What is a weak hydrogen bond?

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What is a hydrogen bond?

Under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms instead of only one, so that it may be considered to be acting as a bond between them (Pauling, 1939).

Other hydrogen bond definitions, X–H…A

A hydrogen bond is said to exist when (1) there is evidence of a bond, and (2) there is evidence that this bond sterically involves a hydrogen atom already bonded to another atom.

Pimentel and McClellan (1960)

Any cohesive interaction where H carries a positive charge and A a negative charge (partial or full) and the charge on H is more positive than on X

Steiner and Saenger (1993)

Eccentricities of nomenclature

D—H.....A

H accepts electrons

H donates a hydrogen bond

DONOR

A donates electrons

A accepts a hydrogen bond

ACCEPTOR

Weak (or non-conventional) hydrogen bonds
Historical survey, 1937-1982.

1937. Glasstone. $Cl_3C–H…O=CMe_2$ complex

1939. Pauling definition

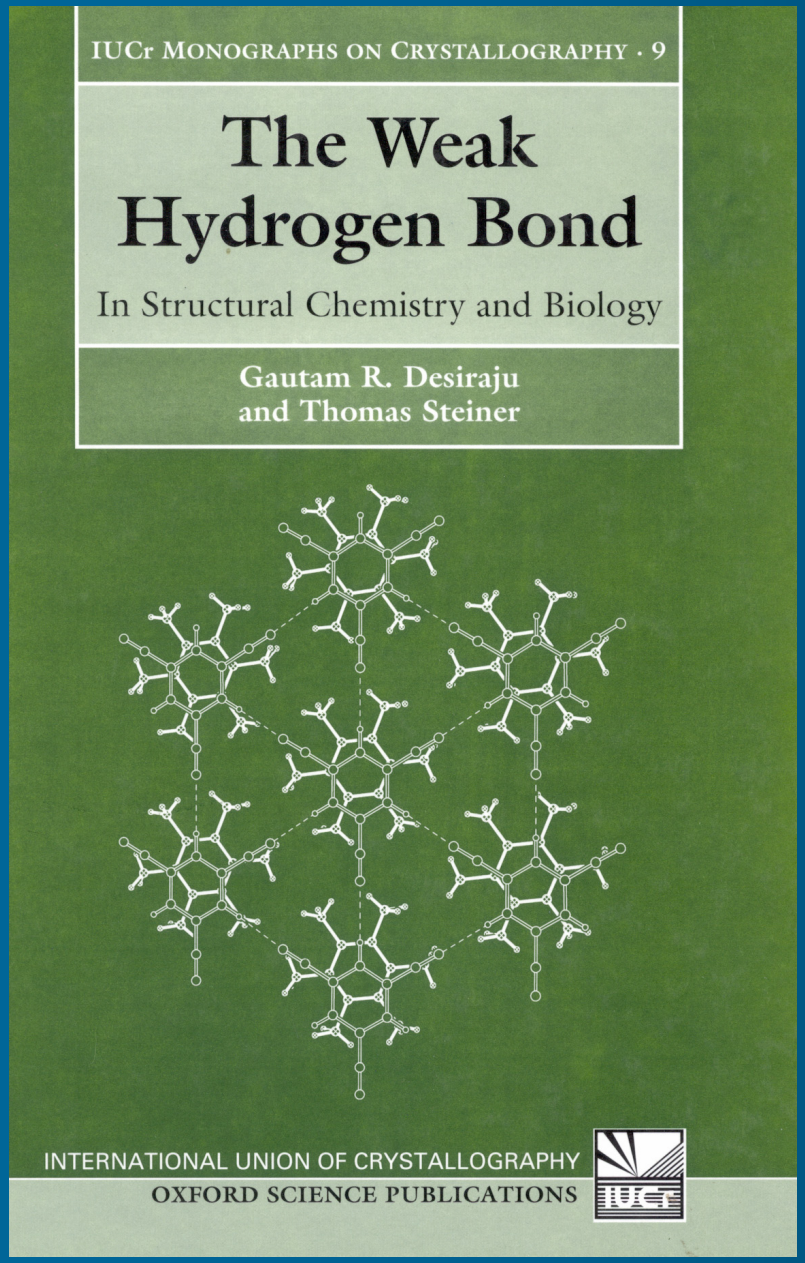
1962. Sutor and the C–H…O hydrogen bond. (Nature).

1967. Oki and Iwamura. O–H…π interactions (JACS)

1968. Donohue criticism of Sutor

1976. Leiserowitz review on carboxylic acids (Acta Cryst)

1982. Taylor–Kennard paper (JACS)



The weak hydrogen bond is an interaction X–H···A wherein a hydrogen atom forms a bond between two structural moieties X and A, of which one or even both are of moderate to low electronegativity (1999)

Bibliography

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- G. R. Desiraju, Chem. Comm., 2996, 2005.
- T. Steiner, Cryst. Rev., 6, 1, 1996.

Different types of hydrogen bond

D—H·····A Very strong

D—H·····A Strong

D—H·····A Weak

Hydrogen bond

Any cohesive interaction X–H•••A where H carries a positive and A a negative (partial or full) charge and the charge on X is more negative than on H

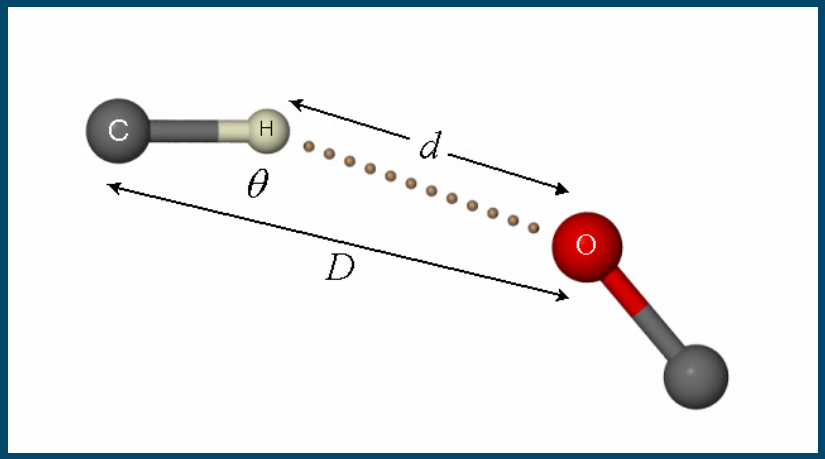
O–H···O(-) O–H···O N–H···O

O–H···π N–H···π C–H···O

Os–H···O C–H···Ni C–H···π

How to assess hydrogen bonds?

- Energy
- Spectroscopy
- Geometry
- Structure
- Function

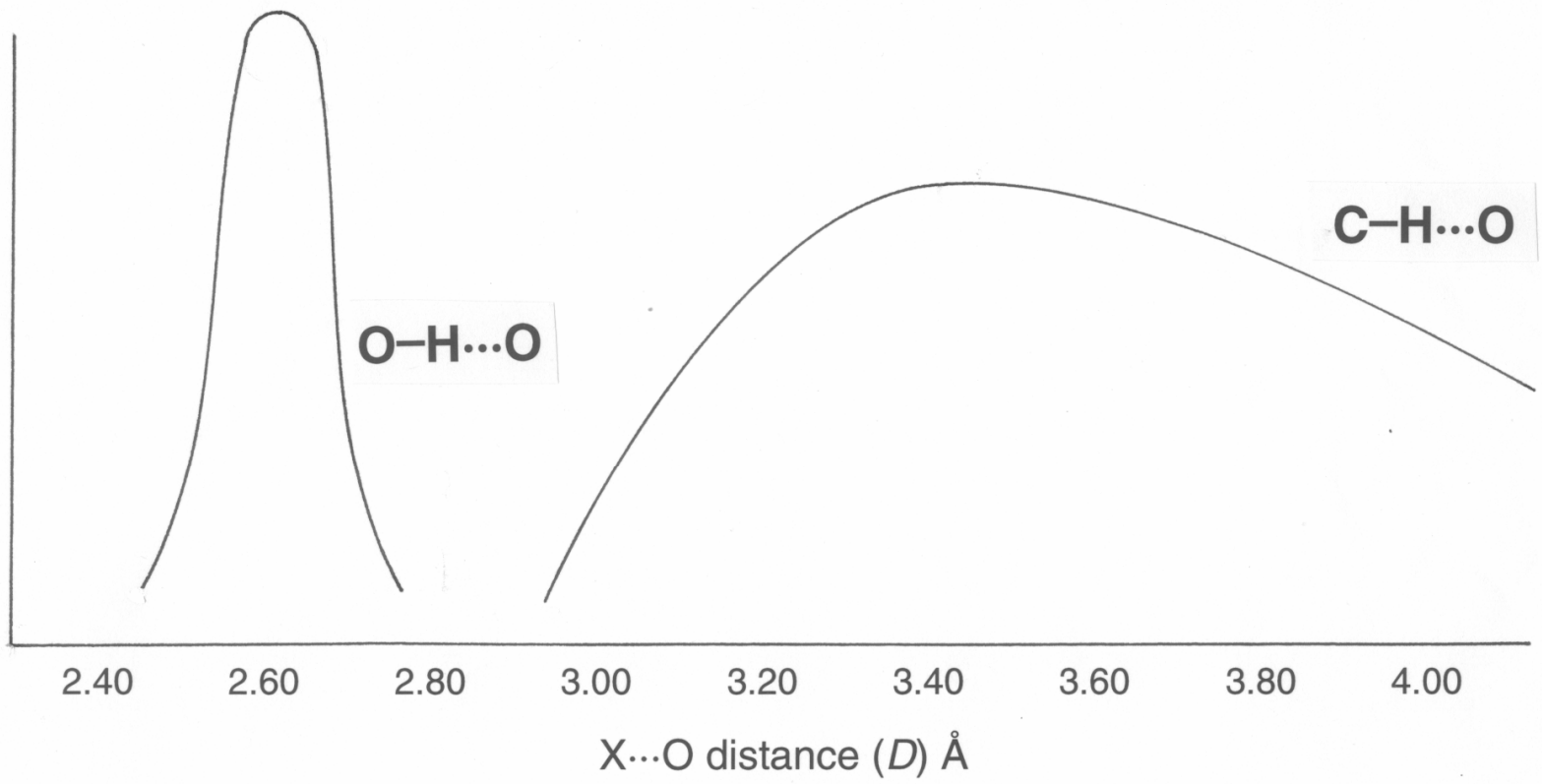


A complex interaction

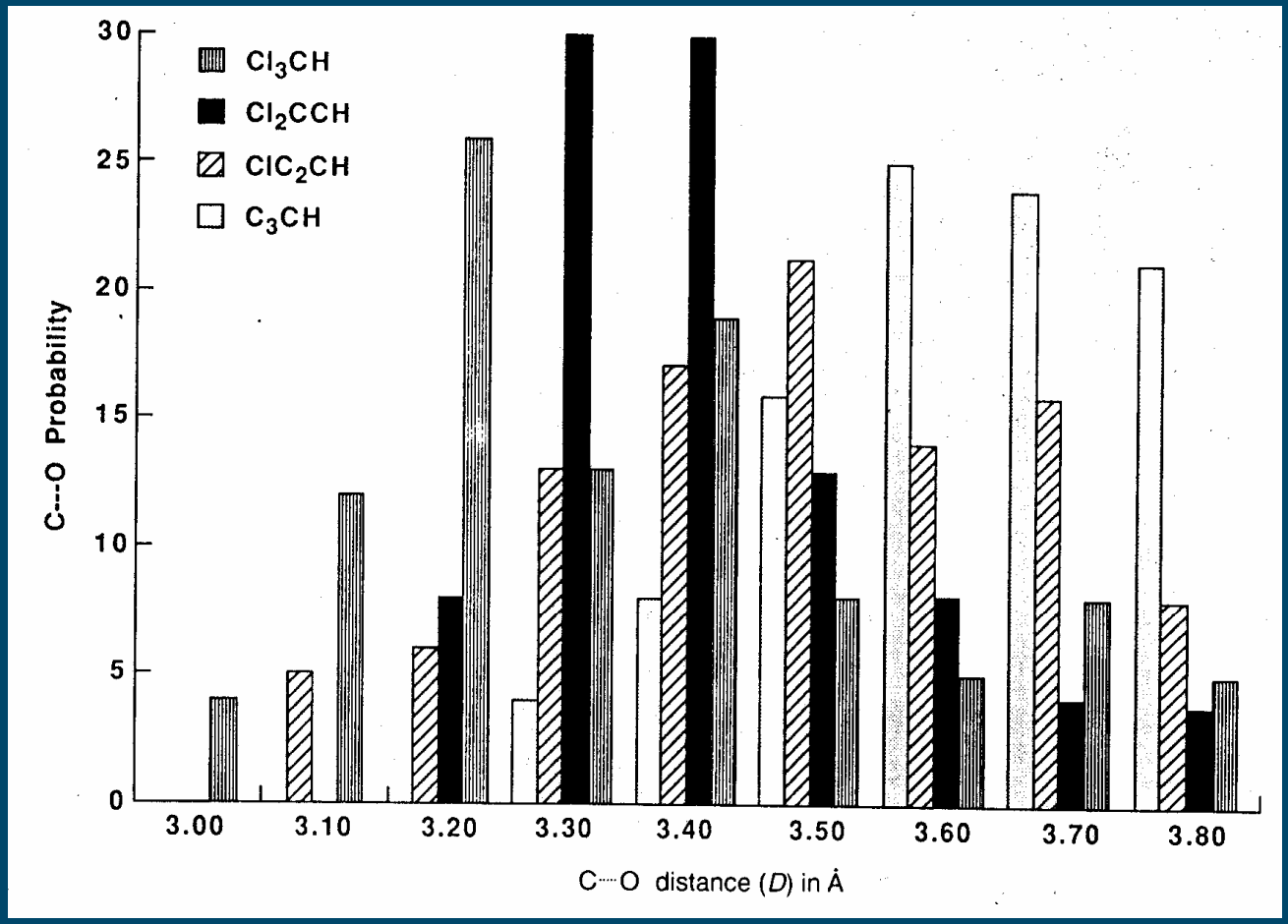
	Very strong	Strong	Weak
	$[F–H…F]^-$	N–H…O=C	C–H…O
Energy (kcal/mol)	–15 to –40	– 4 to – 15	< – 4
IR, ν_s	>25%	5-25%	<5%
Δ(X–H), Å	0.05 to 0.2	0.01 to 0.05	< 0.01
H…A, Å	1.2 to1.5	1.5 to 2.2	2.0 to 3.0
Shorter than van der Waals	100%	~100%	30-80%
Effect on crystal packing	Pronounced	Distinctive	Variable

Strong and Weak Hydrogen Bonds, X–H···O

An important difference



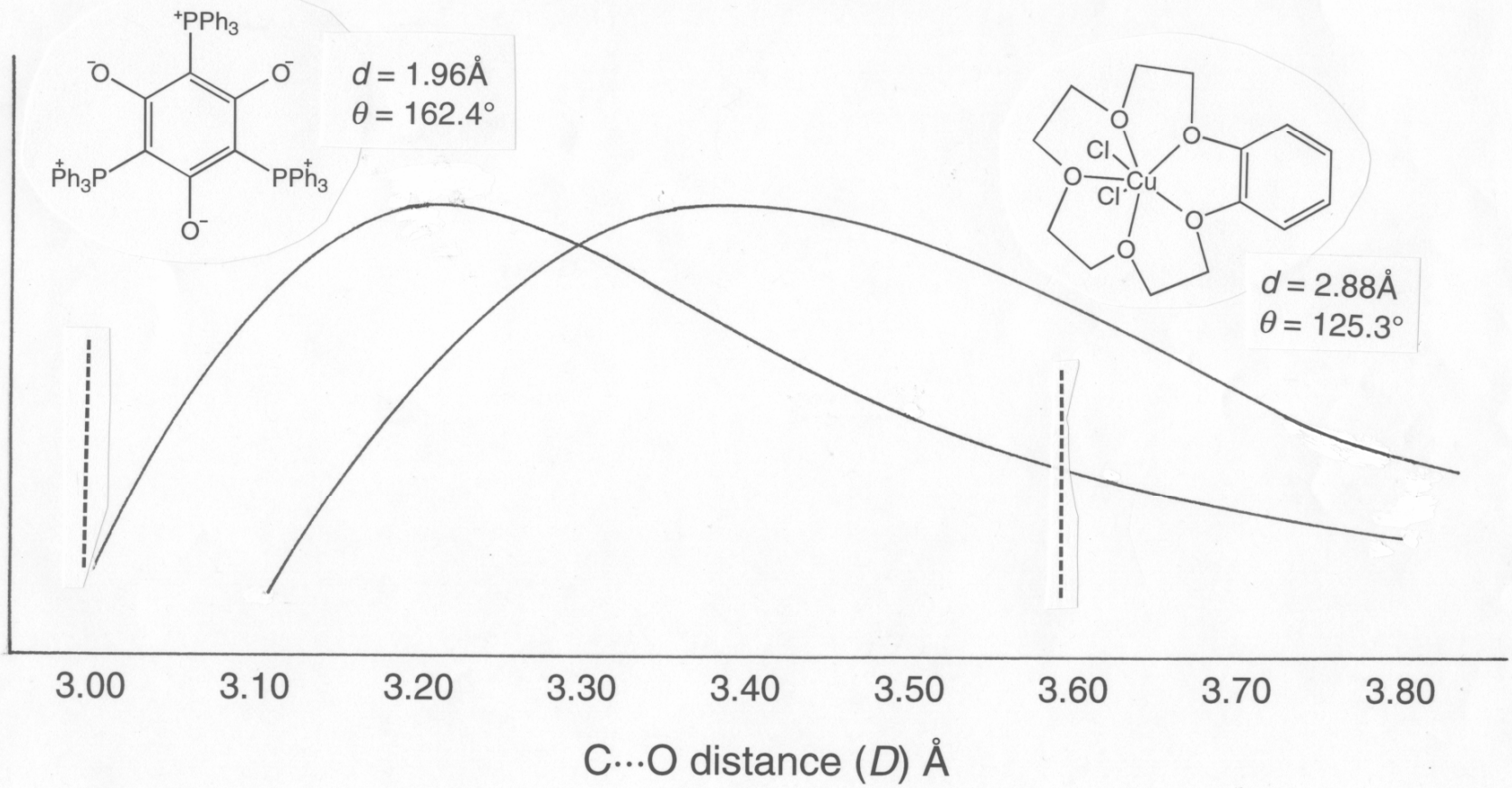
$Cl_{3-n}R_nC–H\ldots O$



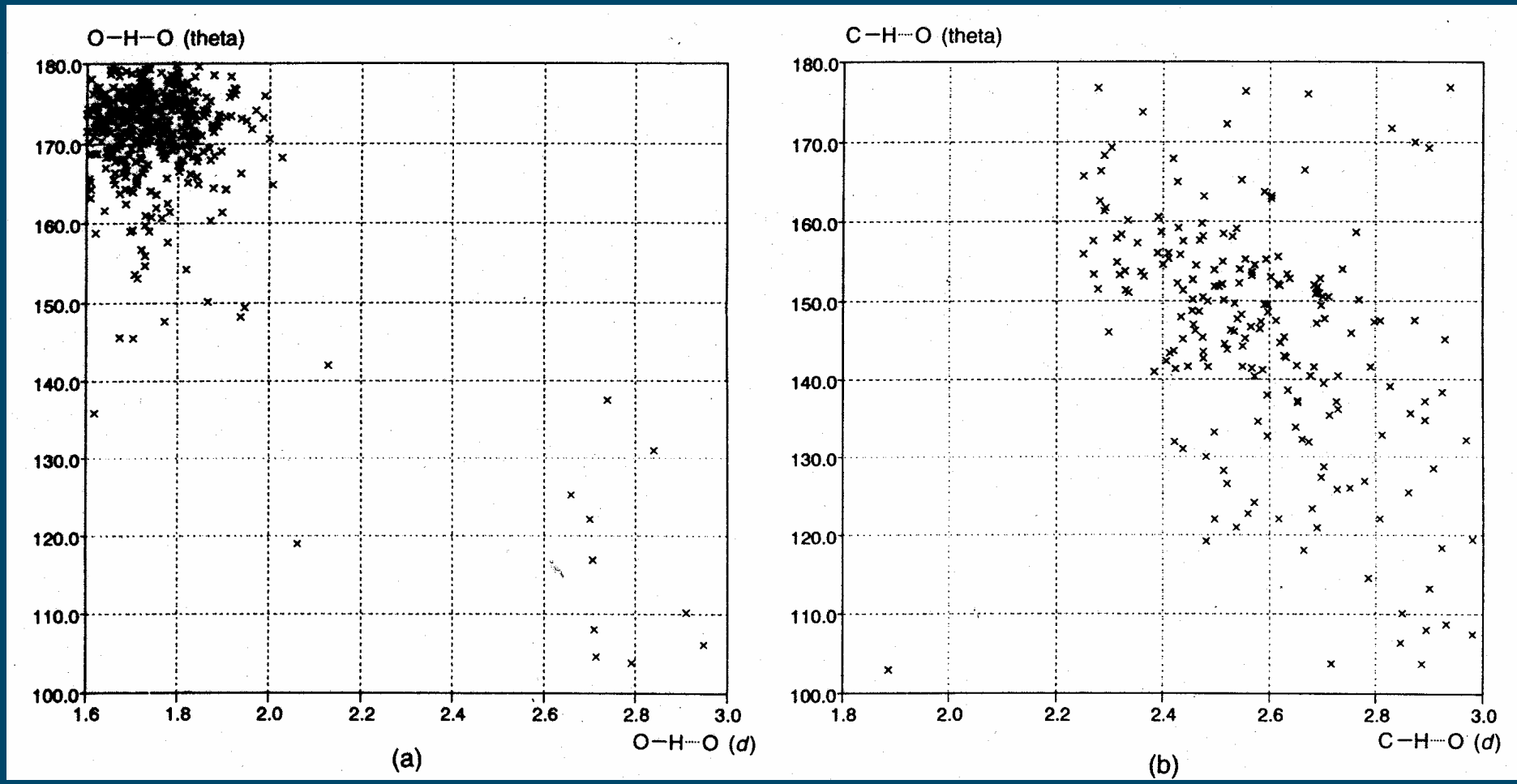
G. R. Desiraju, J. Chem. Soc., Chem. Comm., 179, **1989**

C–H···O Hydrogen Bonds

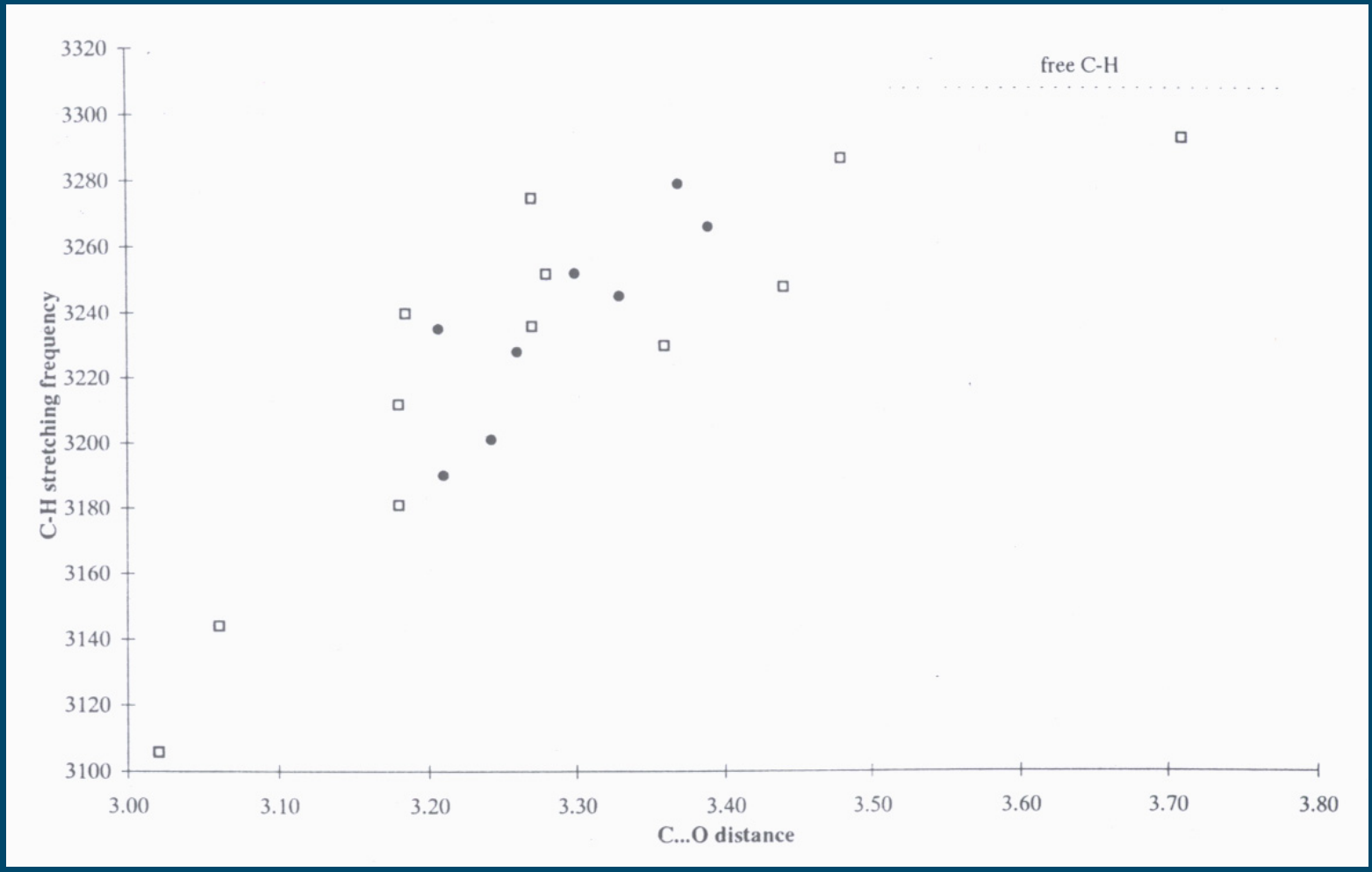
$CHCl_3$ and CH_2Cl_2



Angles, X–H…O

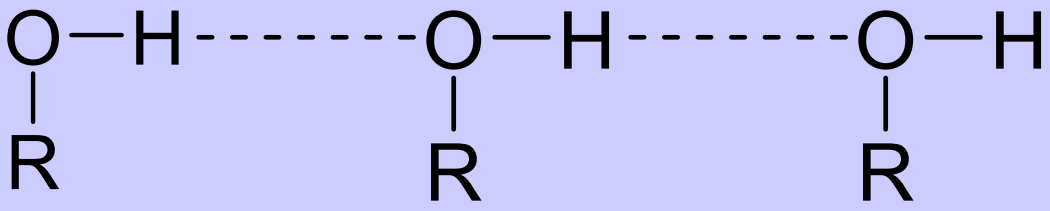

O–H–O (theta)
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
O–H···O (d)
(a)
C–H···O (theta)
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
1.8
2.0
2.2
2.4
2.6
2.8
3.0
C–H···O (d)
(b)

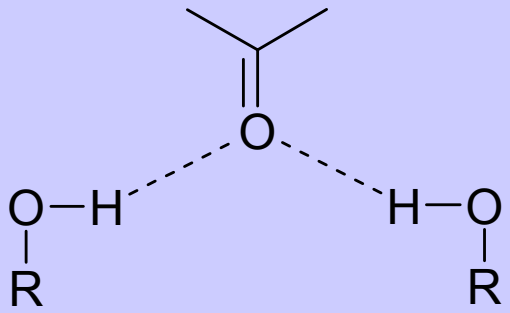
IR bathochromic shifts, C–H…O



G. R. Desiraju and B. N. Murty, Chem. Phys. Lett., 139, 360, **1987**

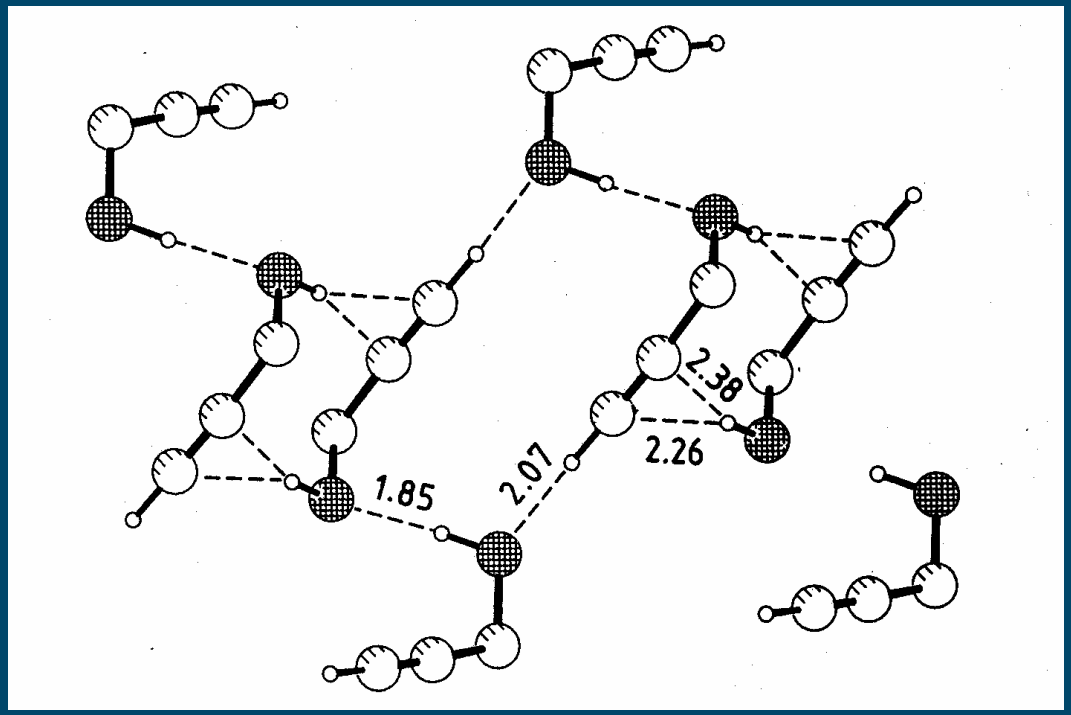
Cooperativity

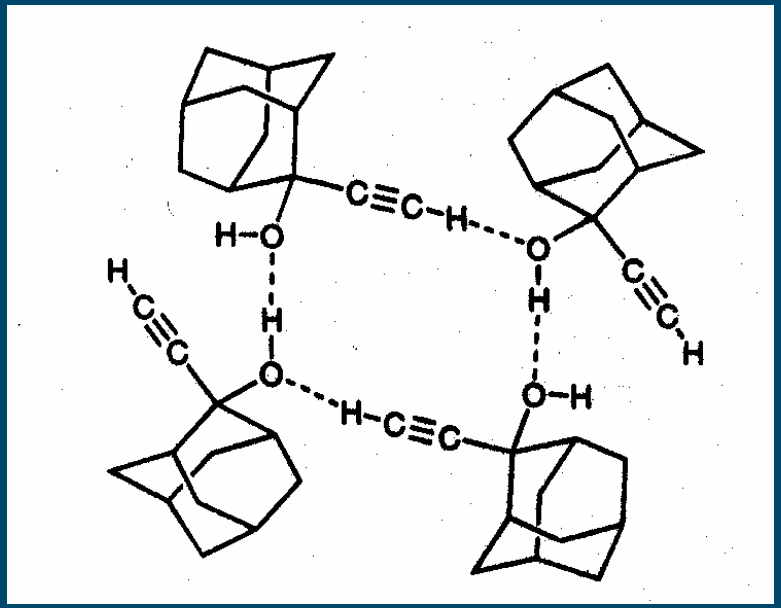




Anti-cooperative

C–H…O cooperativity in ethynyladamantan-2-ol





r_1–r_2 = 0.025(14) Å

Allen et al., J. Am. Chem. Soc., 118, 4081, **1996**

Thermal parameters

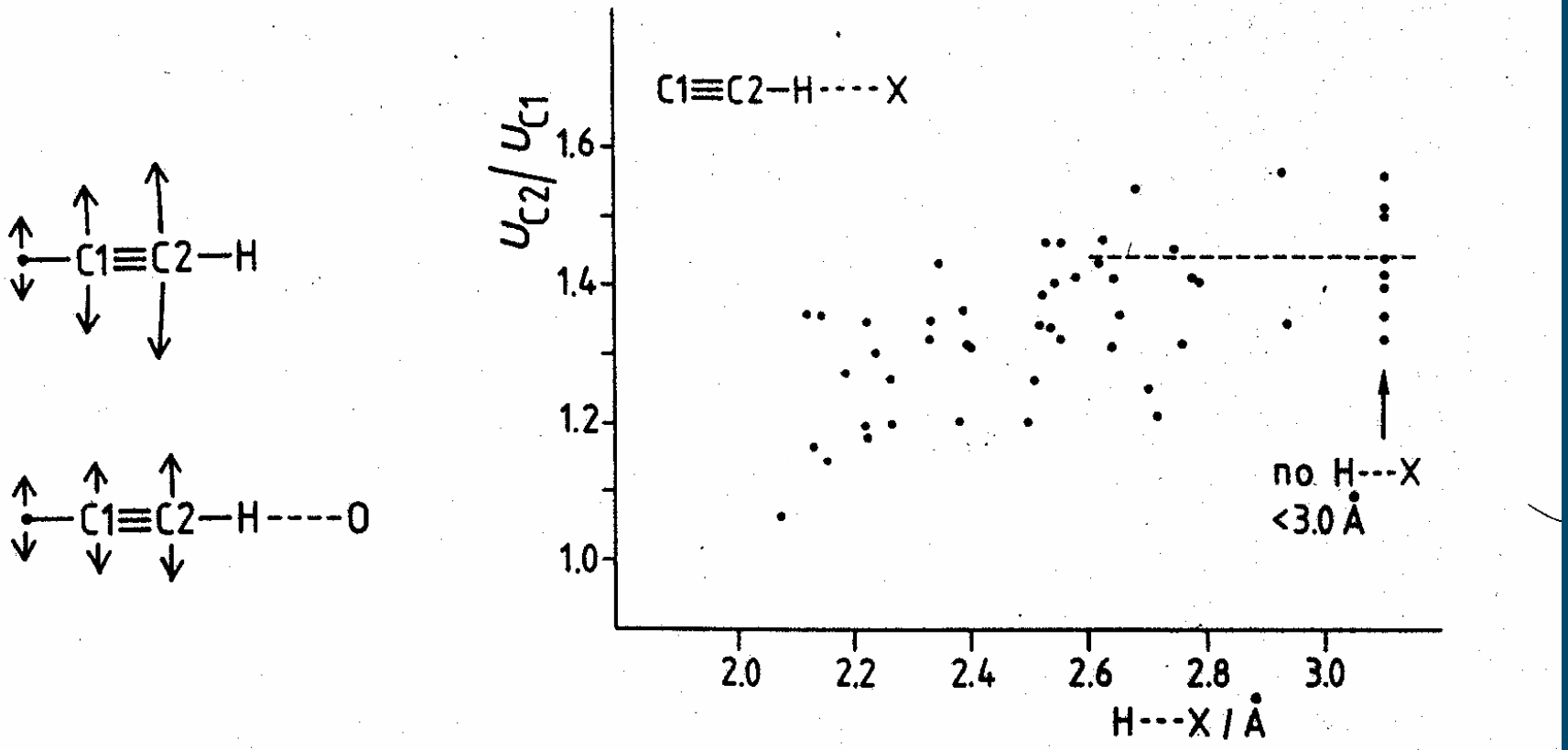
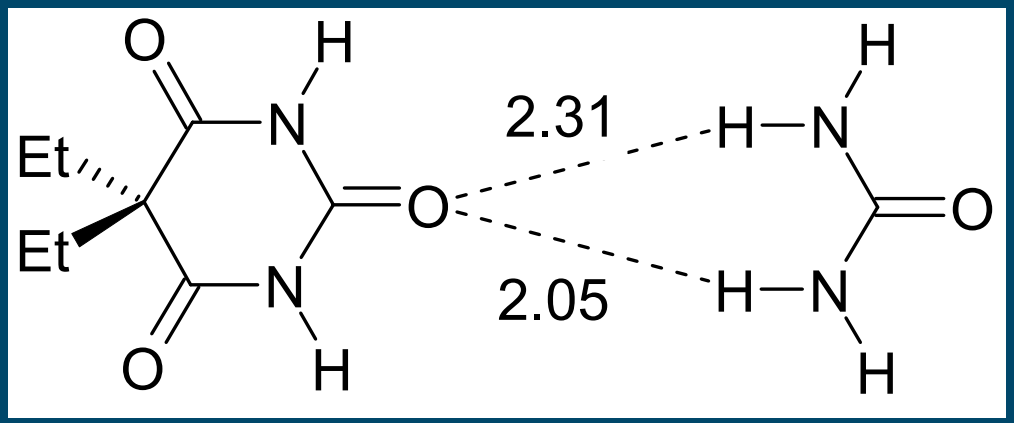
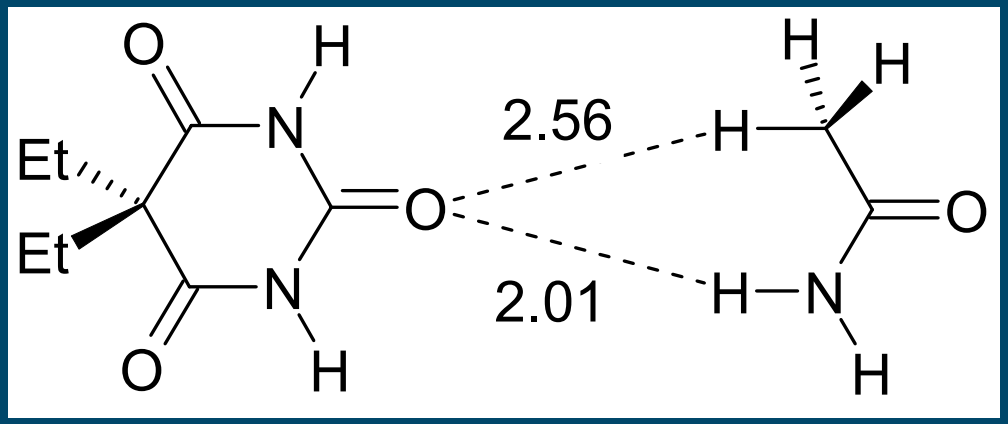


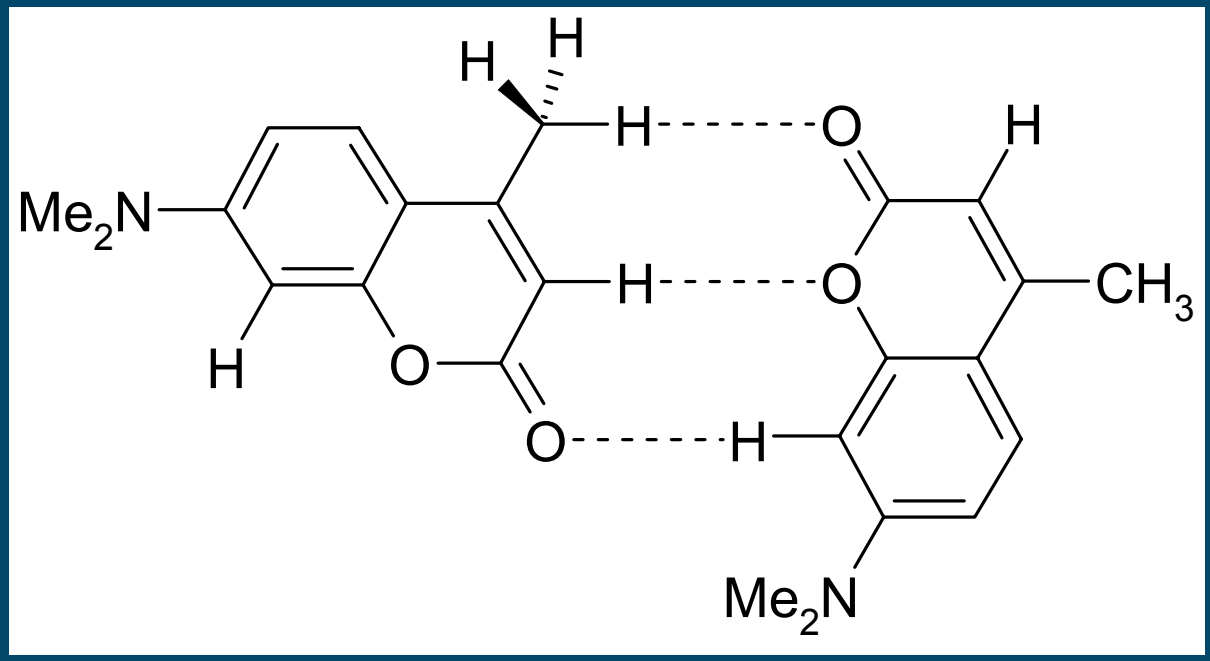
Fig. 2.24. Correlation of the *U*-ratio defined as $U_{eq}(C2)/U_{eq}(C1)$ with the distance *d* in 51 C≡C—H···X hydrogen bonds (X = O, N, π). The horizontal line shows the mean value for C≡C—H groups that donate no hydrogen bond with $d < 2.8$ Å (adapted from Steiner 1994*b*).

Isostructurality





Two molecules in the asymmetric unit (Z'=2)

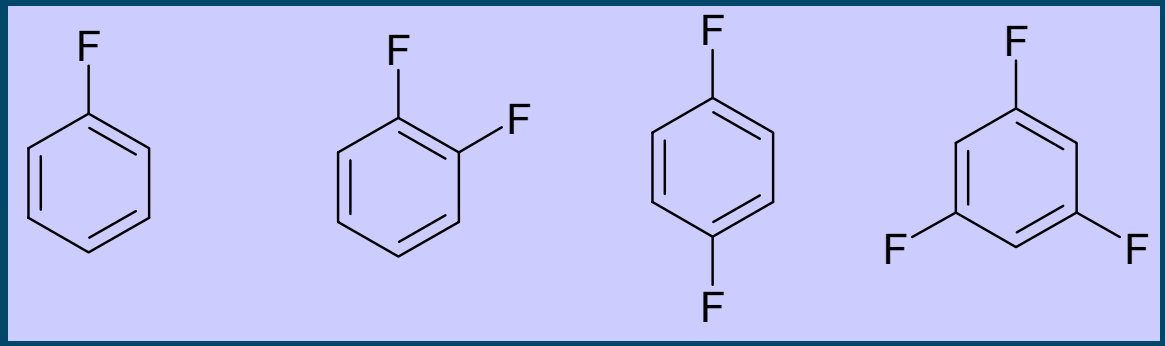


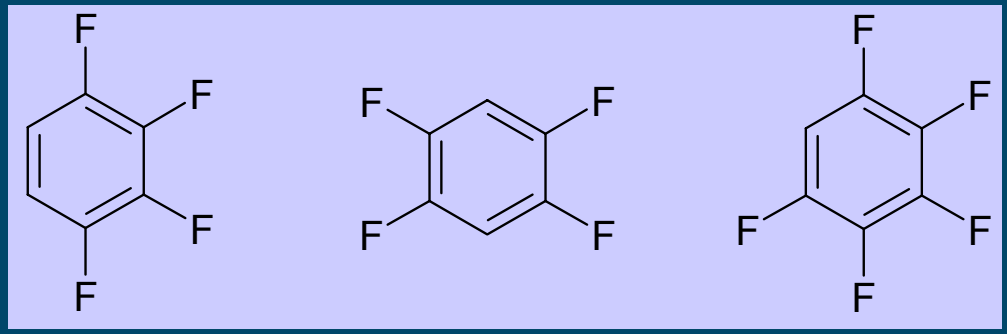
Electronegativity and Hardness

Fluorine

Weak donor **Very weak acceptor**

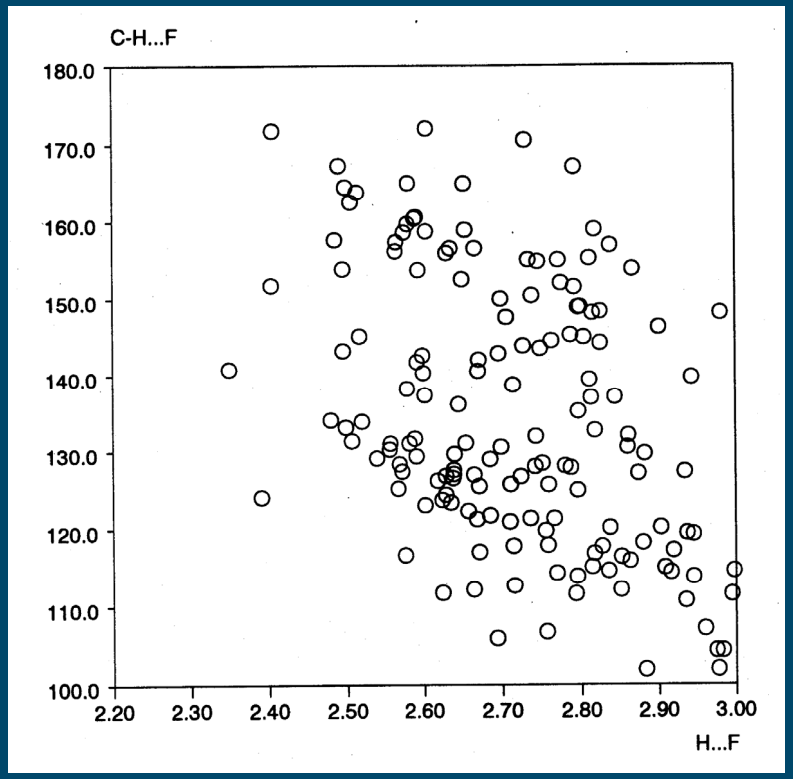
C–H···F–C Interactions in Fluorobenzenes



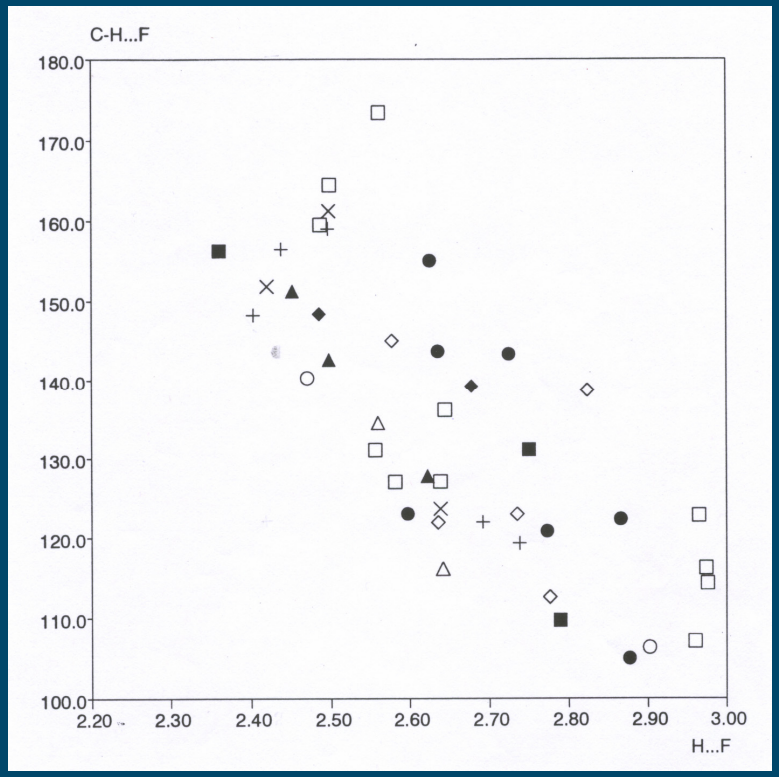


Thalladi, Weiß et al, JACS, 120, 8702, **1998**

C–H···F–C Hydrogen Bonds

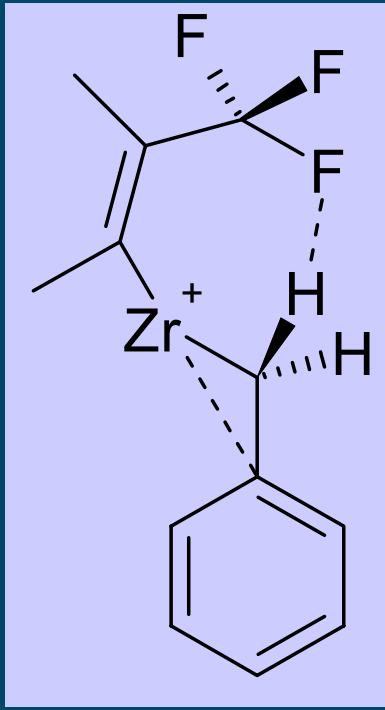


All C, H, F compounds

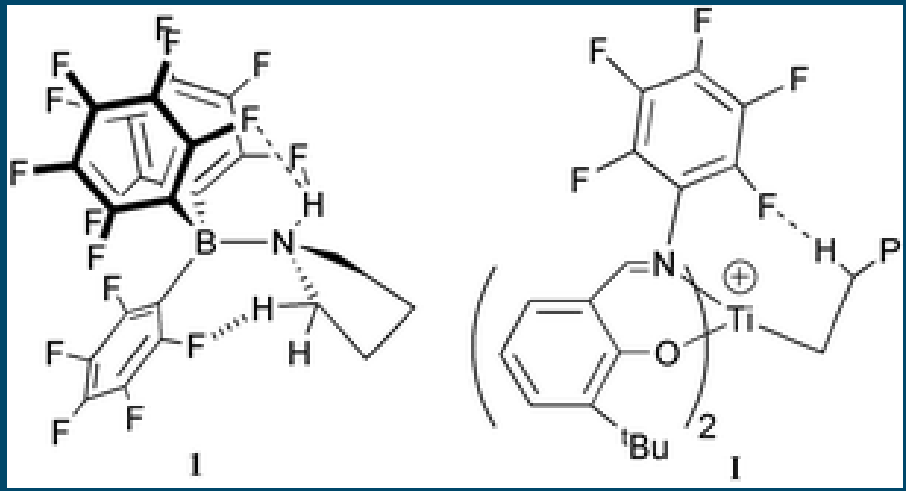


Fluorobenzenes

Weak and reversible C–H···F–C Hydrogen Bridge Applications. Polymerization catalyst.



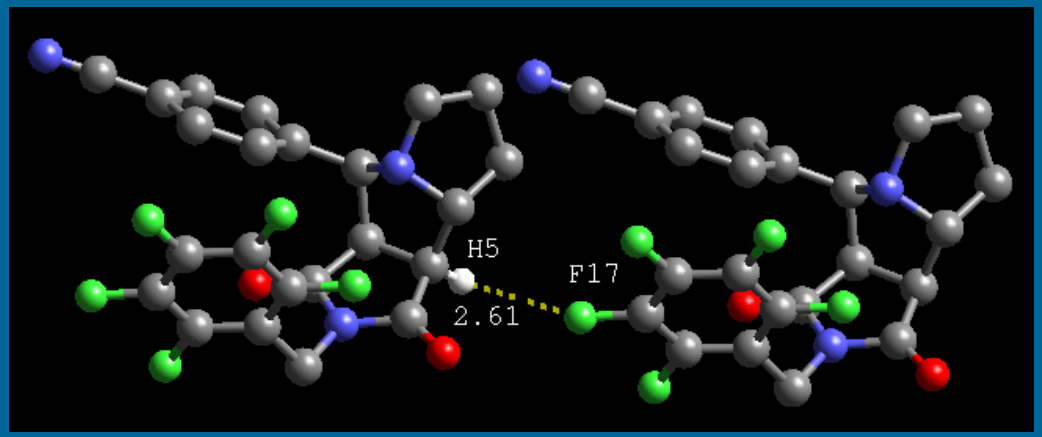
Stereoselective polymerisation
Chan et al,
Angew. Chem. Int. Ed.,
42, 1628, **2003**

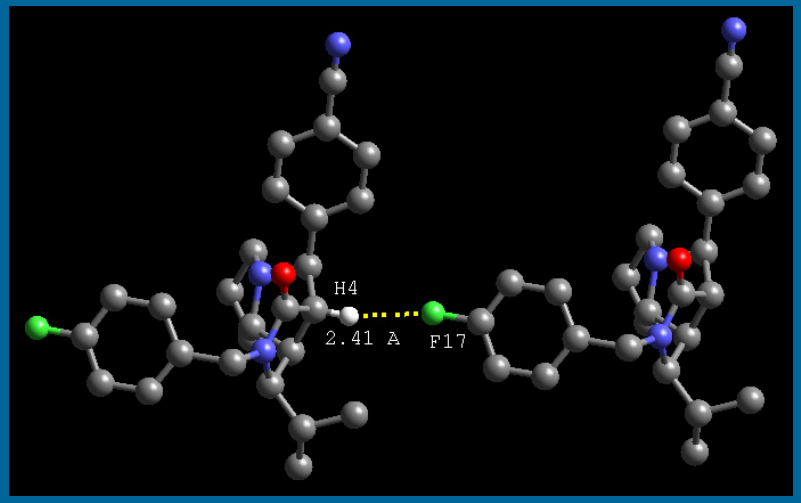


Boron adducts
Lancaster et al, Chem. Comm.,
2148, **2003**

Decrease of β-H transfer
T. Fujita et al,
JACS, 124, 3327, **2002**
JACS, 125, 4293, **2003**

Weak and reversible C–H···F–C Hydrogen Bridge Applications. Molecular recognition.





Binding in thrombin

Diederich et al,

Angew. Chem. Int. Ed.,

42, 2507, **2003**

Hydrogen bridge (*Wasserstoffbrücke)*

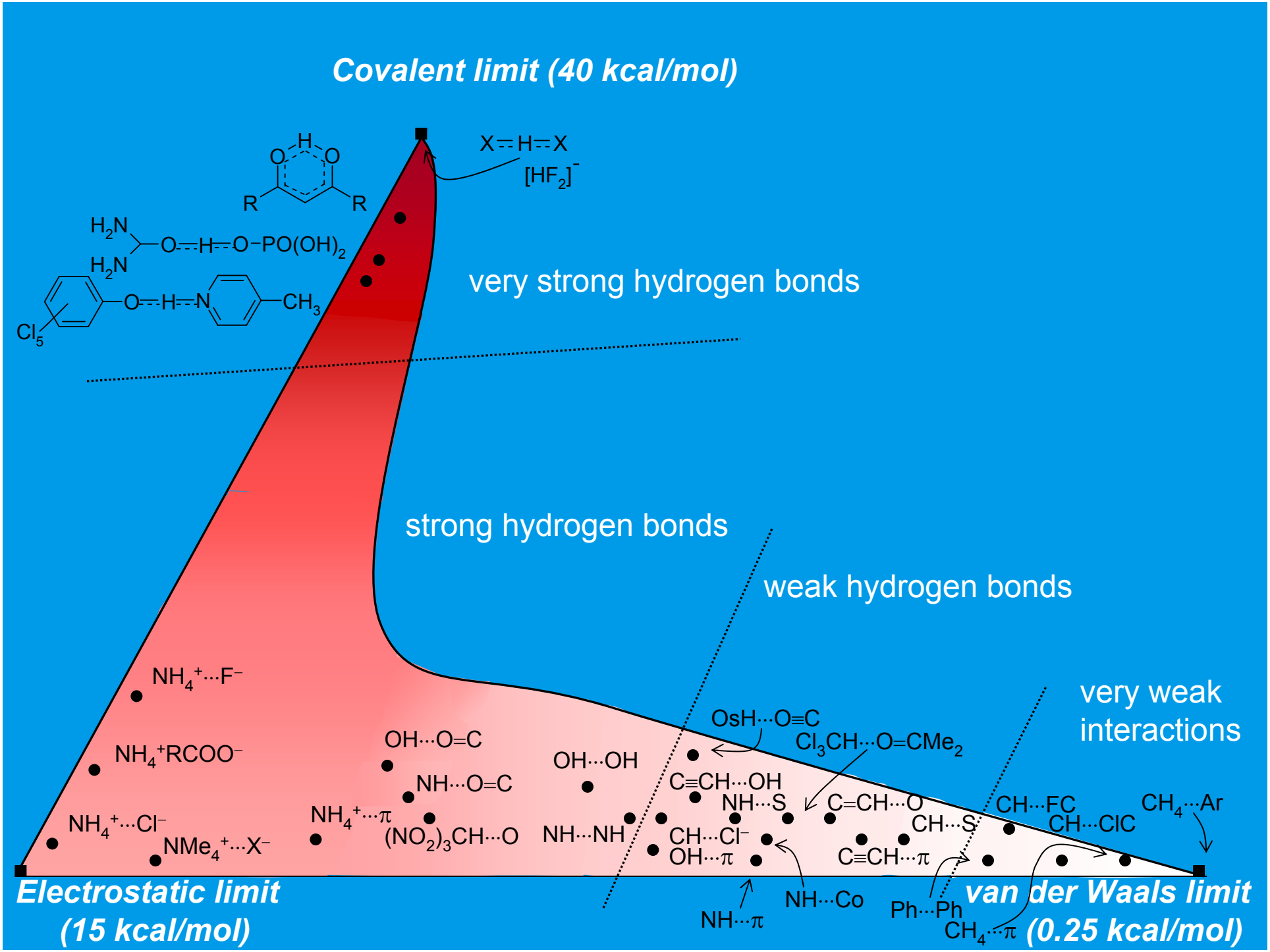
Electrostatics

Charge transfer
(covalency)

Dispersion/repulsion
(van der Waals)

Polarisation

A composite interaction


Covalent limit (40 kcal/mol)
X···H···X
[HF2]-
very strong hydrogen bonds
strong hydrogen bonds
weak hydrogen bonds
very weak interactions
NH4+···F−
NH4+RCOO−
NH4+···Cl−
NMe4+···X−
OH···O=C
NH···O=C
NH4+···π
(NO2)3CH···O
OH···OH
NH···NH
OsH···O≡C
Cl3CH···O=CMe2
C≡CH···OH
NH···S
CH···Cl−
OH···π
NH···π
C=CH···O
C≡CH···π
NH···Co
CH···S
Ph···Ph
CH4···π
CH···FC
CH···ClC
CH4···Ar
Electrostatic limit
(15 kcal/mol)
van der Waals limit (0.25 kcal/mol)

Hydrogen bond

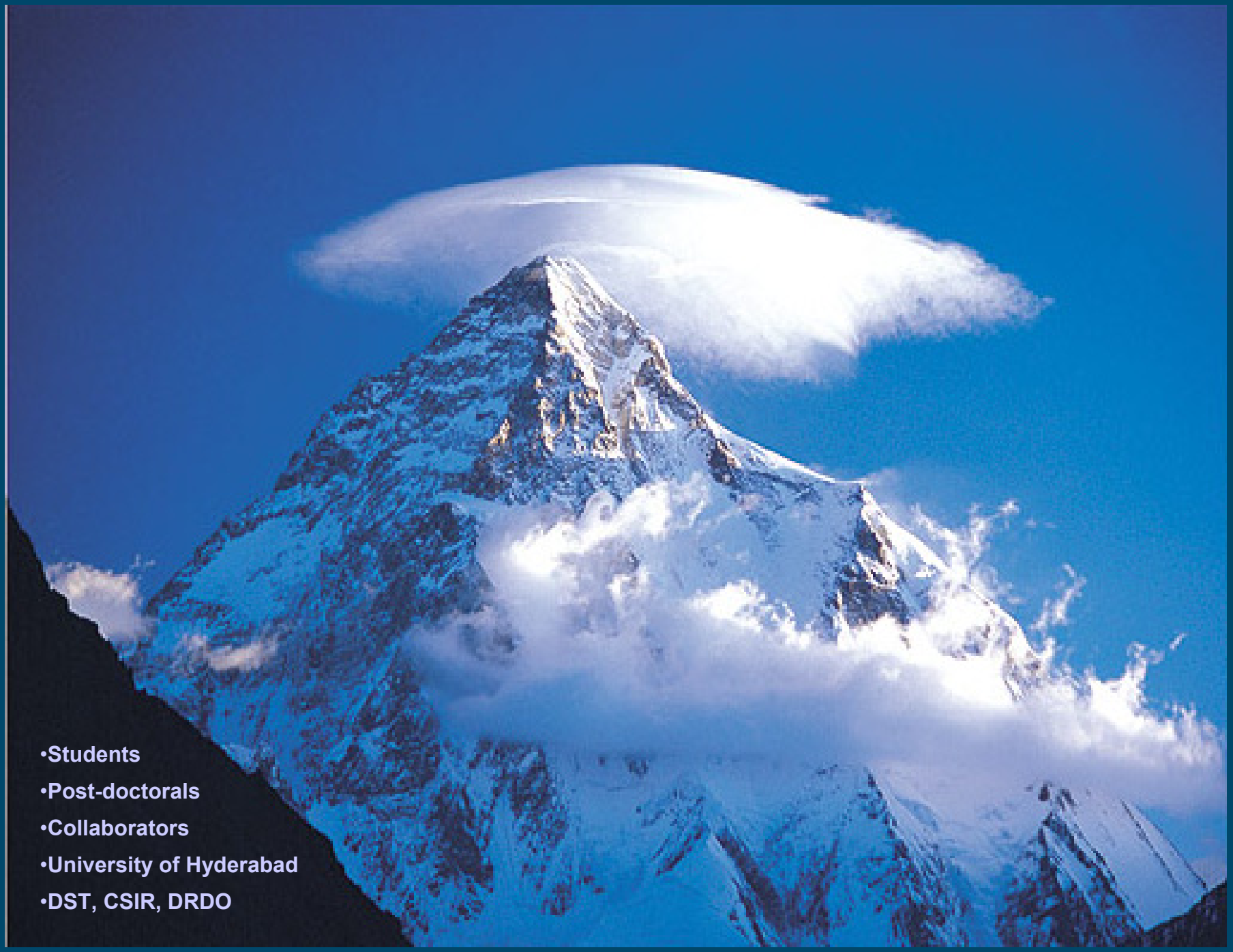
D—H·····A

A composite interaction that spans wide ranges of geometry and energy

Great chemical variations among the donor **D—H** and acceptor **A** groups

However, all hydrogen bonds have several features in common

Notably, their effect on crystal structure and packing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•Collaborators
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•DST, CSIR, DRDO