1
	n = 4: **B–C*ar***	1.606	1.607	0.012	1.596	1.615	41	
	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	

BOND LENGTHS IN CRYSTALLINE ORGANIC COMPOUNDS (continued)

Bond	Substructure	*d*	*m*	σ	q_l	q_u	*n*	Note
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_6Te^{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_3	1.534	1.534	0.011	1.527	1.541	825	
	C#–CH_2–CH_2–C#	1.524	1.524	0.014	1.516	1.532	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	
C*sp*^{3}–C*sp*^{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

BOND LENGTHS IN CRYSTALLINE ORGANIC COMPOUNDS (continued)

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
	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–Car	CH_3–Car	1.506	1.507	0.011	1.501	1.513	454	
	C#–CH_2–Car	1.510	1.510	0.009	1.505	1.516	674	
	$(C\#)_2$–CH–Car	1.515	1.515	0.011	1.508	1.522	363	
	$(C\#)_3$–C–Car	1.527	1.530	0.016	1.517	1.539	308	
	C*–Car (overall)	1.513	1.513	0.014	1.505	1.521	1 813	
	cyclopropyl (C)–Car	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–Car	C=C–Car							
	(conjugated)	1.470	1.470	0.015	1.463	1.480	37	16,18
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)–Car	1.447	1.448	0.006	1.441	1.452	8	10
	Car–C(=O)–C*	1.488	1.489	0.016	1.478	1.500	84	
	Car–C(=O)–Car	1.480	1.481	0.017	1.468	1.494	58	
	Car–COOH	1.484	1.485	0.014	1.474	1.491	75	
	Car–C(=O)(–OC*)	1.487	1.487	0.012	1.480	1.494	218	
	Car–COO^-	1.504	1.509	0.014	1.495	1.512	26	
	Car–C(=O)–NH_2	1.500	1.503	0.020	1.498	1.510	19	
	Car–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	

BOND LENGTHS IN CRYSTALLINE ORGANIC COMPOUNDS (continued)

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
	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	*Car*–C≡C	1.434	1.436	0.006	1.430	1.437	37	
	Car–C≡N	1.443	1.444	0.008	1.436	1.448	31	
Csp^1–Csp^1	C≡C–C≡C	1.377	1.378	0.012	1.374	1.384	21	
Csp^2=Csp^2	C*–CH=CH_2	1.299	1.300	0.027	1.280	1.311	42	
	$(C^*)_2$–C=CH_2	1.321	1.321	0.013	1.313	1.328	77	
	C*–CH=CH–C*							
	(*cis*)	1.317	1.318	0.013	1.310	1.323	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=CH–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-*Car* (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≃*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	
Car≃*Car*	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	

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
	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	
Csp^1≡Csp^1	X–C≡C–X	1.183	1.183	0.014	1.174	1.193	119	15
	C,H–C≡C–C,H	1.181	1.181	0.014	1.173	1.192	104	15
	in C≡C–C(sp^2,*ar*)	1.189	1.193	0.010	1.181	1.195	38	15
	in C≡C–C≡C	1.192	1.192	0.010	1.187	1.197	42	15
	in CH≡C–C#	1.174	1.174	0.011	1.167	1.180	42	15
Csp^3–Cl	Omitting 1,2-dichlorides:							
	$C–CH_2–Cl$	1.790	1.790	0.007	1.783	1.795	13	4
	$C_2–CH–Cl$	1.803	1.802	0.003	1.800	1.807	8	4
	$C_3–C–Cl$	1.849	1.856	0.011	1.837	1.858	5	4
	$X–CH_2–Cl$ (X = C,H,N,O)	1.790	1.791	0.011	1.783	1.797	37	4
	$X_2–CH–Cl$ (X = C,H,N,O)	1.805	1.803	0.014	1.800	1.812	26	4
	$X_3–C–Cl$ (X = C,H,N,O)	1.843	1.838	0.014	1.835	1.858	7	4
	$X_2–C–Cl_2$ (X = C,H,N,O)	1.779	1.776	0.015	1.769	1.790	18	4
	$X–C–Cl_3$ (X = C,H,N,O)	1.768	1.765	0.011	1.761	1.776	33	4
	Cl–CH(–C)–CH(–C)–Cl	1.793	1.793	0.013	1.786	1.800	66	4
	Cl–C($–C_2$)–C($–C_2$)–Cl	1.762	1.760	0.010	1.757	1.765	54	4
	cyclopropyl–Cl	1.755	1.756	0.011	1.749	1.763	64	
Csp^2–Cl	C=C–Cl (C,H,N,O 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
Car–Cl	*Car*–Cl (mono-Cl + *m*,*p*-Cl_2)	1.739	1.741	0.010	1.734	1.745	340	4
	Car–Cl (*o*-Cl_2)	1.720	1.720	0.010	1.713	1.717	364	4
Csp^1–Cl	see HCLENE10 (1.634, 1.646)							
Csp^3–F	Omitting 1,2-difluorides							
	$C–CH_2–F$ and $C_2–CH–F$	1.399	1.399	0.017	1.389	1.408	25	4
	$C_3–C–F$	1.428	1.431	0.009	1.421	1.435	11	4
	$(C^*,H)_2–C–F_2$	1.349	1.347	0.012	1.342	1.356	58	4
	$C^*–C–F_3$	1.336	1.334	0.007	1.330	1.344	12	4
	F–C*–C*–F	1.371	1.374	0.007	1.362	1.375	26	4
	$X_3–C–F$ (X = C,H,N,O)	1.386	1.389	0.033	1.373	1.408	70	4
	$X_2–C–F_2$ (X = C,H,N,O)	1.351	1.349	0.013	1.342	1.356	58	4
	$X–C–F_3$ (X = C,H,N,O)	1.322	1.323	0.015	1.314	1.332	309	4
	$F–C(–X)_2–C(–X)_2–F$ (X = C,H,N,O)	1.373	1.374	0.009	1.362	1.377	30	4
	$F–C(–X)_2–NO_2$ (X = any subst.)	1.320	1.319	0.009	1.312	1.327	18	
Csp^2–F	C=C–F (C,H,N,O subst. on C)	1.340	1.340	0.013	1.334	1.346	34	4
Car–F	*Car*–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
Csp^3–H	$C–C–H_3$ (methyl)	1.059	1.061	0.030	1.039	1.083	83	21
	$C_2–C–H_2$ (primary)	1.092	1.095	0.013	1.088	1.099	100	21
	$C_3–C–H$ (secondary)	1.099	1.097	0.004	1.095	1.103	14	21
	$C_{2,3}–C–H$ (primary and secondary)	1.093	1.095	0.012	1.089	1.100	118	21
	$X–C–H_3$ (methyl)	1.066	1.074	0.028	1.049	1.087	160	21
	$X_2–C–H_2$ (primary)	1.092	1.095	0.012	1.088	1.099	230	21
	$X_3–C–H$ (secondary)	1.099	1.099	0.007	1.095	1.103	117	21
	$X_{2,3}–C–H$ (primary and secondary)	1.094	1.096	0.011	1.091	1.100	348	21
Csp^2–H	C–C=C–H	1.077	1.079	0.012	1.074	1.085	14	21
Car–H	*Car*–H	1.083	1.083	0.011	1.080	1.087	218	21
Csp^3–I	C*–I	2.162	2.159	0.015	2.149	2.179	15	4
Car–I	*Car*–I	2.095	2.095	0.015	2.089	2.104	51	4
Csp^3–N(4)	$C^*–NH_3^+$	1.488	1.488	0.013	1.482	1.495	298	
	$(C^*)_2–NH_2^+$	1.494	1.493	0.016	1.484	1.503	249	
	$(C^*)_3–NH^+$	1.502	1.502	0.015	1.491	1.512	509	
	$(C^*)_4–N^+$	1.510	1.509	0.020	1.496	1.523	319	
	$C^*–N^+$ (overall)	1.499	1.498	0.018	1.488	1.510	1 370	
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

BOND LENGTHS IN CRYSTALLINE ORGANIC COMPOUNDS (continued)

Bond	Substructure	*d*	*m*	σ	q_l	q_u	*n*	Note
	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–*Car*	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	
Car–N(4)	$Car–N^+–(C,H)_3$	1.465	1.466	0.007	1.461	1.470	23	
Car–N(3)	$Car–NH_2$							
	(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
Car–N(3)	Car–NH–C#							
	(Nsp^2: planar)	1.353	1.353	0.007	1.347	1.359	16	23
	(Nsp^3: pyramidal)	1.419	1.423	0.017	1.412	1.432	8	22
	(overall)	1.380	1.364	0.032	1.353	1.412	31	28
	$Car–N–(C\#)_2$							
	(Nsp^2: planar)	1.371	1.370	0.016	1.363	1.382	41	23
	(Nsp^3: pyramidal)	1.426	1.425	0.011	1.421	1.431	22	22
	(overall)	1.390	1.385	0.030	1.366	1.420	69	28
	in indole (N1–C7a)	1.372	1.372	0.007	1.367	1.376	40	
	$Car–NO_2$	1.468	1.469	0.014	1.460	1.476	556	
Car–N(2)	Car–N=N	1.431	1.435	0.020	1.422	1.442	26	
Csp^2=N(3)	in furoxan ($^+$N2=C3)	1.316	1.316	0.009	1.311	1.324	14	
Csp^2=N(2)	Car–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	

BOND LENGTHS IN CRYSTALLINE ORGANIC COMPOUNDS (continued)

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
	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	
$Car \simeq N(3)$	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	
$Car \simeq N(2)$	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	
$Csp^1 \equiv N(2)$	X–S–N≡C⁻ (isothiocyanide)	1.144	1.147	0.006	1.140	1.148	6	
$Csp^1 \equiv N(1)$	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
	Car–C≡N	1.138	1.138	0.007	1.133	1.143	31	
	X–C≡N	1.144	1.141	0.012	1.138	1.151	10	
	(S–C≡N)⁻	1.155	1.156	0.012	1.147	1.165	14	
$Csp^3–O(2)$	in alcohols							
	CH_3–OH	1.413	1.414	0.018	1.395	1.425	17	
	C–CH_2–OH	1.426	1.426	0.011	1.420	1.431	75	
	C_2–CH–OH	1.432	1.431	0.011	1.425	1.439	266	
	C_3–C–OH	1.440	1.440	0.012	1.432	1.449	106	
	C*–OH (overall)	1.432	1.431	0.013	1.424	1.441	464	
	in dialkyl ethers							29
	CH_3–O–C*	1.416	1.418	0.016	1.405	1.426	110	
	C–CH_2–O–C*	1.426	1.424	0.011	1.418	1.435	34	
	C_2–CH–O–C*	1.429	1.430	0.010	1.420	1.437	53	
	C_3–C–O–C*	1.452	1.450	0.011	1.445	1.458	39	
	C*–O–C* (overall)	1.426	1.425	0.019	1.414	1.437	236	5
	in aryl alkyl ethers							29
	CH_3–O–*Car*	1.424	1.424	0.012	1.417	1.431	616	
	C–CH_2–O–*Car*	1.431	1.430	0.013	1.422	1.438	188	
	C_2–CH–O–*Car*	1.447	1.446	0.020	1.435	1.466	58	
	C_3–C–O–*Car*	1.470	1.469	0.018	1.456	1.483	55	
	C*–O–*Car* (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	
$Csp^3–O(2)$	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	

BOND LENGTHS IN CRYSTALLINE ORGANIC COMPOUNDS (continued)

Bond	Substructure	*d*	*m*	σ	q_l	q_u	*n*	Note
	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–OH	1.333	1.331	0.017	1.324	1.342	53	
	in enol esters: C=C–O–C*	1.354	1.353	0.016	1.341	1.363	40	
	in acids:							
	C*–C(=O)–OH	1.308	1.311	0.019	1.298	1.320	174	
	C=C–C(=O)–OH	1.293	1.295	0.019	1.279	1.307	22	
	C*ar*–C(=O)–OH	1.305	1.311	0.020	1.291	1.317	75	
	in esters:							
	C*–C(=O)–O–C*	1.336	1.337	0.014	1.328	1.346	551	12,29
	C=C–C(=O)–O–C*	1.332	1.331	0.011	1.324	1.339	112	
	C*ar*–C(=O)–O–C*	1.337	1.335	0.013	1.329	1.344	219	12
	C*–C(=O)–O–C=C	1.362	1.359	0.018	1.351	1.374	26	
	C*–C(=O)–O–C=C	1.407	1.405	0.017	1.394	1.420	26	
	C*–C(=O)–O–C*ar*	1.360	1.359	0.011	1.355	1.367	40	12
	in anhydrides: O=C–O–C=O	1.386	1.386	0.011	1.379	1.393	70	
	in ring systems:							
	furan (O1–C2, O1–C5)	1.368	1.369	0.015	1.359	1.377	125	
	isoxazole (O1–C5)	1.354	1.354	0.010	1.345	1.360	9	
	β-lactones: C*–C(=O)–O–C*	1.359	1.359	0.013	1.348	1.371	4	13
	γ-lactones: C*–C(=O)–O–C*	1.350	1.349	0.012	1.342	1.359	110	12
	δ-lactones: C*–C(=O)–O–C*	1.339	1.339	0.016	1.332	1.347	27	12
C*ar*–O(2)	in phenols: C*ar*–OH	1.362	1.364	0.015	1.353	1.373	551	
	in aryl alkyl ethers: C*ar*–O–C*	1.370	1.370	0.011	1.363	1.377	920	29,32
C*ar*–O(2)	in diaryl ethers: C*ar*–O–C*ar*	1.384	1.381	0.014	1.375	1.391	132	
	in esters: C*ar*–O–C(=O)–C*	1.401	1.401	0.010	1.394	1.408	40	12
C*sp*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	
	C*ar*–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	
	C*ar*–C≃O_2^-	1.255	1.253	0.010	1.249	1.262	22	
	HOOC–C≃O_2^- (hydrogen oxalate)	1.243	1.247	0.015	1.232	1.256	26	
	$^-O_2$≃C–C≃O_2^- (oxalate)	1.251	1.251	0.007	1.248	1.254	18	

BOND LENGTHS IN CRYSTALLINE ORGANIC COMPOUNDS (continued)

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
	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:							
	$(NH)_2$–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
C*sp*^{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	
C*sp*^{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	
C*sp*^{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
C*sp*^{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	
C*sp*^{3}–S(2)	C*–SH	1.808	1.805	0.010	1.800	1.819	6	
	CH_3–S–C*	1.789	1.787	0.008	1.784	1.794	9	
C*sp*^{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	
C*sp*^{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	
Car–S(4)	*Car*–SO_2–C	1.763	1.764	0.009	1.756	1.769	96	
	Car–SO_2–O–X	1.752	1.750	0.008	1.749	1.756	27	
	Car–SO_2–N–X_2	1.758	1.759	0.013	1.749	1.765	106	35
Car–S(3)	*Car*–S(=O)–C	1.790	1.790	0.010	1.783	1.798	41	
	Car–S^+–X_2	1.778	1.779	0.010	1.771	1.787	10	
Car–S(2)	*Car*–S–C*	1.773	1.774	0.009	1.765	1.779	44	
	Car–S–*Car*	1.768	1.767	0.010	1.762	1.774	158	
	Car–S–*Car* (in phenothiazine)	1.764	1.764	0.008	1.760	1.769	48	

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
	Car–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)	**$(N{\equiv}C{-}S)^-$**	1.630	1.630	0.014	1.619	1.641	14	
Csp^2=S(1)	**$(C^*)_2$–C=S**: see IPMUDS (1.599)							
	$(Car)_2$–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_2N–C(=S)–S–X	1.660	1.660	0.016	1.648	1.674	38	
	$(X_2N)_2$–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	
Car–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	
Car–Si(4)	**Car–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	
Car–Te	**Car–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	
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$^+$$\simeq$N2)	1.350	1.349	0.010	1.345	1.361	7	

BOND LENGTHS IN CRYSTALLINE ORGANIC COMPOUNDS (continued)

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
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	
	Car–N=N–*Car*	1.255	1.253	0.016	1.247	1.262	13	
	X–N=N=N (azides)	1.216	1.226	0.028	1.202	1.237	19	
N(2)=N(1)	X–N=N=N (azides)	1.124	1.128	0.015	1.114	1.137	19	
N(3)–O(2)	$(C,H)_2$–N–OH (Nsp^2: planar)	1.396	1.394	0.012	1.390	1.401	28	
	C_2–N–O–C							
	(Nsp^3: pyramidal)	1.463	1.465	0.012	1.457	1.468	22	
	(Nsp^2: planar)	1.397	1.394	0.011	1.388	1.409	12	
	in furoxan (N2–O1)	1.438	1.436	0.009	1.430	1.447	14	
N(3)–O(1)	$(C\simeq)_2N^+$–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)(Csp^2)–C=N–OH	1.390	1.390	0.011	1.380	1.401	20	
	(C#)(Csp^2)–C=N–OH	1.402	1.403	0.010	1.393	1.410	18	
	$(Csp^2)_2$–C=N–OH	1.378	1.377	0.017	1.365	1.393	16	
	$(C,H)_2$–C=N–OH (overall)	1.394	1.395	0.018	1.379	1.408	67	
	in furazan (O1–N2, O1–N5)	1.385	1.383	0.013	1.378	1.392	12	
	in furoxan (O1–N5)	1.380	1.380	0.011	1.370	1.388	14	
	in isoxazole (O1–N2)	1.425	1.425	0.010	1.417	1.434	9	
N(3)=O(1)	in nitrate ions NO_3^-	1.239	1.240	0.020	1.227	1.251	105	
	in nitro groups							
	C*–NO_2	1.212	1.214	0.012	1.206	1.221	84	
	C#–NO_2	1.210	1.210	0.011	1.203	1.218	251	
	Car– 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)–NX_2							
	Nsp^2: planar	1.652	1.651	0.024	1.634	1.670	205	
	Nsp^3: pyramidal	1.683	1.683	0.005	1.680	1.686	6	
	(overall)	1.662	1.662	0.029	1.639	1.682	358	
	subsets of this group are:							
	O_2–P(=S)–NX_2	1.628	1.624	0.015	1.615	1.634	9	
	C–P(=S)–$(NX_2)_2$	1.691	1.694	0.018	1.678	1.703	28	
	O–P(=S)–$(NX_2)_2$	1.652	1.654	0.014	1.642	1.664	28	
	P(=O)–$(NX_2)_3$	1.663	1.668	0.026	1.640	1.679	78	
N(3)–P(3)	–NX–P(–X)–NX–P(–X)– (P_2N_2 ring)	1.730	1.721	0.017	1.716	1.748	20	
	–NX–P(=S)–NX–P(=S)– (P_2N_2 ring)	1.697	1.697	0.015	1 690	1.703	44	
	in *P*-substituted phosphazenes:							
	$(N\simeq)_2$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	
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–SO_2–NH_2	1.600	1.601	0.012	1.591	1.610	14	35
	C–SO_2–NH–C#	1.633	1.633	0.019	1.615	1.652	47	35
	C–SO_2–N–$C(\#)_2$	1.642	1.641	0.024	1.623	1.659	38	35
N(3)–S(2)	C–S–NX_2 Nsp^2: planar	1.710	1.707	0.019	1.698	1.722	22	23
	(for Nsp^3 pyramidal see MODIAZ: 1.765)							
	X–S–NX_2 Nsp^2: planar	1.707	1.705	0.012	1.699	1.715	30	23
N(2)–S(2)	C=N–S–X	1.656	1.663	0.027	1.632	1.677	36	
N(2)≃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–NX_2 (overall)	1.748	1.746	0.022	1.735	1.757	170	
	subsets of this group are:							
	X_3–Si–NHX	1.714	1.719	0.014	1.702	1.727	16	
	X_3–Si–NX–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	

Bond	Substructure	*d*	*m*	σ	q_l	q_u	*n*	Note
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)	$X–P–(OX)_4$							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)	$C–O–P(\simeq O)_3^{2-}$	1.621	1.622	0.007	1.615	1.628	12	
	$(H–O)_2–P(\simeq O)_2^-$	1.560	1.561	0.009	1.555	1.566	16	
	$(C–O)_2–P(\simeq O)_2^-$	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	
	$(Car–O)_3–P=O$	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)	$(N\simeq)_2P–O–C$ (N ≃ P aromatic)	1.573	1.573	0.011	1.563	1.584	16	
O(1)=P(4)	$C–O–P(\simeq O)_3^{2-}$ (declocalized)	1.513	1.512	0.008	1.508	1.518	42	
	$(H–O)_2–P(\simeq O)_2^-$ (delocalized)	1.503	1.503	0.005	1.499	1.508	16	
	$(C–O)_2–P(\simeq O)_2^-$ (delocalized)	1.483	1.485	0.008	1.474	1.490	16	
	$(C–O)_3–P=O$	1.449	1.448	0.007	1.446	1.452	18	
	$C_3–P=O$	1.489	1.486	0.010	1.481	1.496	72	
	$N_3–P=O$	1.461	1.462	0.014	1.449	1.470	26	
	$(C)_2(N)–P=O$	1.487	1.489	0.007	1.479	1.493	5	
	$(C,N)_2(O)–P=O$	1.467	1.465	0.007	1.462	1.472	33	
	$(C,N)(O)_2–P=O$	1.457	1.458	0.009	1.454	1.462	35	
O(2)–S(4)	$C–O–SO_2–C$	1.577	1.576	0.015	1.566	1.584	41	
	$C–O–SO_2–CH_3$	1.569	1.569	0.013	1.556	1.582	7	
	$C–O–SO_2–Car$	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	
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	1.614	1.631	70	
	$X_3–Si–O–O–Si–X_3$	1.680	1.676	0.008	1.673	1.688	10	
O(2)–Te(6)	$(X–O)_6–Te$	1.927	1.927	0.020	1.908	1.942	16	
O(2)–Te(4)	$(X–O)_2–Te–X_2$	2.133	2.136	0.054	2.078	2.177	12	
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	

Bond	Substructure	d	m	σ	q_l	q_u	n	Note
S(2)–Te	X–S–Te (any)	2.405	2.406	0.022	2.383	2.424	10	
	X=S–Te (any)	2.682	2.686	0.035	2.673	2.694	28	
Se(2)–Se(2)	X–Se–Se–X	2.340	2.340	0.024	2.315	2.361	15	
Se(2)–Te(2)	see BAWFUA, BAWGAH (2.524—2.561)							†
Si(4)–Si(4)	X_3–Si–Si–X_3 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. $p(\pi)$–$p(\pi)$ 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≃C3 and C3≃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 ⩾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.	BIBLAZ	*Zh. Strukt. Khim.*, 1981, **22**, 118.
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BALXOB	*J. Am. Chem. Soc.*, 1981, **103**, 4587.	BIRGUE10	*Z. Naturforsch., Teil B*, 1983, **38**, 20.
BAPPAJ	*Inorg. Chem.*, 1981, **20**, 3071.	BIRHAL10	*Z. Naturforsch., Teil B*, 1982, **37**, 1410.
BARRIV	*Acta Chem. Scand., Ser. A*, 1981, **35**, 443.	BIZJAV	*J. Organomet. Chem.*, 1982, **238**, C1.
BAWFUA	*Cryst. Struct. Commun.*, 1981, **10**, 1345.	BOGPOC	*Z. Naturforsch., Teil B*, 1982, **37**, 1402.
BAWGAH	*Cryst. Struct. Commun.*, 1981, **10**, 1353.	BOGSUL	*Z. Naturforsch., Teil* B, 1982, **37**, 1230.
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BELNIP	*Z. Naturforsch., Teil B*, 1982, **37**, 299.	BOJPUL	*Acta Chem. Scand., Ser. A*, 1982, **36**, 829.
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