Comparing the strength of covalent bonds, intermolecular hydrogen bonds and other intermolecular interactions for organic molecules. X-ray diffraction data and quantum chemical calculations

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SUPPLEMENTARY INFORMATION

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Units are Å for distances, kJ mol^{-1} for energies and kJ $mol^{-1}Å^{-2}$ for force constants.

SUPPLEM1 Intramolecular bond lengths

SUPPLEM1.1 Retrieval of crystal structures from the Cambridge Structural Database and preparation of the databases for the present work

A master dataset for was created from the CSD under the following conditions: radiation source: X-rays; year: after 1980 (exclude visual/photographic methods); heaviest element Cl; $Z' \leq 2$ (where Z' is the number of molecules in the asymmetric unit; this excludes suspicious materials); number of atoms in molecule ≤ 35; number of residues = 1 (exclude molecular complexes, solvates); average σ(C-C bonds) < 0.005; conventional crystallographic R-factor ≤ 5%; no disorder, no errors, no polymeric structures, no powder data, only organic compounds. Structures at non-ambient pressure were screened out by negating the text qualifier 'pressure'. This yielded 25423 hits. The CLP modules Retcif, Rtecor, Retcha and Clpcry (see http://users.unimi.it/ gavezzot, the CLP program suite and its reference manual) check for correct interatomic connectivity (formal atomic valence), for cases with dubious electron counts, or for structures with suspiciously short intermolecular contacts , reducing the size of the dataset to 23248 crystal structures. For each group of duplicate determinations of the same crystal structure, only the one with the lowest R-factor was kept, leaving 21712 crystal structures irrespective of temperature of the Xray determination (T-ALL data set), or12532 entries with 201<T<320 K ("T-ROOM" data set), and 9679 entries with 0<T<200 K ("T-LOW" data set). The total room-T+low-T (22211) is greater than the number in the all-T database because many structures have been determined both at low and high temperature. With slightly more tolerant criteria, keeping only one best entry for duplicates but without temperature screening, datasets of 1017 bromine-containing structures and 411 iodine-containing structures were retrieved "BR" and "IOD" databases, respectively). Neutron diffraction crystal structure data were retrieved with the limits of R< 5%, one residue (excluding salts, where H-atoms in charged species are often in special electronic environments, and hydrates), for 217 hits, reduced to 119 best unique, without temperature screening (the "NEU" database). Unfortunately the number of neutron determinations is very small. CSD Refcode names for all the structures in the databases above are available from the author upon request. Table S1 shows the types of atom considered with their labeling.

The database for hydrogen-bonding studies, the "HBDON" database, was prepared from the T-ALL dataset by requesting the presence of at least one of the hydrogen-bonding donor atoms (H5 , H6, H7 or H8 in Table S1). This gave 11429 entries.

Table S1. Atomic species considered and their indicator label in the data treatment software

hydrogen	indicator	
acetylene ≡CH	1	to sp carbon
$=CH_2$, =CH*X*, aromatic CH	2	to sp^2 carbon
aliphatic CH, CH_2, CH_3	3	to sp^3 carbon
R-OH, R-SH	5	alcohol, thiol
COO-H	6	acid
CON)-H	7	amide
R_2NH, RNH_2, $(R_3N^+)H$	8	amine, ammonium
carbon		
C=(O)	10	carbonyl carbon (ketone, aldehyde, acid, amide)
≡C-	11	sp carbon
sp^2 C	12	ethylenic, allene, aromatic
sp^3 C	13	
C(node)	14	aromatic core, e.g. 9-10 in naphthalene
nitrogen		

$(R_nH_{4-n})N^+$	16	ammonium
$(R_nH_{3-n})N$	17	sp^3 nitrogen
arom.N, R=N(H)	18	sp^2 nitrogen
-C≡N,-N=N	19	
nitro N	20	
amide N ($CONH,CONH_2$)	21	
oxygen		
-O-	23	ether
C=O, COO^-	27	carbonyl oxygen (ketone, aldehyde, acid, amide)
(C=O)-OH	28	hydroxyl oxygen in acids
R-OH	29	alcohol oxygen
N=O	30	
S=O	31	
P=O	32	
sulfur		
-S-	34	thioether
(C)=S	35	sulfide
(O)=S	36	sulfone, sulfoxide, sulfonate
R-S(H)	37	thiol
heteroatoms		
F	41	
Cl	42	
Br	43	
I	44	

SUPPLEM1.2 Average or Gaussian-fit derived best bond distances for intramolecular bonds. For each set of distances, a Scheme with indication of the bond under consideration (the central horizontal one), a Table of bond length values, and some examples of the N(R) profiles with Gaussian fit and difference between experintal N(R) and Gaussian fit. T-ROOM database, 201<T<320, 12532 entries.

SUPPLEM1.2.1 The carbonyl carbon

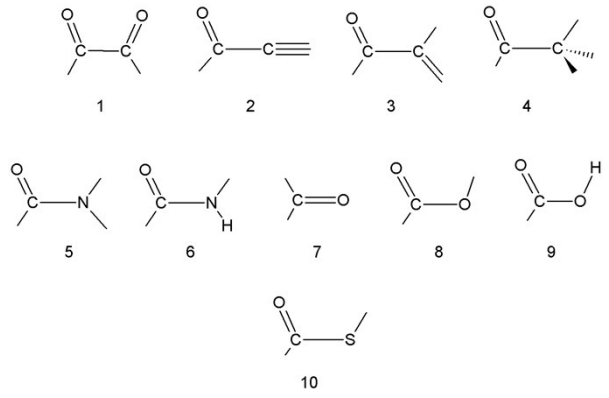
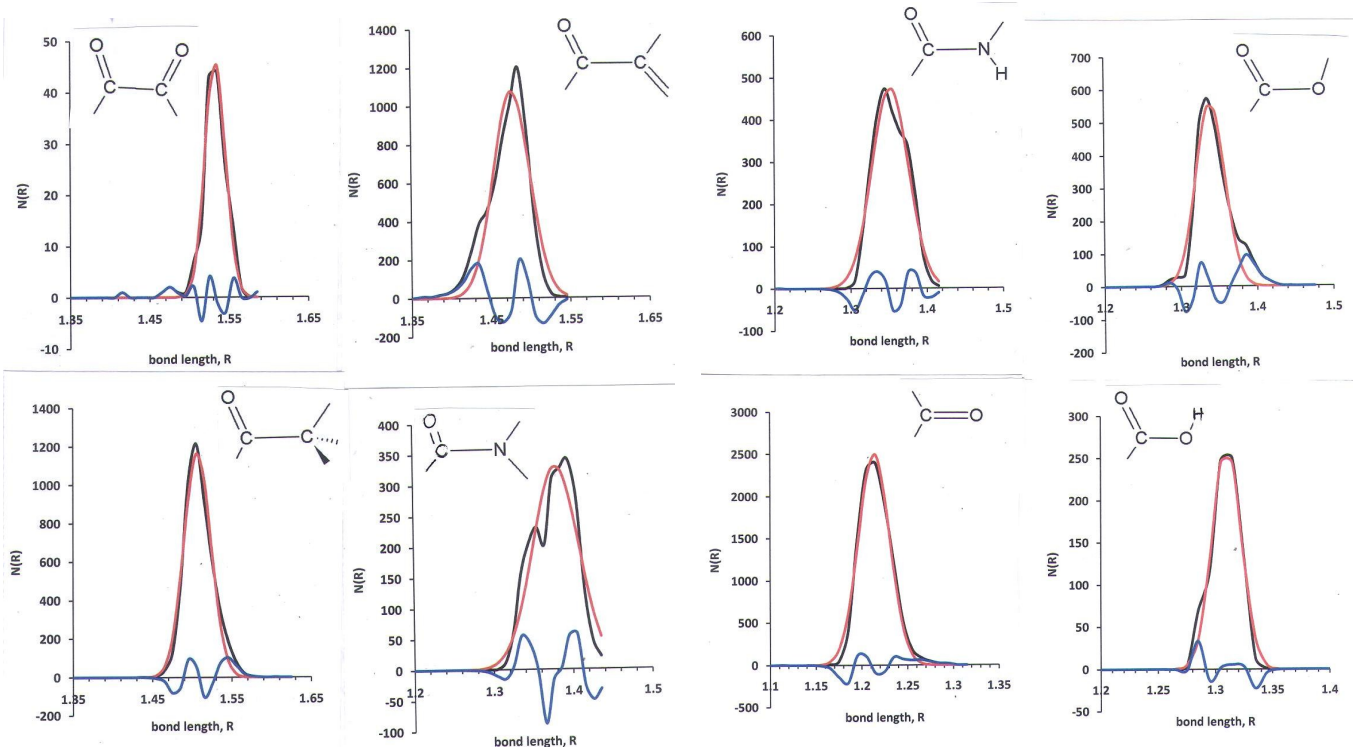


Table S2					
bond scheme	total hits	average[a]	gaussian fit[b]	linkage number[c]	species Table 1
(O=)C − C(=O)	157	1.531(19)	1.532(13)	1	10-10

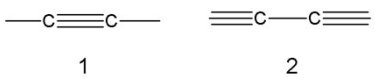
(O=)C − C(sp^2)	6423	1.470(26)	1.447(20)sh 1.485(15)	3	10-12
(O=)C − C(sp^3)	5075	1.509(18)	1.507(17)	4	10-13
(O=)C − N(X_2)	2358	1.378(28)	1.349(16)sh 1.391(17)	5	10-17
(O=)C − N(H*X*),N(H_2), C-N amide	2870	1.353(23)	1.352(24)	6	10-21
(O=)C − O*X* C-O ester	2836	1.345(23)	1.337(16) 1.379(16)sh	8	10-23
C=O carbonyl (any)	10677	1.216(18)	1.214(17)	7	10-27
(O=)C − OH,C-O carboxylic acid	831	1.308(12)	1.310(13)	9	10-28
(O=)C−SH, C-S thioester	151	1.774(16)	1.773(14)	10	10-34

[a]Average of all data, irrespective of profile shape. *X* is any non-hydrogen atom, mostly carbon. [b]Profile fit by gaussian(s); more than one entry means multimodal profile. '*sh*' indicates that the feature is a shoulder, not a separate peak. [c]Entries in parentheses are from scattered or too few data for significant statistics. [c]See Scheme.

Profiles of the N(R) functions in Table S2.
Black: experimental, red: Gaussian fitting, blue: difference exptl-fit.



SUPPLEM1.2.2 The *sp*-hybridized carbon



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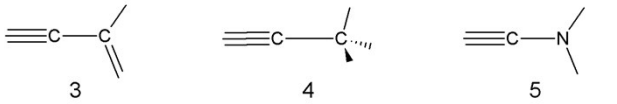

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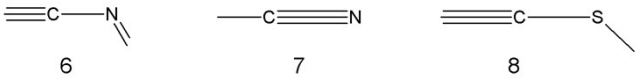
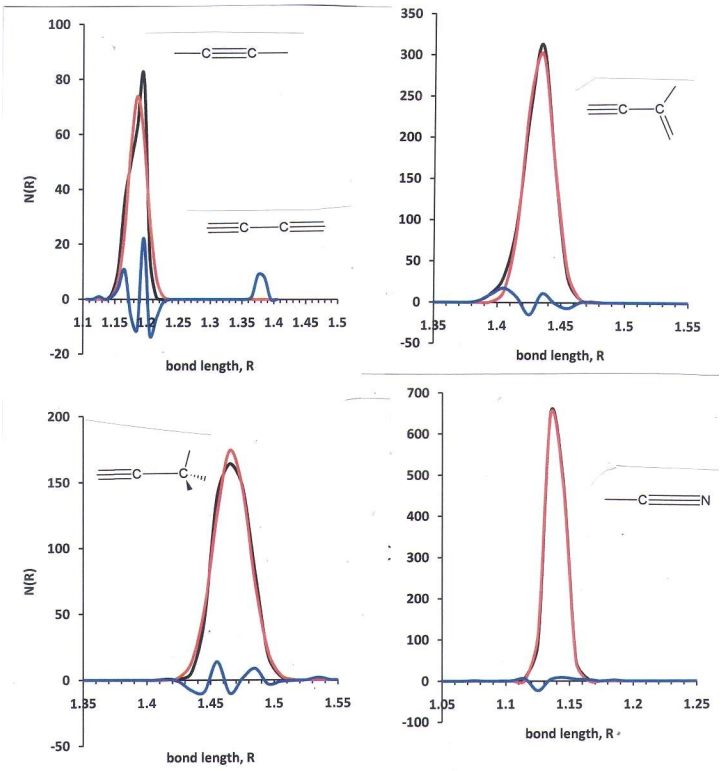


6 7 8

Table S3	total hits	average	gaussian fit	linkage number	species (Table 1)
C≡C ≡C−C≡	260 18	1.183(13) [1.38]	-	1 2	11-11
C(*sp*) −C(sp^2)	877	1.431(12)	1.433(11)	3	11-12
C(*sp*)−C(sp^3)	609	1.467 (14)	1.467(14)	4	11-13
C(*sp*)−N(sp^3)	10	[1.34]		5	11-17
C(*sp*)−N(sp^2)	37	[1.27 scatter]		6	11-18
C≡N	1287	1.139 (7)	1.139(7)	7	11-19
C(*sp*)−S(*X*)	26	[1.69]		8	11-34



SUPPLEM1.2.3 The sp2-hybridized carbon

Number 4 is for the central bond in naphthalene rings or for the C(sp2)-benzene bond.

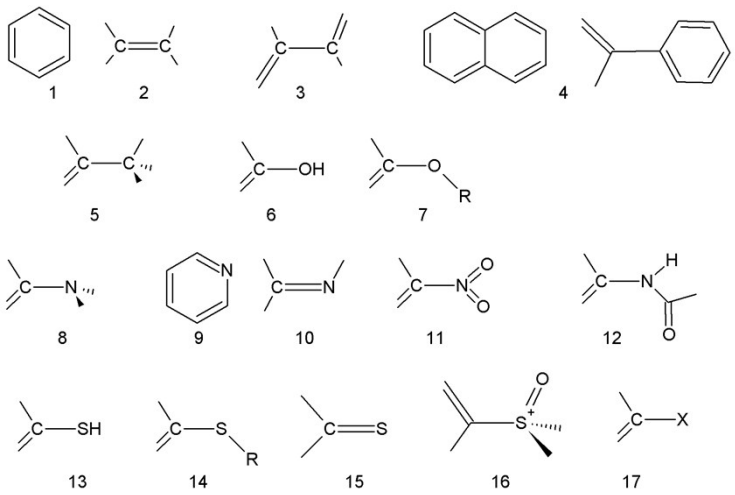
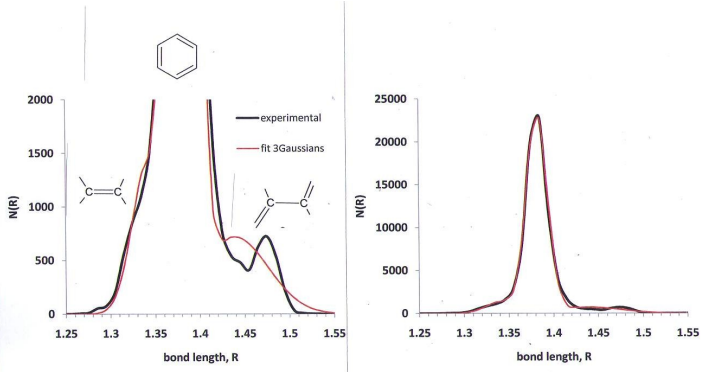
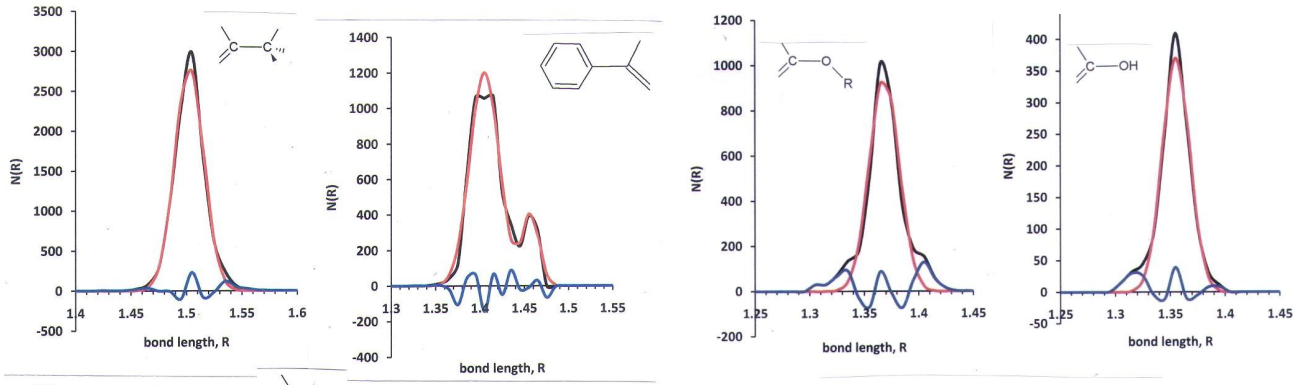


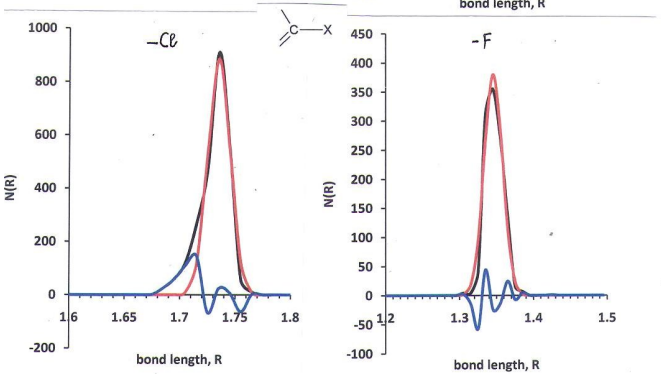
Table S4.

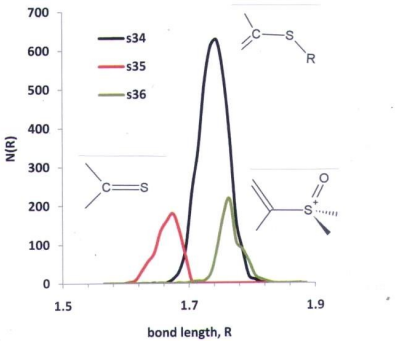
bond type	total hits	average	gaussian fit	linkage number	species Table 1
C(sp^2)−C(sp^2) >C=C< --C---C-- aromatic =C − C= single	79737	-	 1.342(18) 1.382(12) 1.439(38)	 2 1 3	12-12
C(sp^2)−C(sp^2,*node*)	5795	1.413 (24)	-	4	12-14
C(sp^2)−C(sp^3)	9436	1.503(15)	1.503(13)	5	12-13
C(sp^2)−N(sp^3) C−N(H_2, RH, R_2) Ph − N	8687	1.371(35)	 1.363(30) 1.428(14)sh	8	12-17
C(sp^2)−N(sp^2) >C=N- double aromatic -N---N-	9813	-	 1.289(18) 1.331(14)	 10 9	12-18
C(sp^2)−N(*nitro*) mostly Ph-NO_2	1227	1.457 (23)	1.466(12)	11	12-20
C(sp^2)−N(*amide*)	1078	1.385 (35)	1.402(20)	12	12-21
C(sp^2)−O*X* ether	3600	1.369 (19)	1.369(14)	7	12-23
C(sp^2)−OH mostly phenols	1257	1.354 (15)	1.356(13)	6	12-29
C(sp^2)−S*X* thioether	3691	1.739 (23)	1.740(22)	14	12-34
C(sp^2)=S	859	1.665 (19)	1.669(19)	15	12-35
C(sp^2)−S(=O_x)	840	1.765(22)	1.764(17)	16	12-36
C(sp^2)−F	1148	1.347 (12)	1.346(13)	17	12-41
C(sp^2)−Cl	2465	1.731 (14)	1.735(10)	17	12-42
C(sp^2)−Br	1038	1.892(14)	-	17	12-43
C(sp^2)−I	400	2.095(15)	-	17	12-44
C(node)-C(node)	601	1.425 (19)	1.423(16)	4	14-14

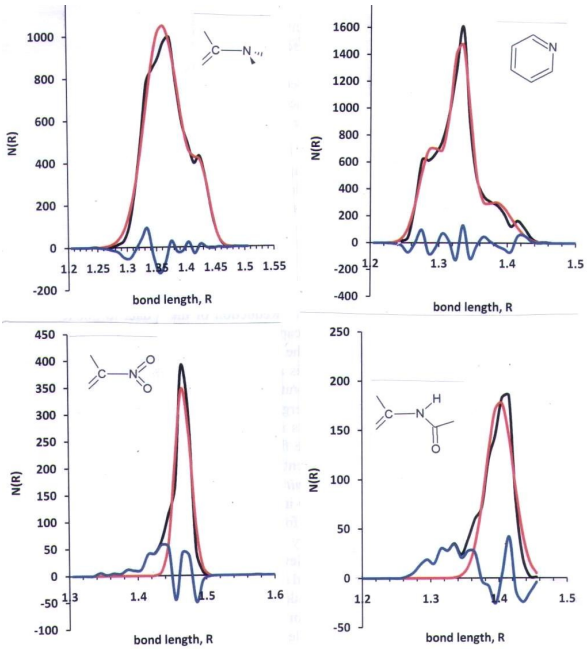


Csp^2-Csp^2 magnification overall profile

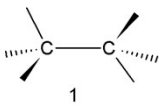








SUPPLEM1.2.4 The sp^3-hybridized carbon



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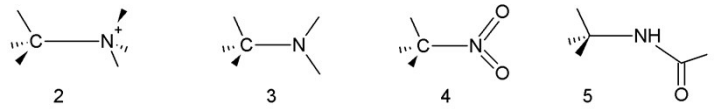

2 3 4 5

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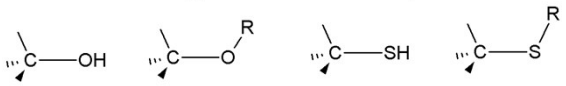
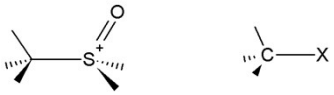
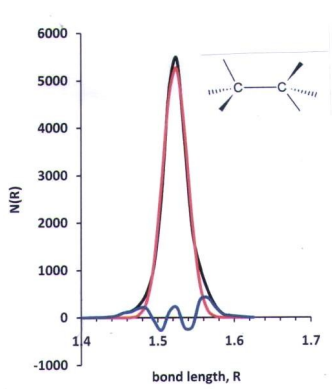


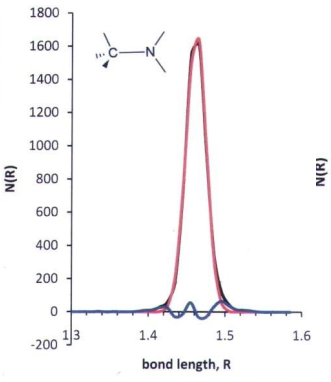
8 9 10 11

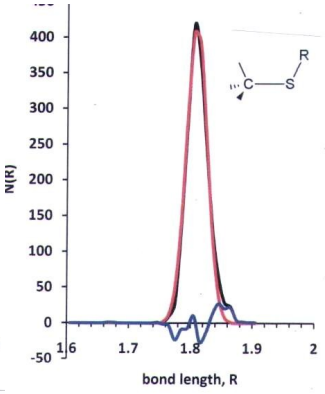


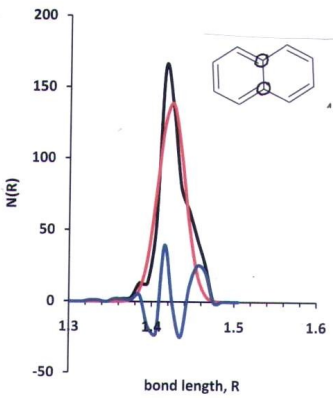
12 13

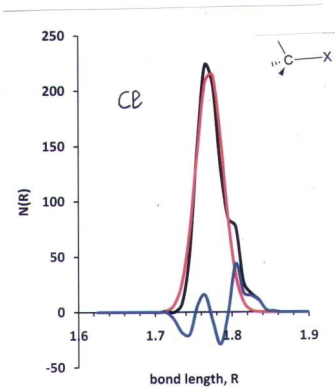
Table S5.	total hits	average	gaussian fit	linkage number	species Table 1
C(sp^3)− C(sp^3)	22828	1.523(21)	1.523(16)	1	13-13
C(sp^3)− N$^+$(sp^3) ammonium	289	1.494(13)	1.492(11)	2	13-16
C(sp^3)− N(sp^3) C-N(X_2)	5744	1.462 (16)	1.461(13)	3	13-17
C(sp^3)− N(sp^2)	275	1.471 (21)	1.469(13)	6,7	13-18
C(sp^3)−N(*nitro*)	218	1.514 (25)	1.514(27)	4	13-20
C(sp^3)−N(*amide*)	531	1.454(12)	1.454(11)	5	13-21
C(sp^3)− O*X* ether	8375	1.435 (20)	1.435(19)	9	13-23
C(sp^3)− OH alcohol	2571	1.420 (14)	1.422(11)	8	13-29
C(sp^3)− S*X* *thioether*	1756	1.812 (19)	1.809(17)	11	13-34
C(sp^3)− S(=O$_x$) sulfone,sulfoxide	621	1.794(35)	1.749(6) 1.795(32)	12	13-36
C(sp^3)− F main peak F-cycloalkanes	1316	1.336 (26)	1.328(12) 1.367(21)sh	13	13-41
C(sp^3)− Cl	993	1.776 (20)	1.771(18)	13	13-42
C(sp^3)− Br	304	1.960(20)	-	13	13-43
C(sp^3)− I	87	2.164(29)	-	13	13-44

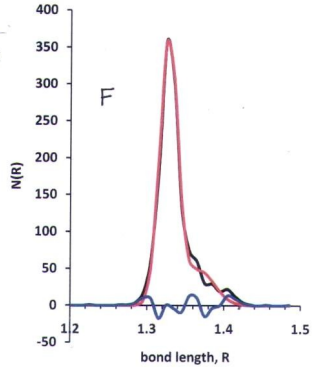

N(R)
bond length, R

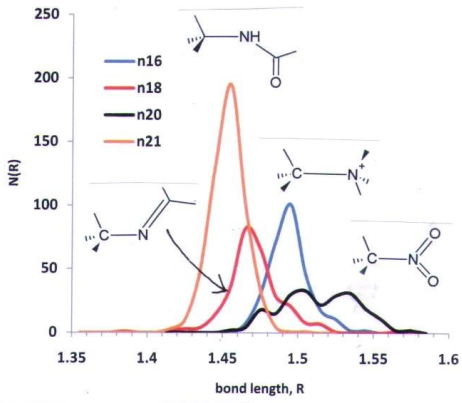

N(R)
bond length, R

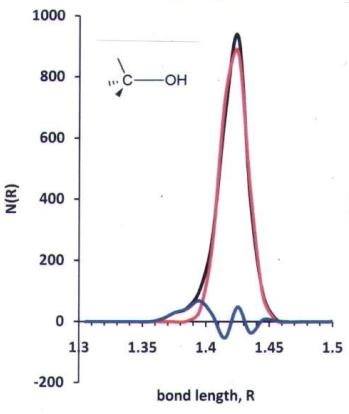

N(R)
bond length, R

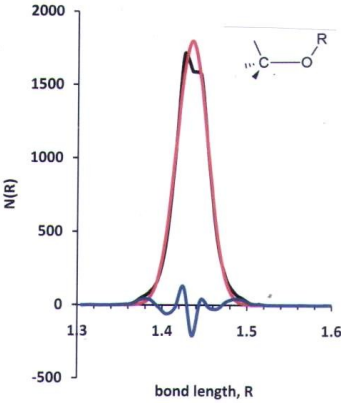

N(R)
bond length, R


Cl
N(R)
bond length, R


F
N(R)
bond length, R


n16
n18
n20
n21
N(R)
bond length, R


N(R)
bond length, R


N(R)
bond length, R

SUPPLEM1.2.5 Nitrogen

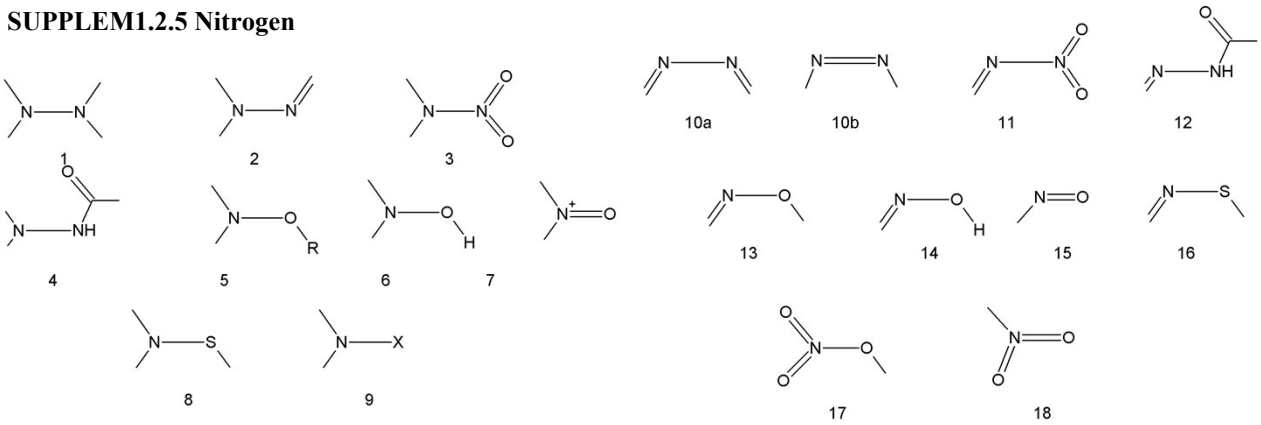


Table S6.	total hits	average	Gaussian fit	linkage number	species Table 1
N(sp^3) −N(sp^3) >N−N<	223	1.400 (31)	1.403(17)	1	17-17
N(sp^3) −N(sp^2) >N−N=	1557	1.361 (29)	1.364(21)	2	17-18
N(sp^3) −N(*nitro*)	109	1.376 (30)	-	3	17-20
N(sp^3) −N(*amide*)	78	1.398 (28)	-	4	17-21
N(sp^3) −O*X*	129	1.427 (38)	-	5	17-23
N(sp^3) −O(H)	68	1.399 (29)	-	6	17-29
N(sp^3) →O	165	1.280 (34)	-	7	17-30

Table S7	total hits	average	Gaussian fit	linkage number	species Table 1
N(sp^2) −N(sp^2) =C-N=N-C= -N=N- double =N-N= single	882	-	1.249(16) 1.299(14) 1.373(32)	10b 10b 10a	18-18
N(sp^2)=N (*terminal*) =N=N	99	1.119 (12)	-		18-19
N(sp^2) −N(*amide*)	293	1.372 (29)	-	12	18-21
N(sp^2) −O =N−O*X*	322	1.399 (25)	-	13	18-23
=N−OH	162	1.395 (16)	-	14	18-29
-N=O nitro group	3204	1.218(12)	1.218(10)	18	20-30
N(sp^2) −S*X*	264	1.631(45)	-	16	18-34

SUPPLEM1.2.6 Sulfur

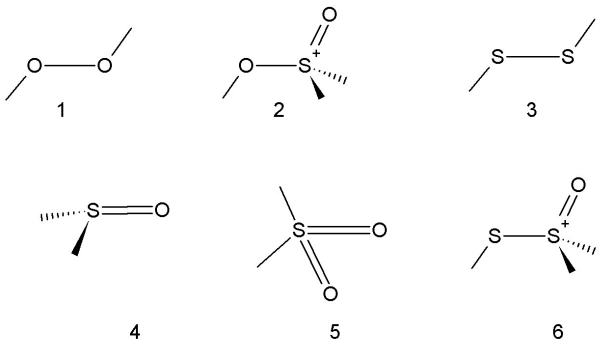
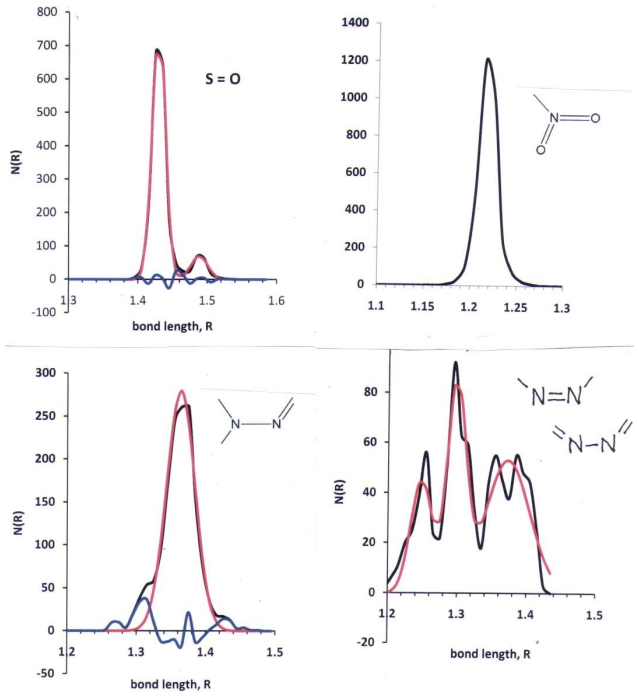


Table S8	total hits	average	Gaussian fit	linkage number	species Table 1
-O−O- peroxide	24	[1.48]	-	1	23-23
-O−S(O_2), -O−S=O sulfonate	125	[1.60 scatter]	-	2	23-36
>S-O >S=(O_2) >S=O	2015	1.436(21)	 1.429(10) 1.489(12)	 5 4	31-36
-S−S-	220	2.054 (29)	-	3	
-S−S(O_2), -S−S(O_3)	21	[2.10]	-	6	



SUPPLEM1.2.7. Average bond distances involving hydrogen, from neutron diffraction data.

Table S9	total hits	average
C(sp2)−H	307	1.077(31)
C(sp3) −H	670	1.085(26)
R-O−H	93	0.975(27)
(CO)-O−H	11	1.015
(CO)-N−H	37	1.018
$N(sp3)^+$ −H	29	1.034(14)
N(sp3) −H	40	1.018(14)

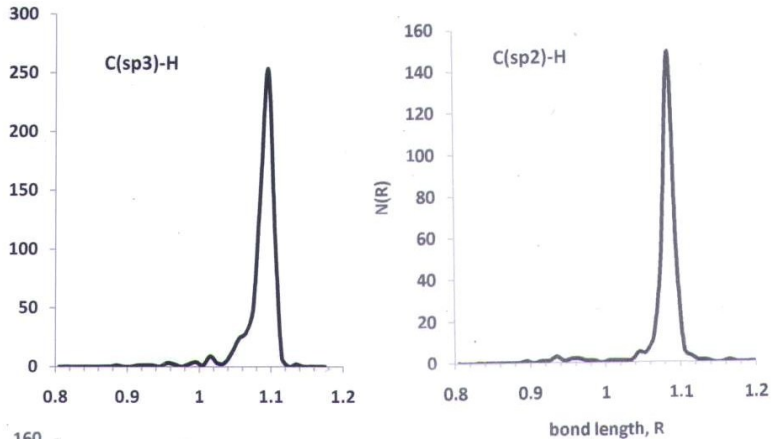


Table S10. Average C–C bond lengths in comparison with older surveys. A.G.Orpen, L.Brammer, F.H.Allen, O.Kennard, D.G.Watson and R.Taylor, in Structure Correlation, H.-B.Buergi and J.D.Dunitz, Eds., VCH, Weinheim 1994, vol. 2, Appendix A.

experimental X-ray, present			1994 survey[a]
bond type	R_G or R_{Av}	σ_G or σ_{Av}	
-C≡C-	1.183	13	1.183
>C=C<	1.342	18	1.331
≡C – C≡	1.378	6	1.377
C_{arom}---C_{arom}	1.382	12	1.380
≡C – Csp^2	1.433	11	1.431
Csp^2 – Csp^2	1.439	38	1.460
≡C – Csp^3	1.467	14	1.466
Csp^2 – Csp^3	1.503	13	1.507
Csp^3 – Csp^3	1.523	16	1.530

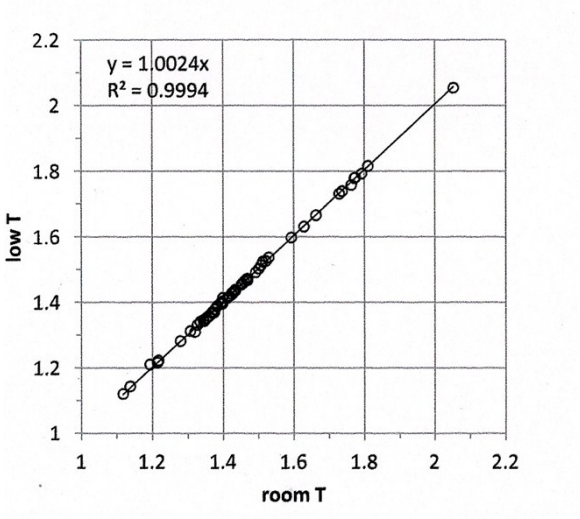


Figure S1. The relationship between low-T and room-T experimental determination. Low-T bond lengths are slightly longer due to a systematic error in the treatment of X-ray data.

SUPPLEM1.3 Calculations of bond stretching profiles by ab initio MP2/6-31G**

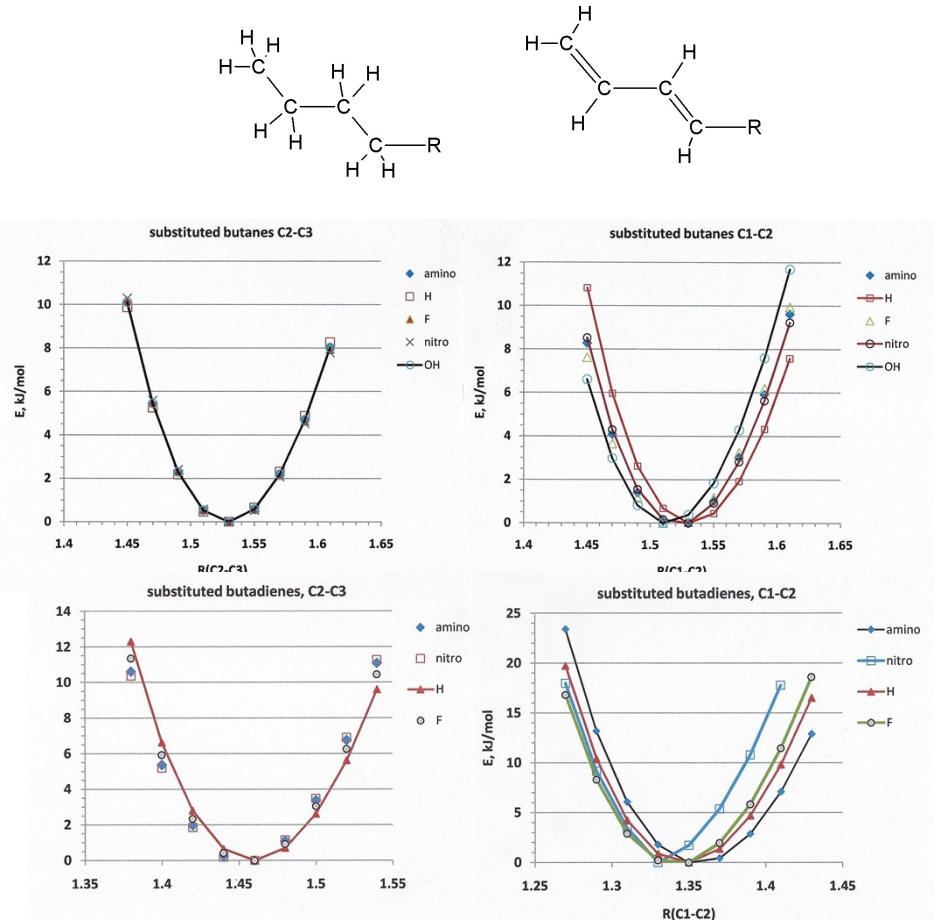


Figure S2. Bond stretching profiles for carbon-carbon bonds in 1-substituted butanes and butadienes. The C2-C3 central bond is in both cases quite insensitive to substitution. The C1-C2 bond, close to the substitution point, is marginally sensitive to substitution, but without a clear trend as a function of the electronic character of the substituent. All curves are strictly harmonic within 0.1 Å from the minimum. Note the different energy scale for the C1-C2 (double) bond in butadiene.

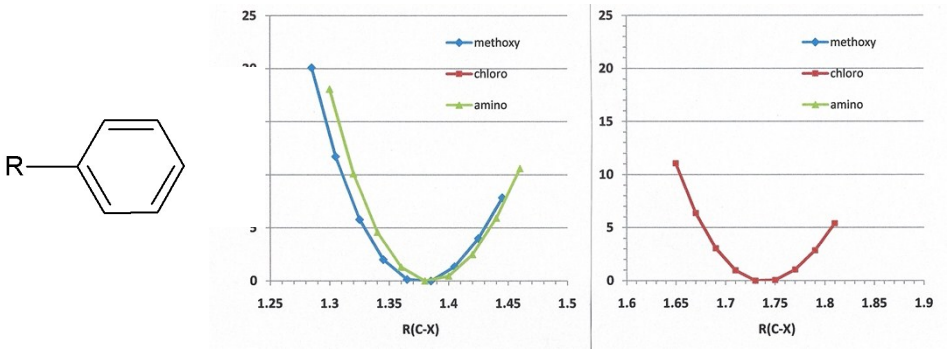


Figure S3. Bond stretching profiles for the C-substituent bond in substituted benzenes. All curves are strictly harmonic within 0.1 Å from the minimum.

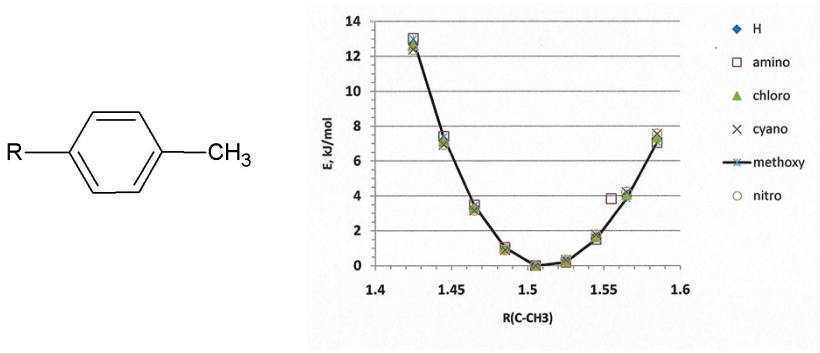


Figure S4. Bond stretching profiles for the C-CH_3 bond in p-substituted toluenes. Bond length and force constant are insensitive to substitution. All curves are strictly harmonic within 0.1 Å from the minimum.

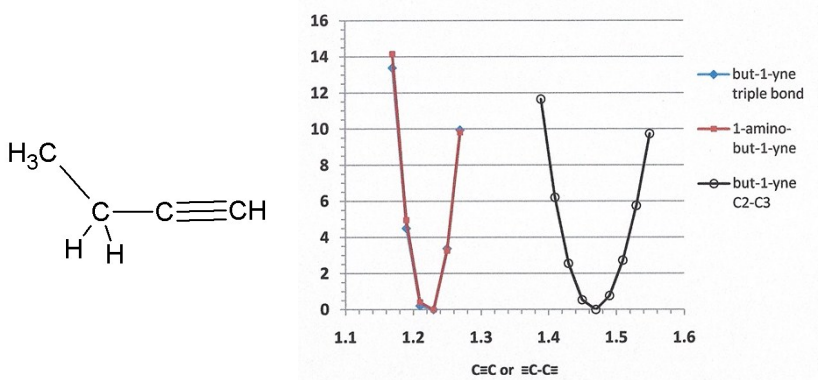


Figure S5. Bond stretching profiles in acetylenic compounds. The profile for triple bond is extremely narrow as expected, and is insensitive to substitution.

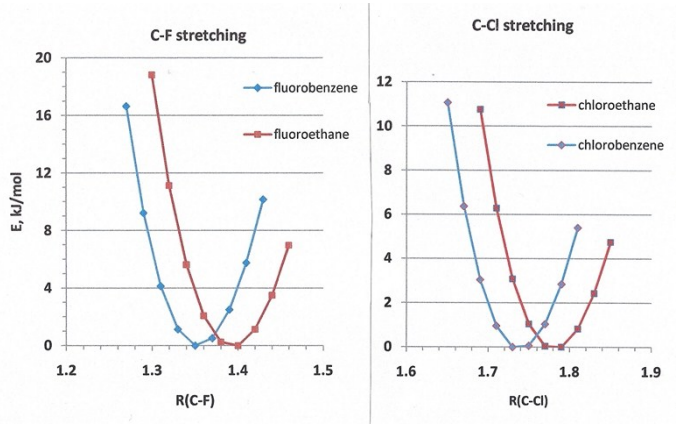


Figure S6. Bond stretching profiles for carbon-halogen bonds.

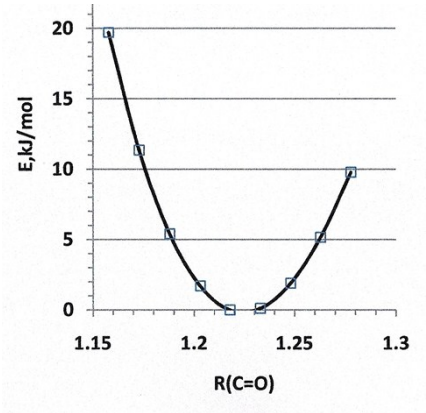
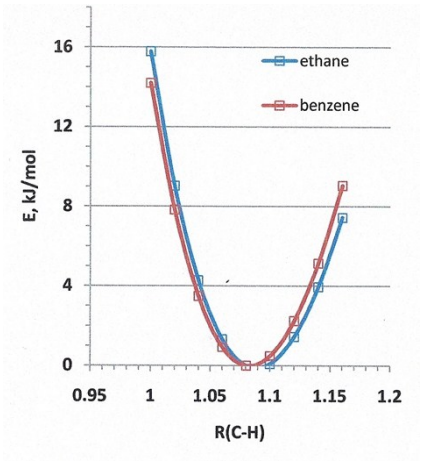


Figure S7. Bond stretching profile for the C=O bond in acetone.

Figure S8. Bond stretching profiles for C-H bonds.



SUPPLEM1.4 Calculation of approximate vibrational frequencies and vibrational level spacings from bond stretching force constants

In a first approximation the bond stretching can be assimilated to that occurring in a diatomic molecule:

$$\nu(\mathrm{Hz}) = 1/(2\pi)\,[k\,10^{23}/\mu]^{1/2} \quad ; \quad \Delta E = h\nu$$

with k in kJ/(mol Å^2) and the reduced mass μ in kg. Assuming as a reference the ethane molecule as a diatomic molecule formed by two methyl groups, m = 0.0075 kg and for k = 3000 one gets ν = 3 10^{13} Hz, or approximately a wavenumber of 1000 cm^{-1}, and ΔE = 12 kJ/mol.

SUPPLEM2. The intermolecular hydrogen bond

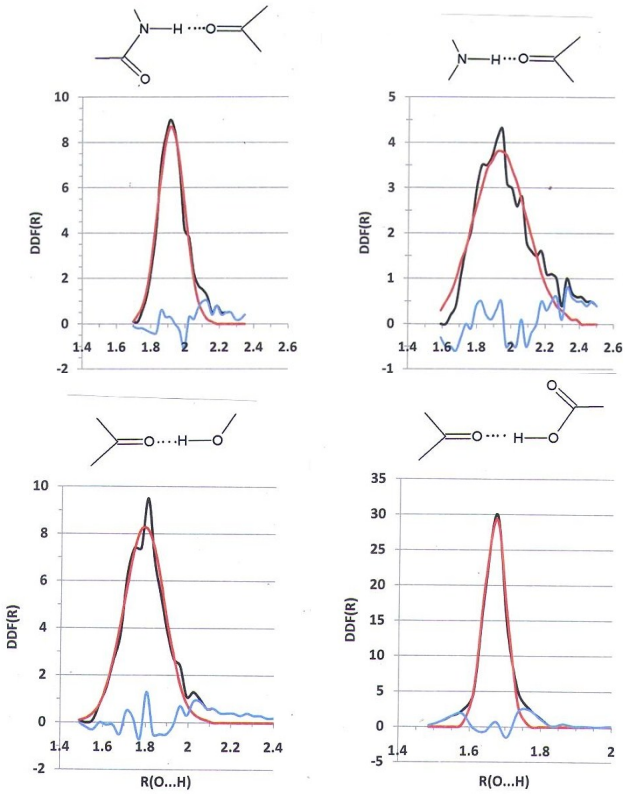
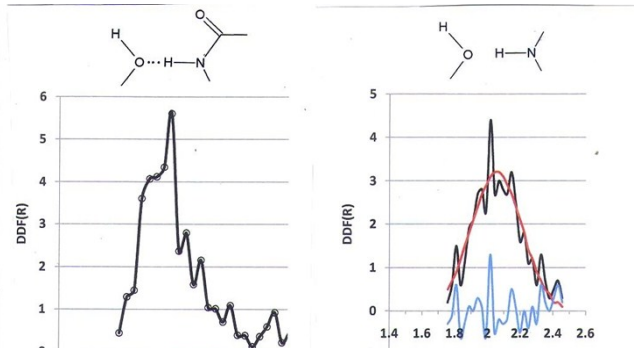


Figure S9. Distance density function (DDF) plots, with Gaussian fitting, for the distribution of hydrogen bonding distances of the carbonyl group with several donors. Black, experimental DDF, red: Gaussian fitting, blue: difference. Dangling bonds are to non-H atoms (mostly carbon).



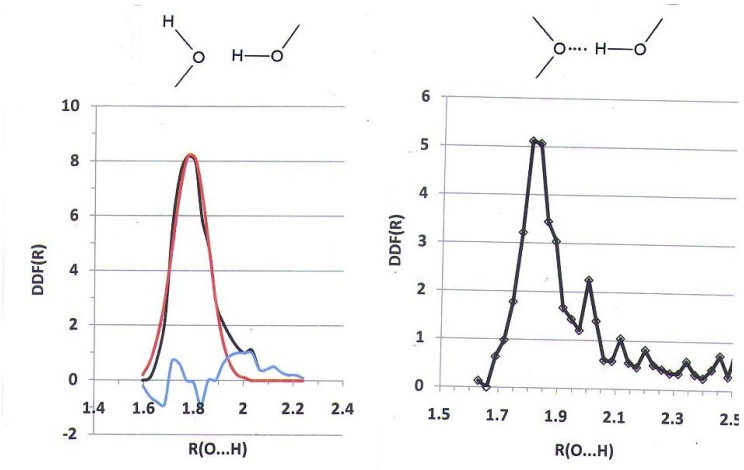


Figure S10. Distance density plots for the distribution of hydrogen bonding distances of the alcohol or ether group with several donors. Black, experimental DDF, red: Gaussian fitting, blue: difference. No Gaussian fitting when the distributions are multimodal and/or too noisy because of the small number of data. Dangling bonds are to non-H atoms (mostly carbon).

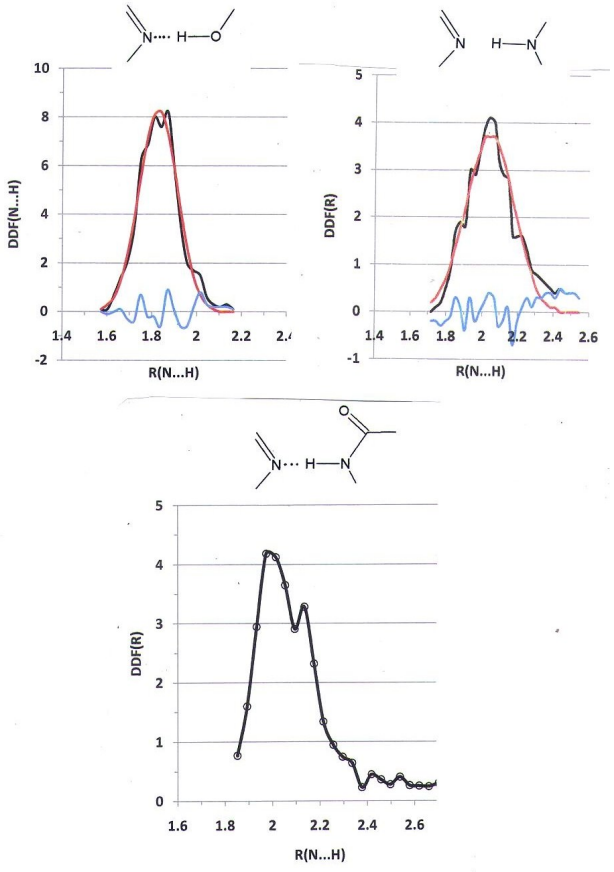
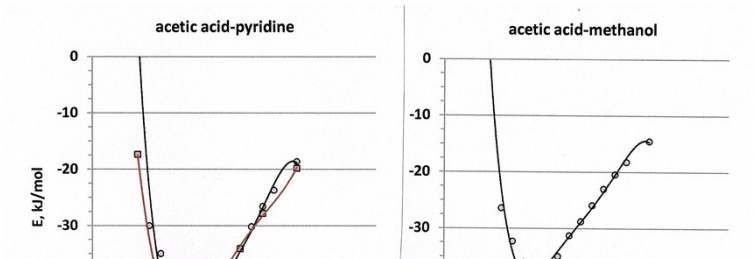
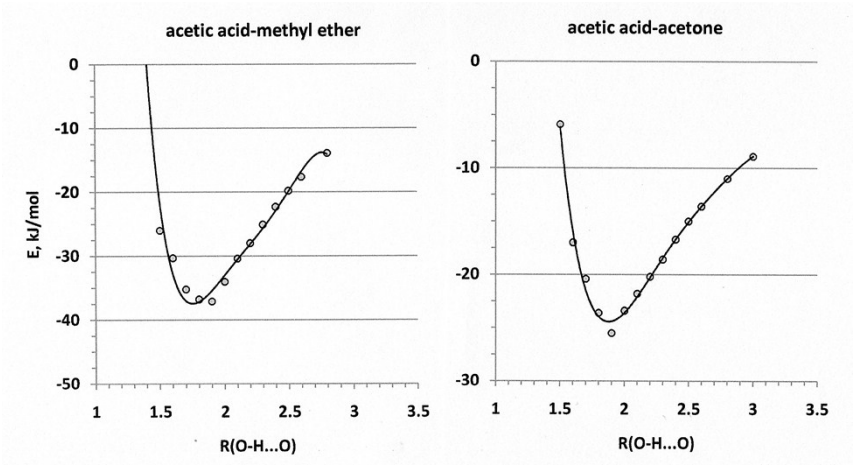


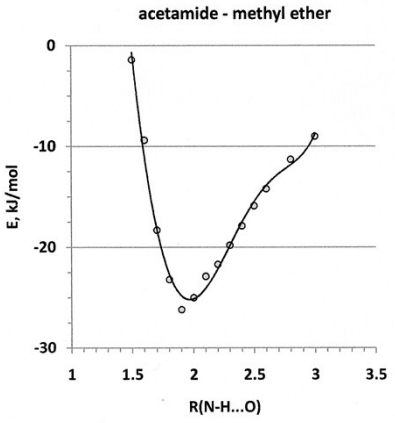
Figure S11. Distance density plots for the distribution of some N-H...O or N-H...N hydrogen bonding distances. Black, experimental DDF, red: Gaussian fitting, blue: difference. No Gaussian fitting when the distributions are multimodal and/or too noisy because of the small number of data. Dangling bonds are to non-H atoms (mostly carbon).

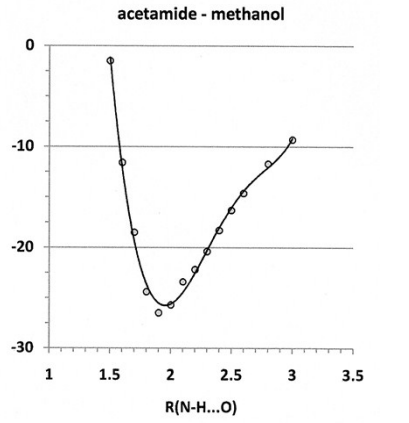
Figures S12-S15. Calculated hydrogen-bond energy profiles for model compounds.

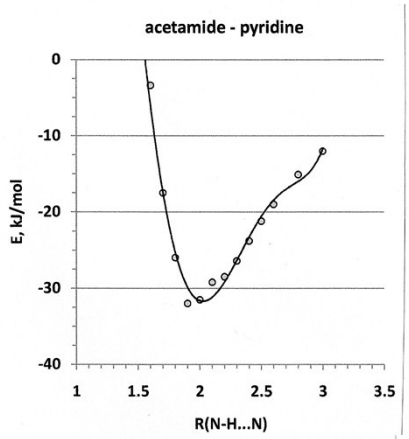


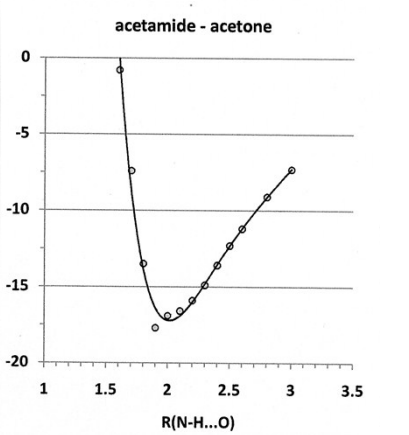

acetic acid-methyl ether
E, kJ/mol
0
-10
-20
-30
-40
-50
1
1.5
2
2.5
3
3.5
R(O-H...O)

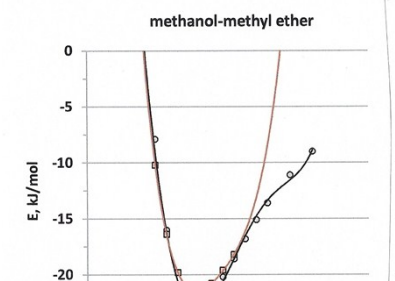
acetic acid-acetone
0
-10
-20
-30
1
1.5
2
2.5
3
3.5
R(O-H...O)

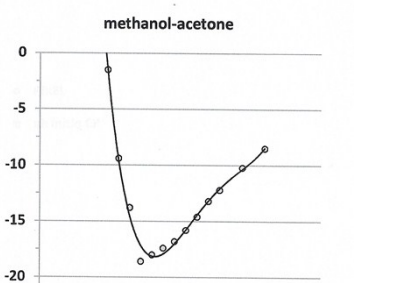

acetamide - methyl ether
E, kJ/mol
0
-10
-20
-30
1
1.5
2
2.5
3
3.5
R(N-H...O)


acetamide - methanol
0
-10
-20
-30
1
1.5
2
2.5
3
3.5
R(N-H...O)


acetamide - pyridine
E, kJ/mol
0
-10
-20
-30
-40
1
1.5
2
2.5
3
3.5
R(N-H...N)


acetamide - acetone
0
-5
-10
-15
-20
1
1.5
2
2.5
3
3.5
R(N-H...O)


methanol-methyl ether
E, kJ/mol
0
-5
-10
-15
-20


methanol-acetone
0
-5
-10
-15
-20

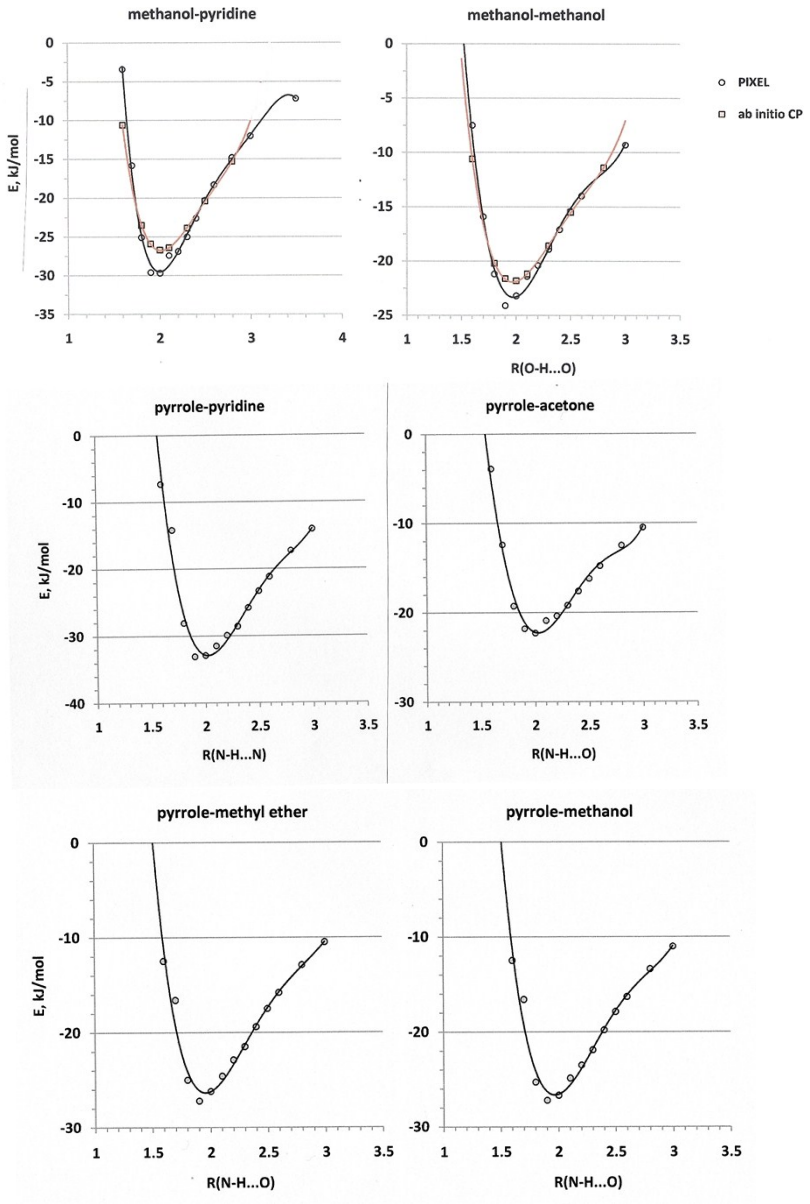

methanol-pyridine
methanol-methanol
PIXEL
ab initio CP
E, kJ/mol
R(O-H...O)
pyrrole-pyridine
pyrrole-acetone
R(N-H...N)
R(N-H...O)
pyrrole-methyl ether
pyrrole-methanol
R(N-H...O)
R(N-H...O)

Table S11. First line: experimental top-frequency bond distance for common types of hydrogen bonding; 11429 crystal structures in the "HB-donor" data set. Second line: equilibrium distance, cohesive energy in kJ mol^{-1} and stretching force constant calculated by PIXEL for pairing of the indicated model molecules. Third line: same by ab initio MP2/6-31G**

	O-H alcohol exptl. (methanol)	COO-H acid exptl. (acetic acid)
acceptor (exptl) (model molecule)		
=N-or --N--arom (pyridine)	1.826(86) 2.00 30 214 2.02 27 125	- 1.85 49 342 1.82 47 227
- O - ether (dimethyl ether)	1.838(79) 1.97 23 146 1.95 22 125	- 1.82 39 283
(R)O(H) alcohol (methanol)	1.784(71) 1.92 25 241 1.95 23 152	- 1.82 40 286

Table S12. Experimental top-frequency bond distance for common types of hydrogen bonding; 11429 crystal structures in the "HB-donor" data set, with the number of hits for each type.

	donor			
	O-H alcohol	COO-H acid	CON-H amide	R_2N-H
acceptor				
=N-or --N--arom	1.826(86)[a] 893[c]	-	[1.98][b] 394	2.041(134) 2150
- O - ether	1.838(79) 751	-	-	-
(R)O(H) alcohol	1.784(71) 2987	-	[1.97] 326	2.055(155) 584
(C)=O carbonyl	1.790(95) 2046	1.669(31) 1171	1.918(77) 3143	1.933(157) 2150

[a]R_G and σ_G from a Gaussian fit of the DDF. [b]From visual estimation from the graph (too few data for Gaussian fitting). [c] Number of data points.

SUPPLEM3 The weak bond

Table S13 Equilibrium distances, binding energies and stretching force constants from cubic fitting for all calculated profiles of hydrogen bonds, halogen bonds and weak bonds. Å, kJ/mol and kJ/(mol $Å^2$) units.

pair	R°	E°	k
hydrogen bonds			
methanol don.-pyridine accpt. pix	2.002	-30.0	214.2
methanol don.-pyridine accpt. ab in	2.020	-27.0	124.6
methanol don.-methyl ether accpt. pix	1.966	-23.2	146.0
methanol don.-methyl ether accpt. ab in	1.948	-21.7	124.6
methanol don.-methanol accpt. pix	1.923	-25.0	241.0
methanol don.-methanol accpt. ab in	1.949	-22.6	151.6
methanol don.-acetone accpt. pix	2.018	-18.4	125.4
acetic acid don.-pyridine accpt. pix	1.850	-49.3	342.8
acetic acid don. pyridine accpt. ab in	1.824	-46.8	227.4
acetic acid don.-methyl ether accpt. pix	1.823	-38.6	283.0
acetic acid don.-methanol accpt. pix	1.821	-39.8	285.5
acetic acid don.-acetone accpt. pix	1.901	-24.7	155.2
acetamide don.-pyridine accpt. pix	2.003	-32.0	220.1

acetamide don.-methyl ether accpt. pix	1.952	-25.7	180.9
acetamide don.-methanol accpt. pix	1.961	-25.9	159.4
acetamide don.-acetone accpt. pix	2.019	-17.7	134.8
pyrrole don.-pyridine accpt. pix	2.027	-32.9	197.6
pyrrole don.-methyl ether accpt. pix	1.969	-26.4	154.0
pyrrole don.-methanol accpt. pix	1.975	-26.7	152.2
pyrrole don.-acetone accpt. pix	2.005	-22.3	144.8
acetic acid-acetic acid pix	1.78	-32.	250.
acetamide-acetamide pix	1.96	-28.	135.
benzamide-benzamide pix	1.95	-27.	140.
pyrazole-pyrazole pix	1.95	-39.	200.
methanol-methanol pix	1.95	-22.	130.
phenol-phenol pix	1.90	-25.	130.

halogen bonds

Bromobenzene pyridine all ab initio	3.197	-7.2	59.0
p-ohBromobenzene pyridine	3.229	-6.7	51.8
no2Brbenzene pyridine ab initio	3.140	-11.4	64.9
nh2Brbenzene pyridine all abinitio	3.252	-5.4	53.2
cnBrbenzene pyridine	3.117	-10.4	62.5
coohBrbenzene pyridine	3.166	-8.8	62.1
c6h5cl benzoquinone abini	3.340	-1.6	16.6
c6f5cl furan ab ini	3.163	-5.2	37.8
c6f5I furan ab ini	3.182	-11.3	66.6
c6f5I benzonitrile	3.175	-16.7	74.5
c6h5i-pyridine	3.192	-13.4	69.1
c6h5br benzonitrile	3.302	-4.0	49.5
c6f5br pyridine	3.010	-15.7	86.0
c6f5br benzoquinone	3.118	-9.0	54.9
c6h5br furan ab ini	3.326	-4.2	28.5

weak bonds

acetone benzene ab initio	2.533	-5.2	32.3
formaldehyde ethylene ab initio	2.602	-3.1	27.9
urea benzene ab initio	2.385	-7.6	54.7
chlorobenzene-chlorobenzene pix	3.501	-2.6	33.2
hexaFclbenz-chlorobenzene pix	3.451	-3.3	38.0
benzene-chlorobenzene H...Cl pix	2.535	-4.9	40.6
benzene acetonitrile pix	2.548	-6.6	36.5

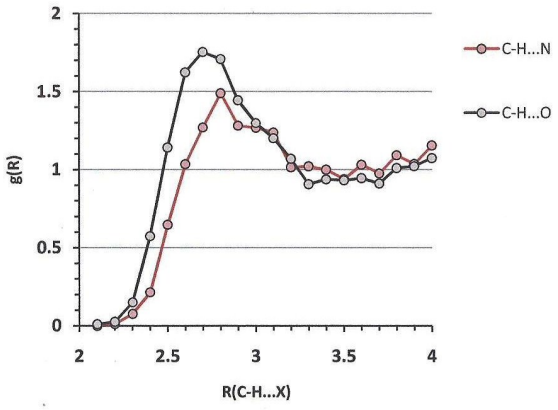


Figure S16. DDF(R) functions for the CH...O and CH...N contacts in crystals

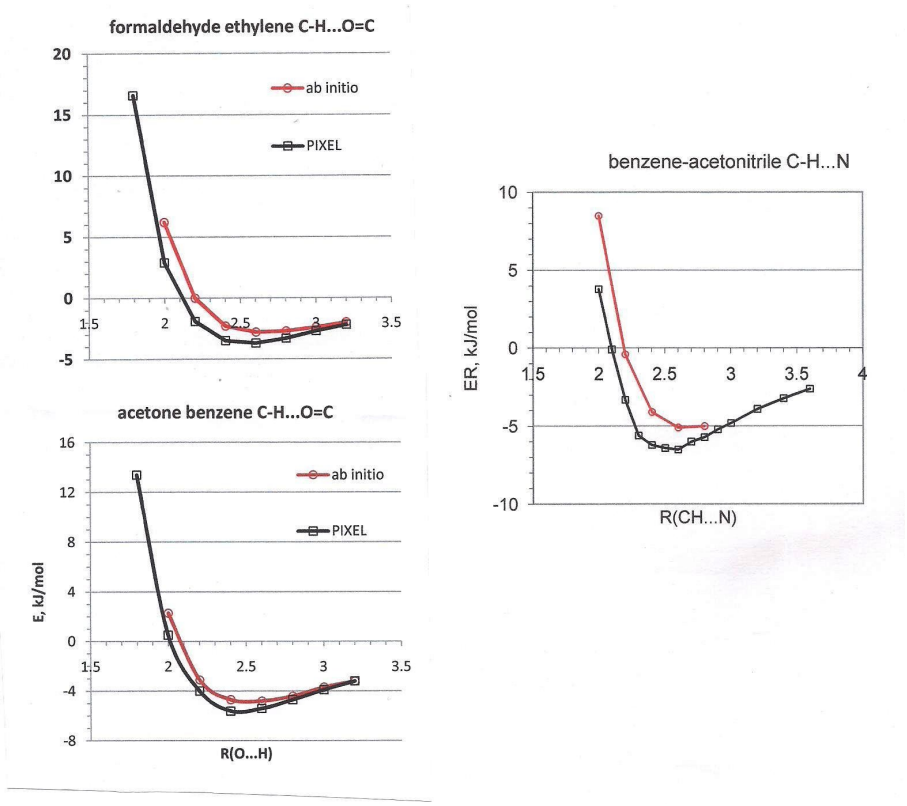


Figure S17. Binding energy profiles for some weak-bond dimers