

**Solid and gas-phase structures:  
the whole is more than the sum of its parts**

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# Phase dependence of molecular structures

## Methods:

	gas phase (GED, MW)	solid state (XRD, NRD)
conditions	volatile compounds	crystalline solids
accuracy	better for smaller molecules	almost size independent
comparability with theory	good	limited
effort to be spent	relatively high (analysis)	standard cases quick sometimes tricky
further possibilities	conformational analysis ...	charge density ...

# Overview: Gas versus solid state

**a) Aggregates**

**b) Weak bonds**

**c) Conformations**

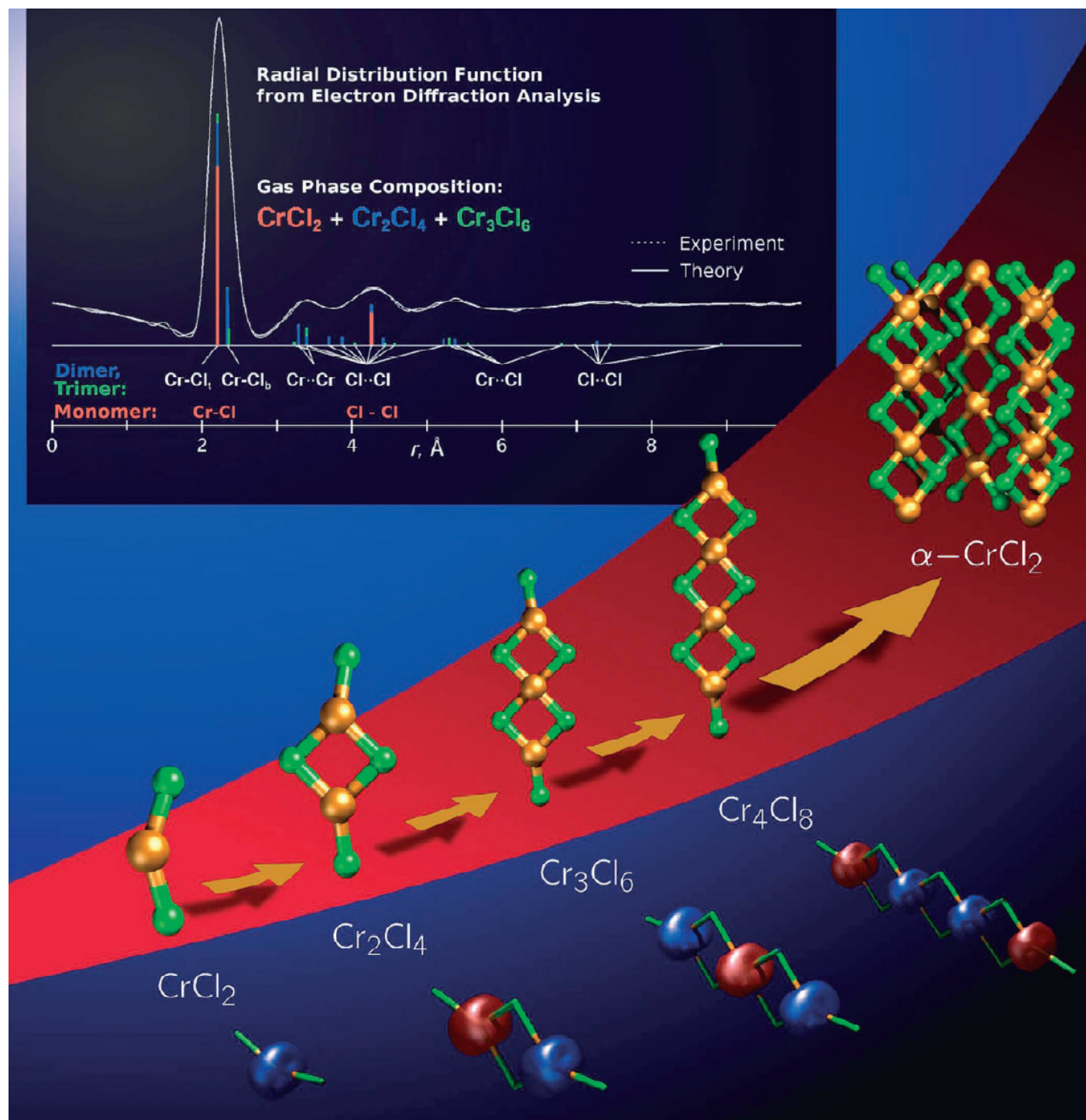
**d) Dative bonds**

**e) Coordinative bonds**

# Gas versus solid - aggregates

## Gas-Phase Structure of $\text{CrCl}_2$ : Stepwise aggregation

B. Vest, Z. Varga, M.  
Hargittai, A. Hermann,  
P. Schwerdtfeger,  
*Chem. Eur. J.*  
2008, 14, 5130





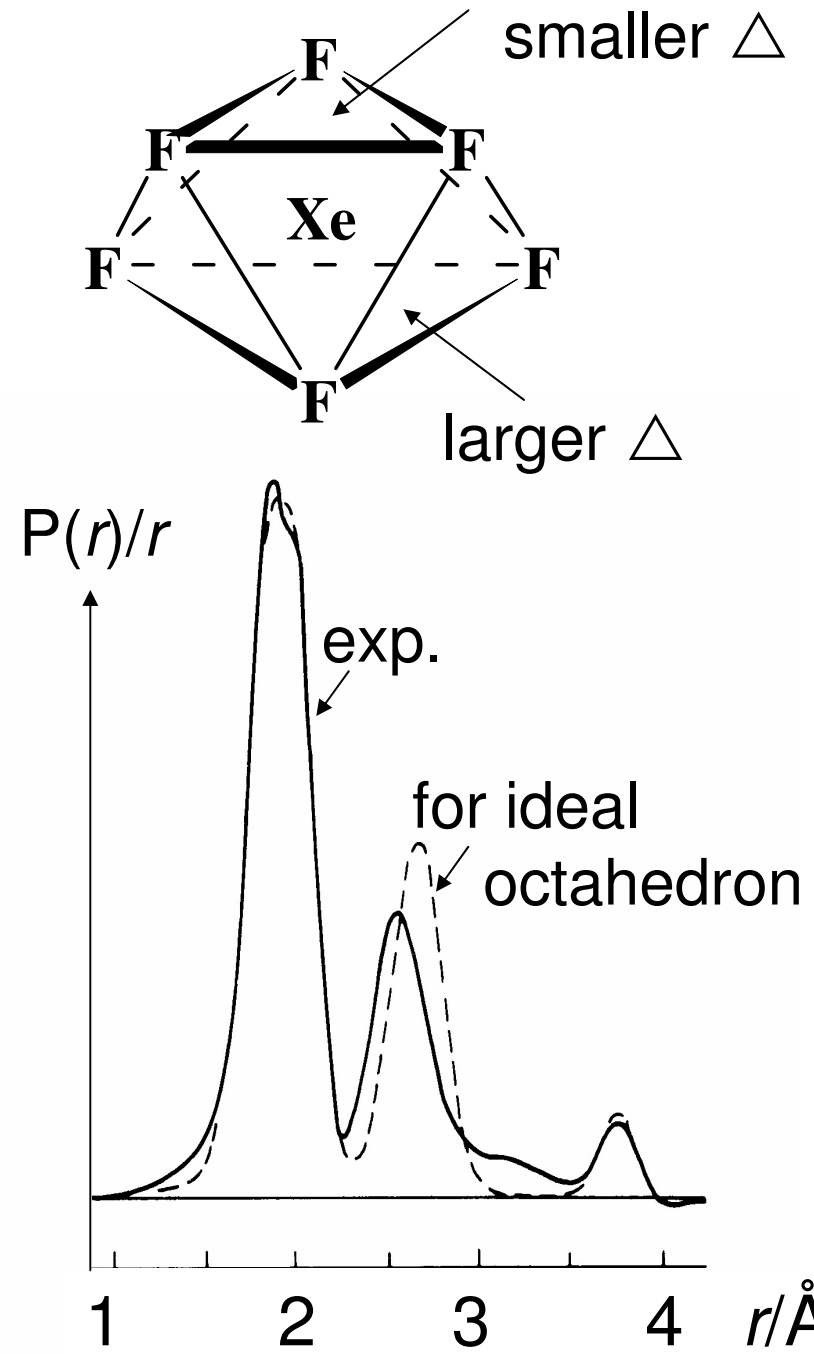
## XeF<sub>6</sub> – Gas phase

### Electron diffraction (GED):

- $C_{3v}$
- distorted octahedron

compare:

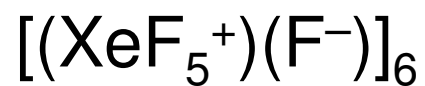
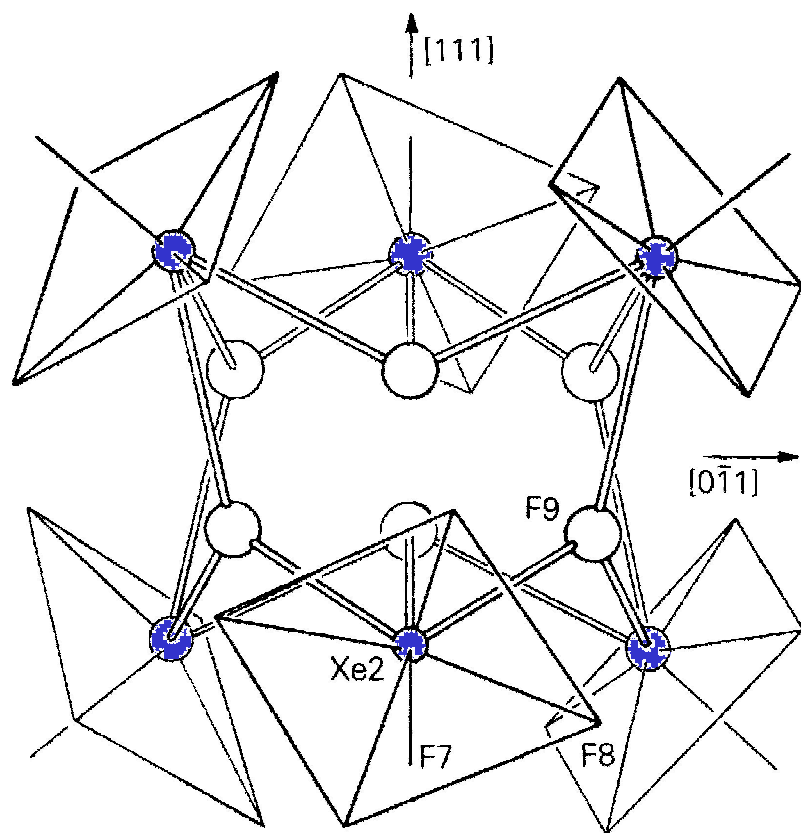
TeCl<sub>6</sub><sup>2-</sup>: regular octahedron  
(stereochemically inactive  
lone pair)



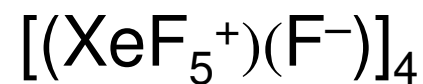
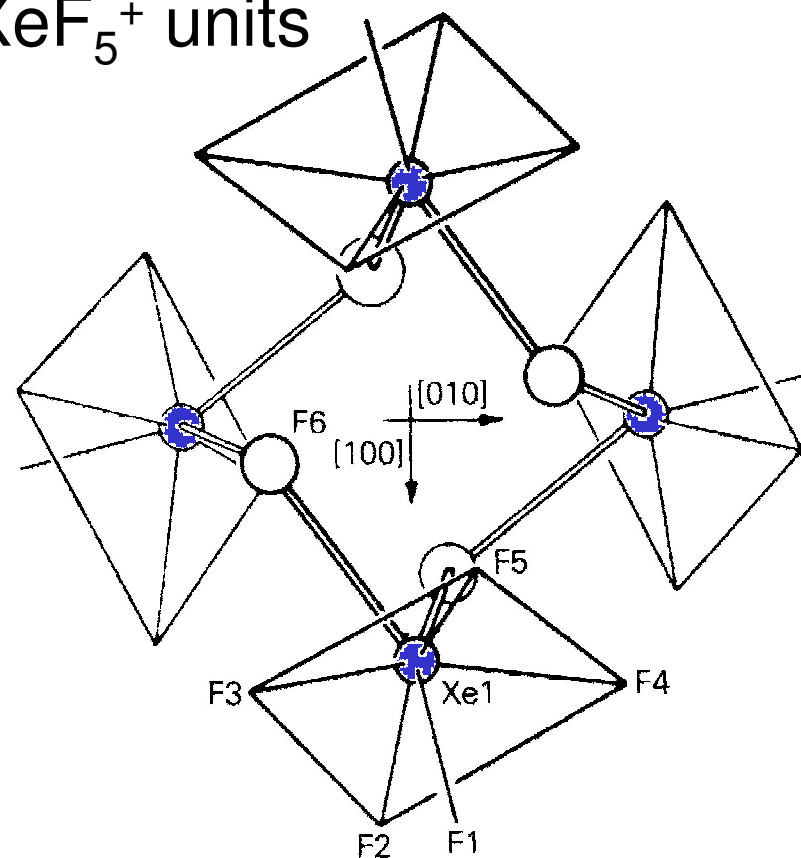
# $(\text{XeF}_6)_x$ – Single crystal X-ray diffraction (XRD)

F<sup>-</sup>-connected

$\text{XeF}_5^+$  units

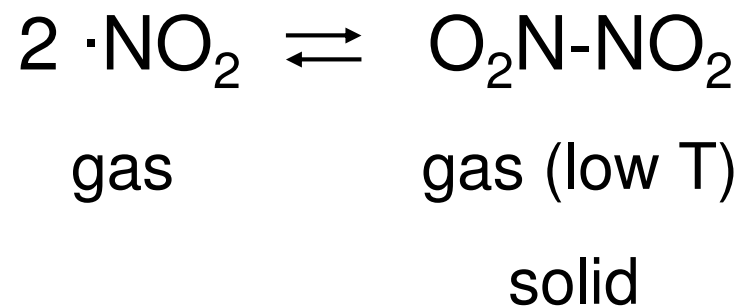
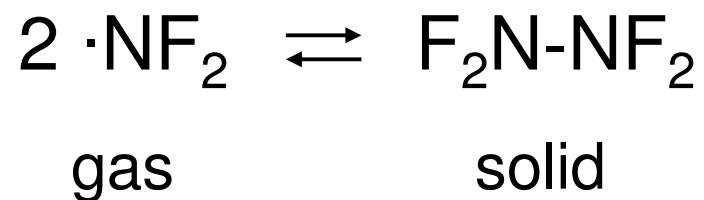


CN = 8



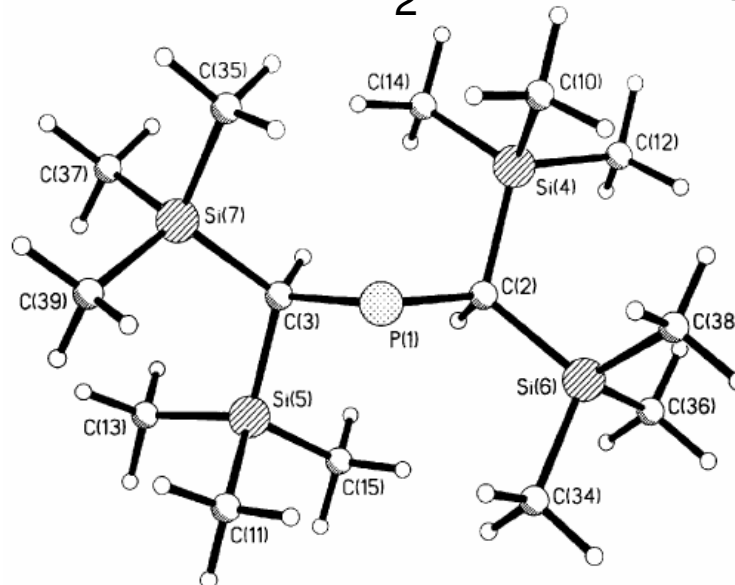
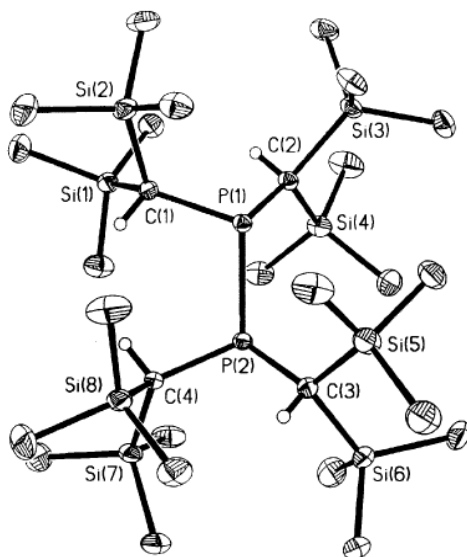
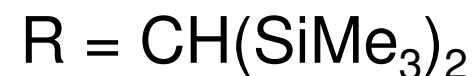
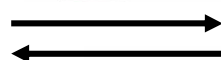
CN = 7

## Gas versus solid - weak bonds



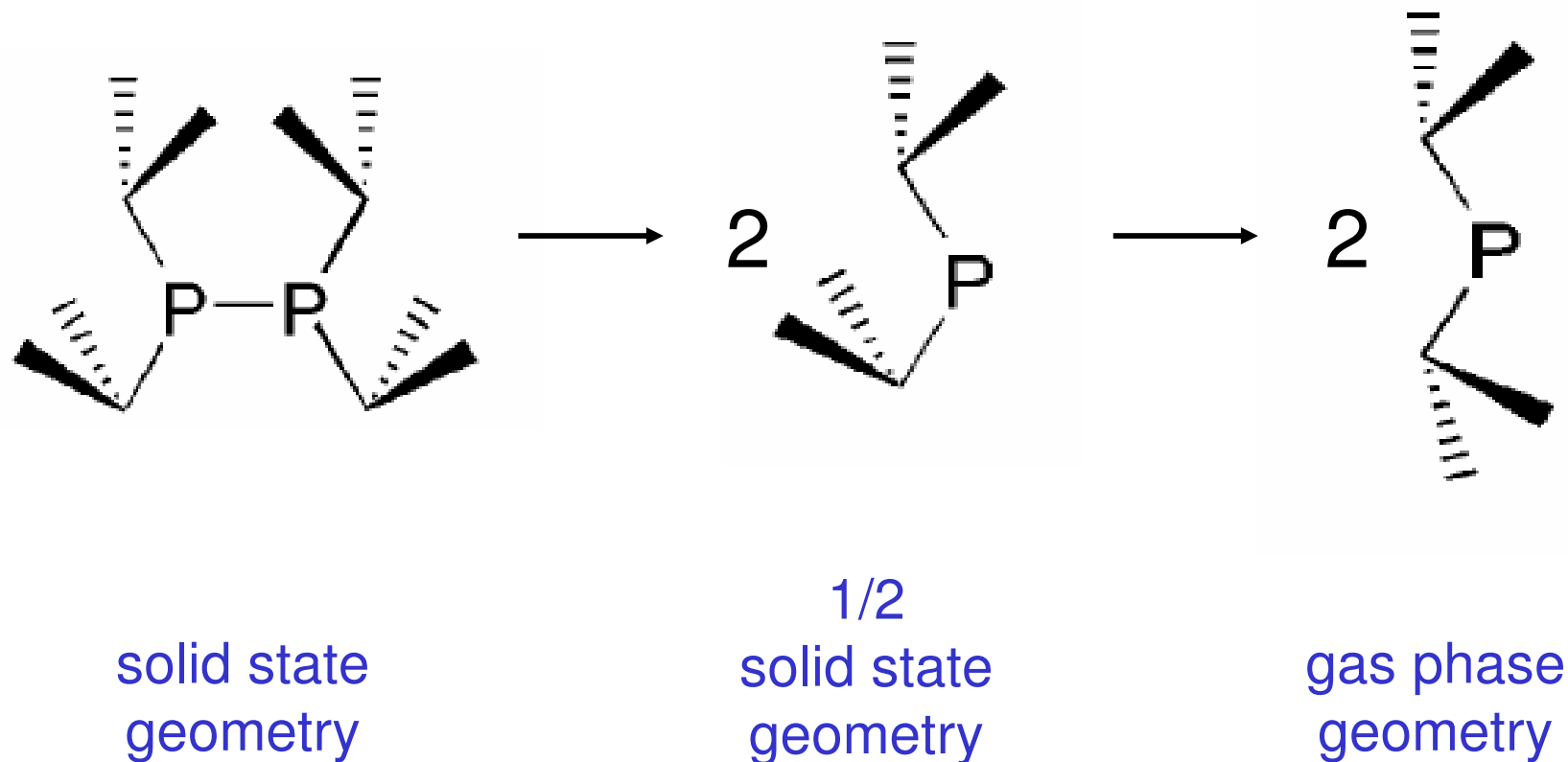
# Persistent phosphinyl radicals from a bulky diphosphine: a molecular jack-in-the-box

P–P 2.310(1) Å



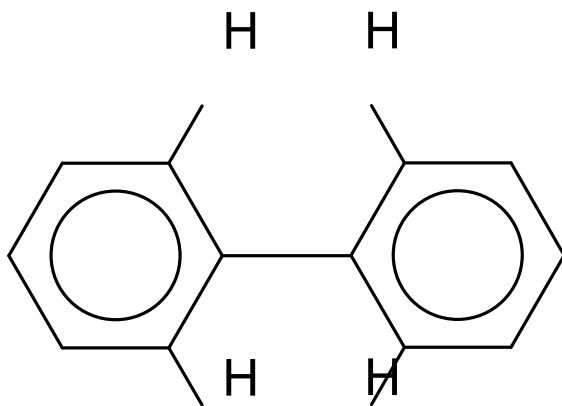
	solid state	gas phase
P–C	1.893(2)-1.896(2)	1.856(9) Å
C–P–C	103.6(1)-107.9(1)	103.9(10)°

## Phosphinyl radicals from a bulky diphosphine

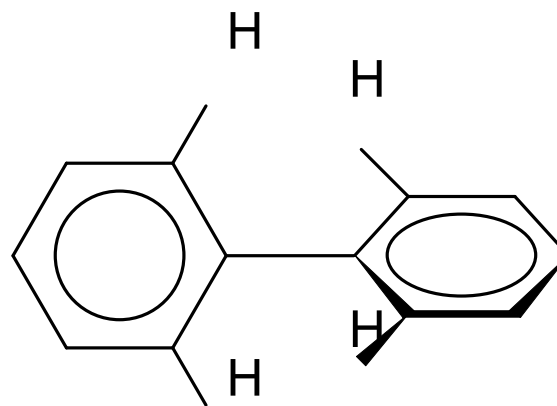


S. L. Hinchley, C. A. Morrison,  
D. W. H. Rankin, C. L. B. Macdonald, R. J. Wiacek, A. H. Cowley, M. F. Lappert,  
G. Gundersen, J. A. C. Clyburnee, P. P. Power, *Chem. Commun.* **2000**, 2045

## Gas versus solid – conformations



solid  
torsion = 0°



gas  
torsion = 44.4°

# Oxalyl chloride and bromide – solid state

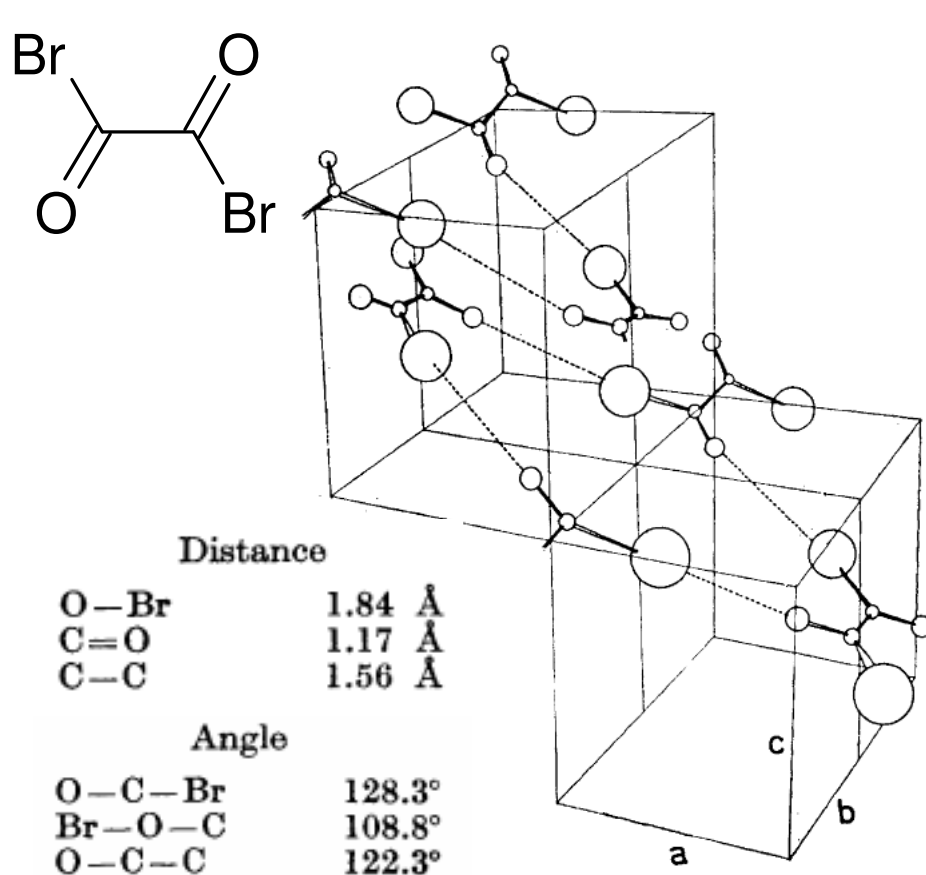


Fig. 2 a. Drawing of the oxalyl bromide structure.

O···Br: 3.27 Å

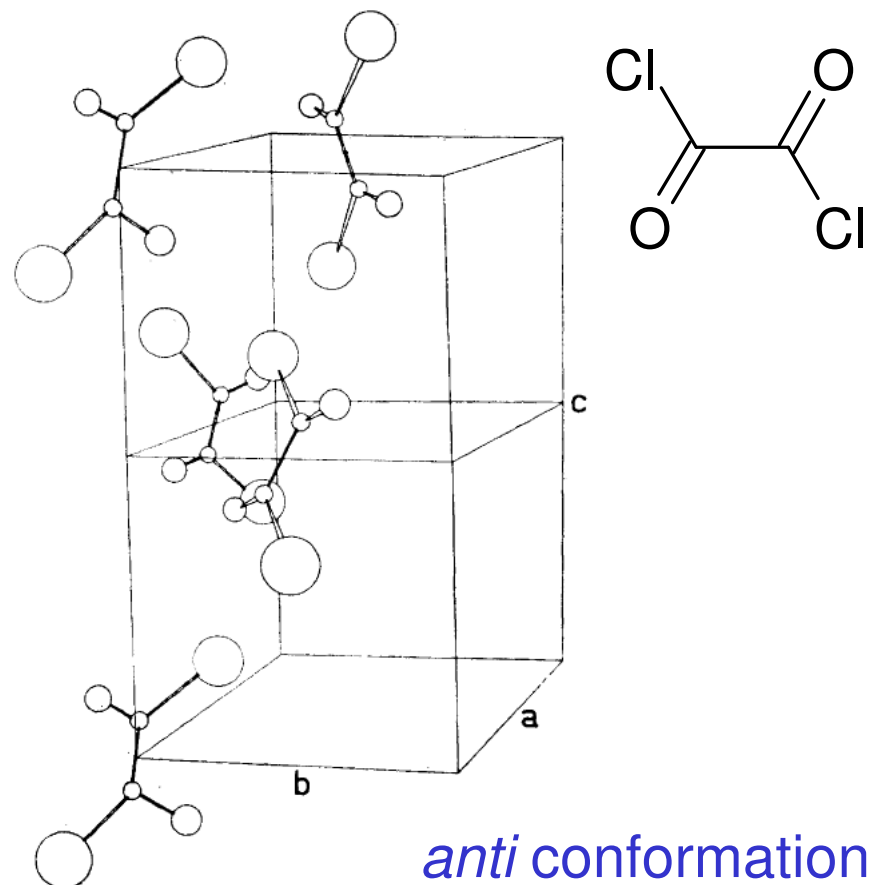
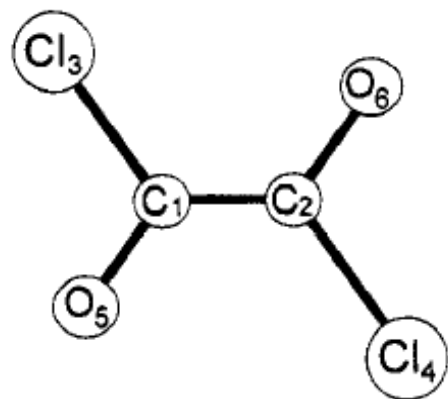
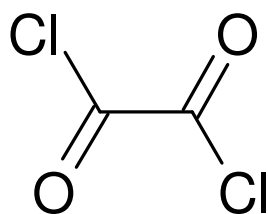


Fig. 2 b. Drawing of the oxalyl chloride structure.

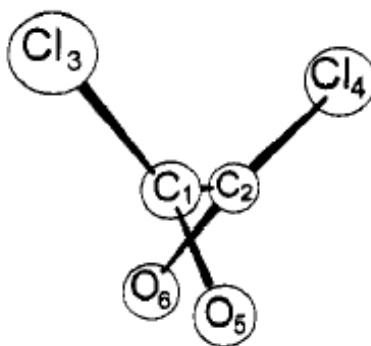
O···Cl: 3.50 Å



# Oxalyl chloride - gas phase



anti



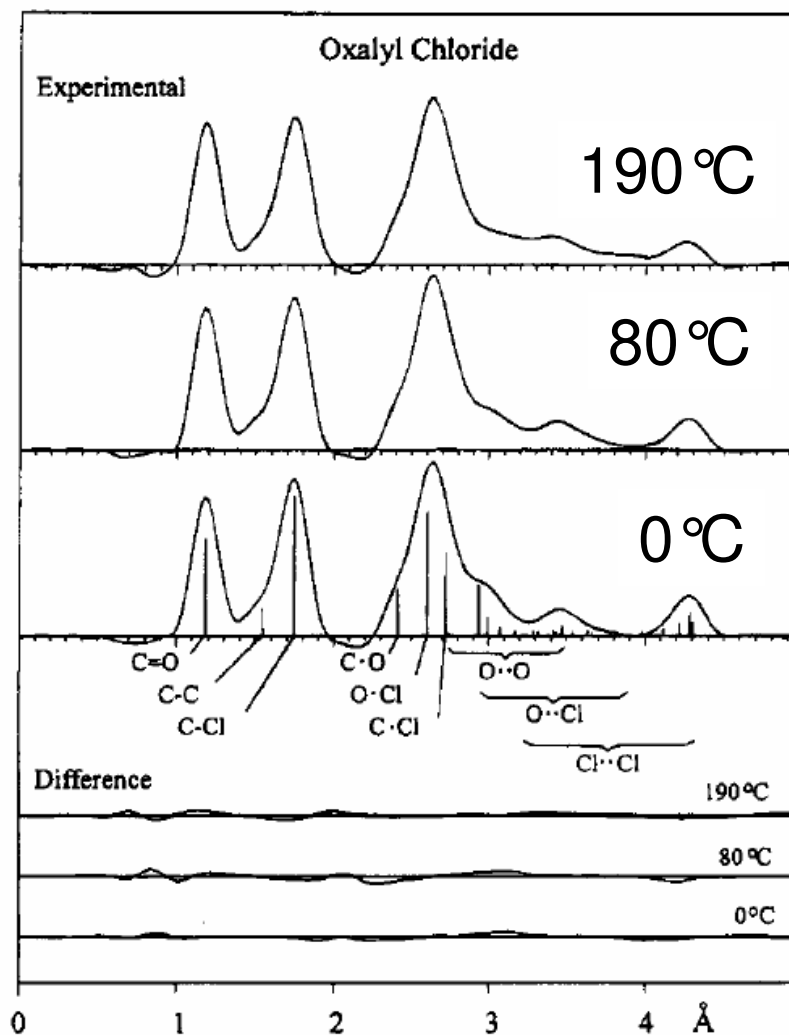
gauche

*anti*

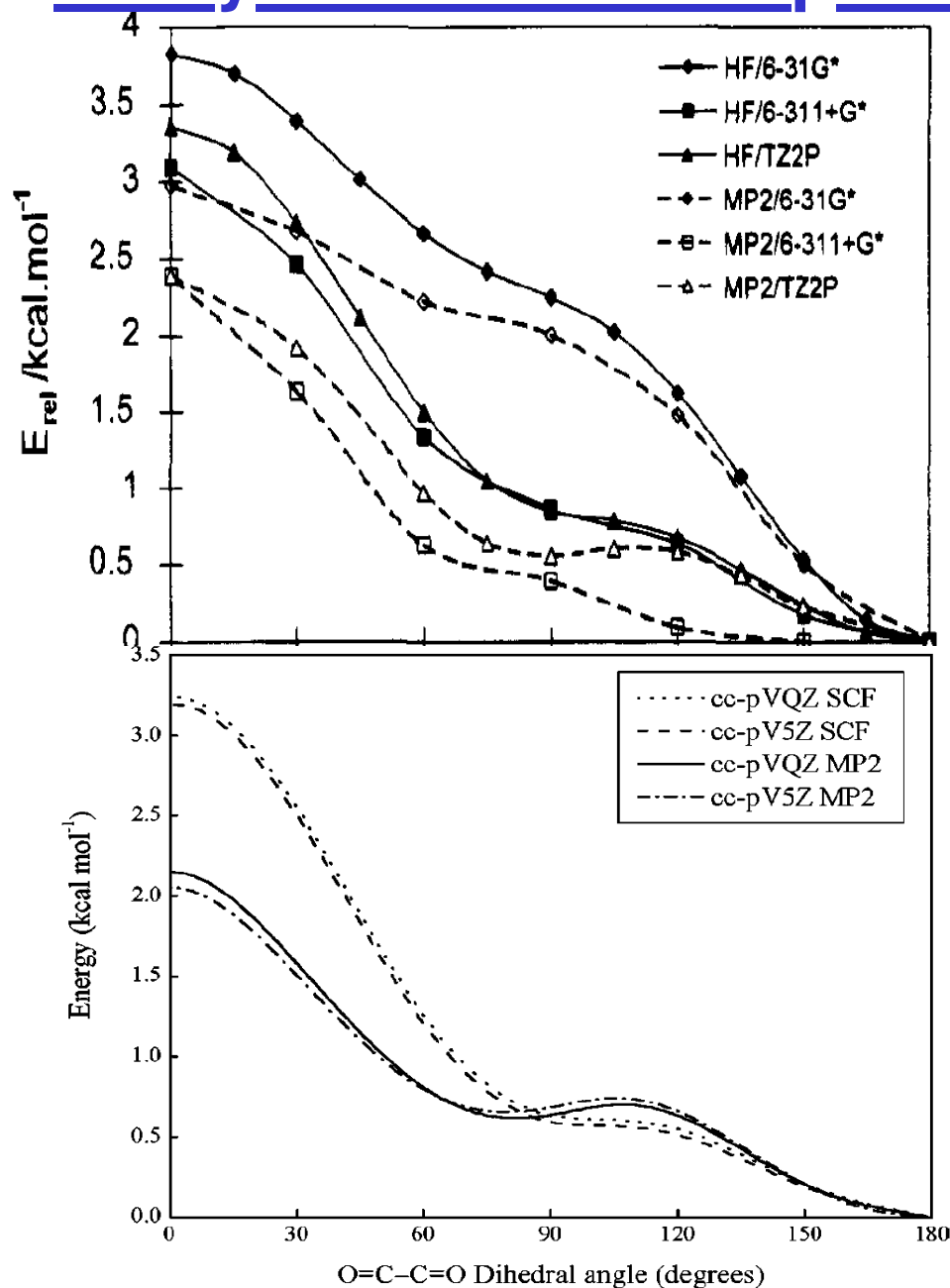
43 %

62 %

67 %

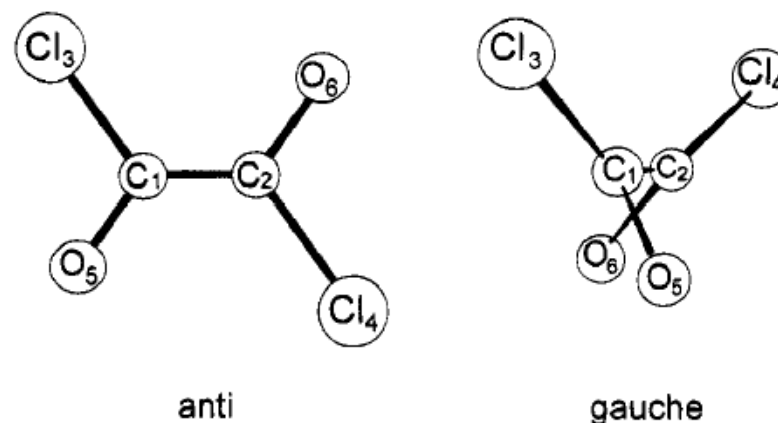


# Oxalyl chloride: Gas phase and theory



< D. D. Danielson, L. Hedberg, K. Hedberg,  
K. Hagen, M. Traetteberg,  
*J. Phys. Chem.* 1995, 99, 9374

GED:  
0.75(50) kcal/mol



IR:  
0.83(32) kcal/mol

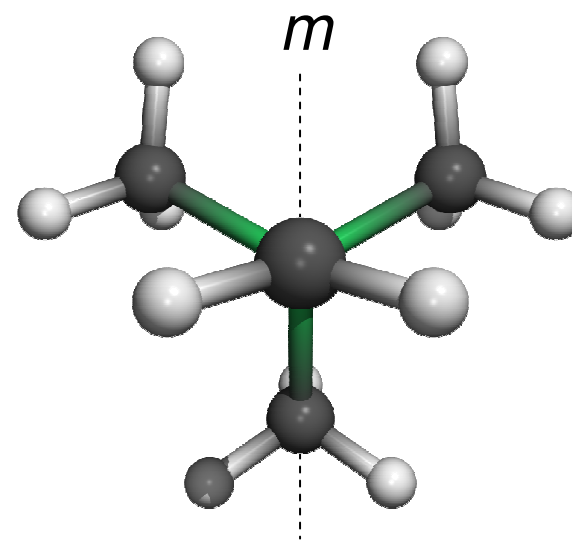
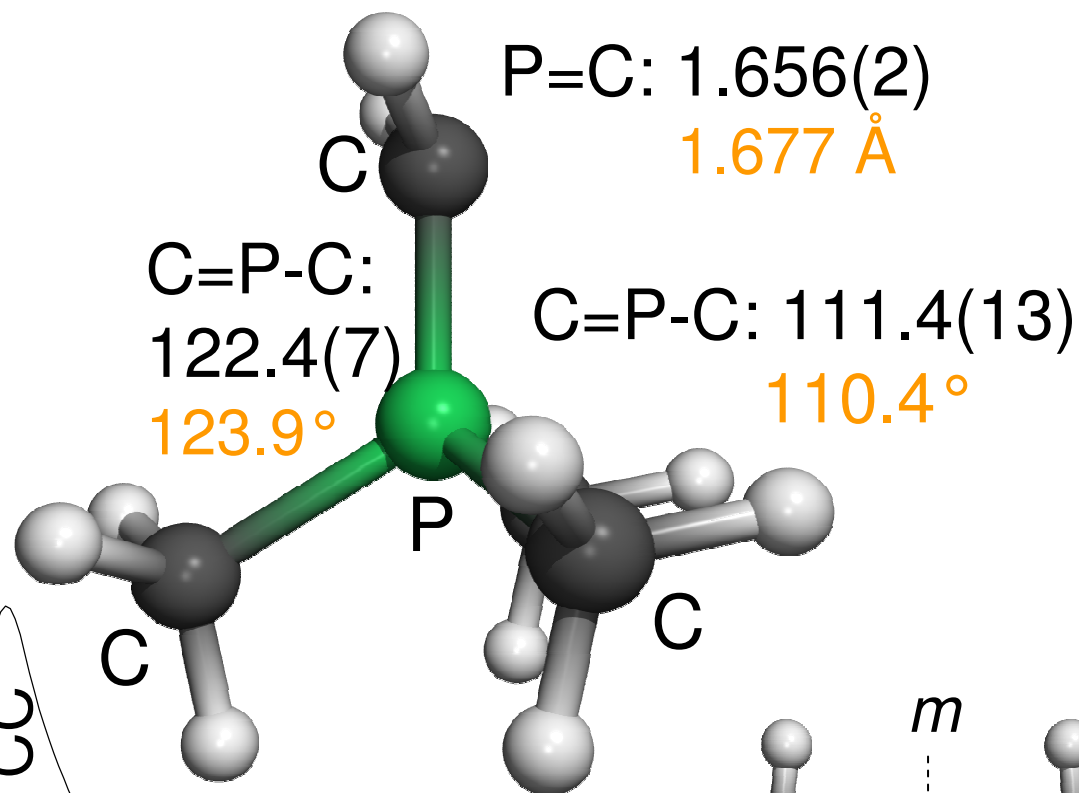
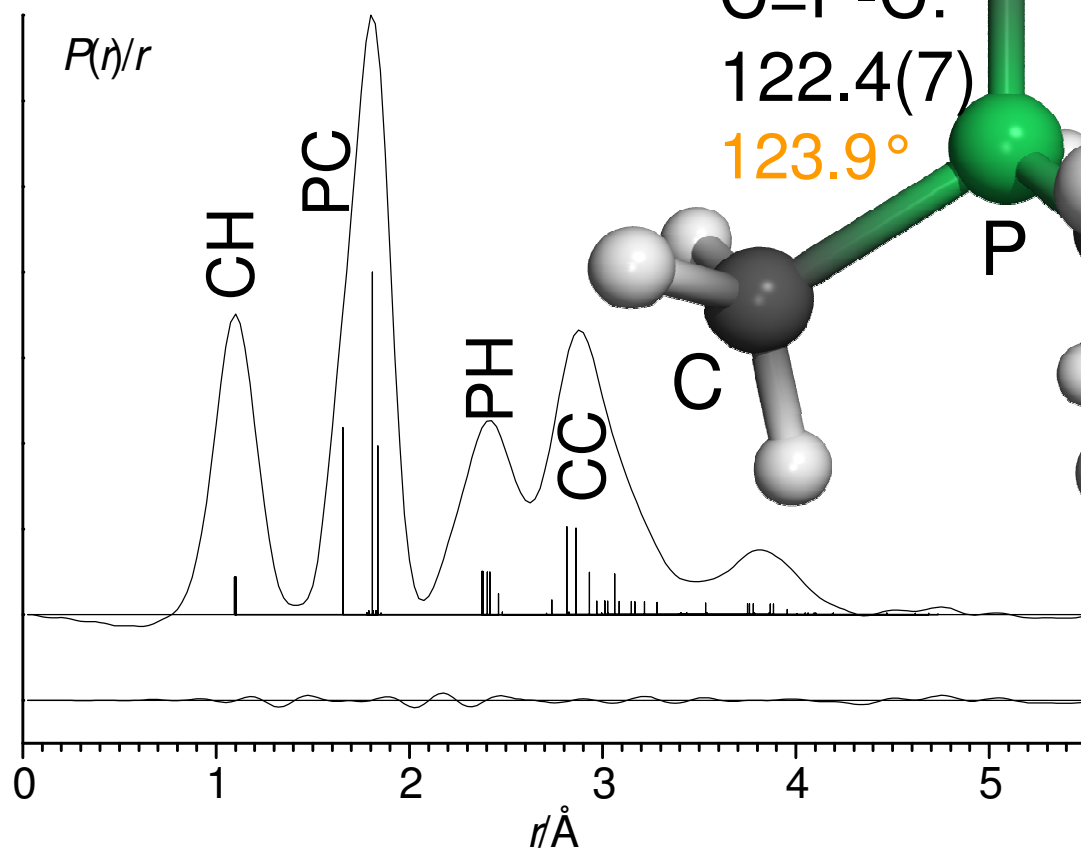
^J. R. Durig, J. F. Davis, A. Wang,  
*J. Mol. Struct.* 1996, 375, 67

< S. Kim, S. E. Wheeler, N. J. DeYonker,  
H. F. Schaefer,  
*J. Chem. Phys.* 2005, 122, 234313

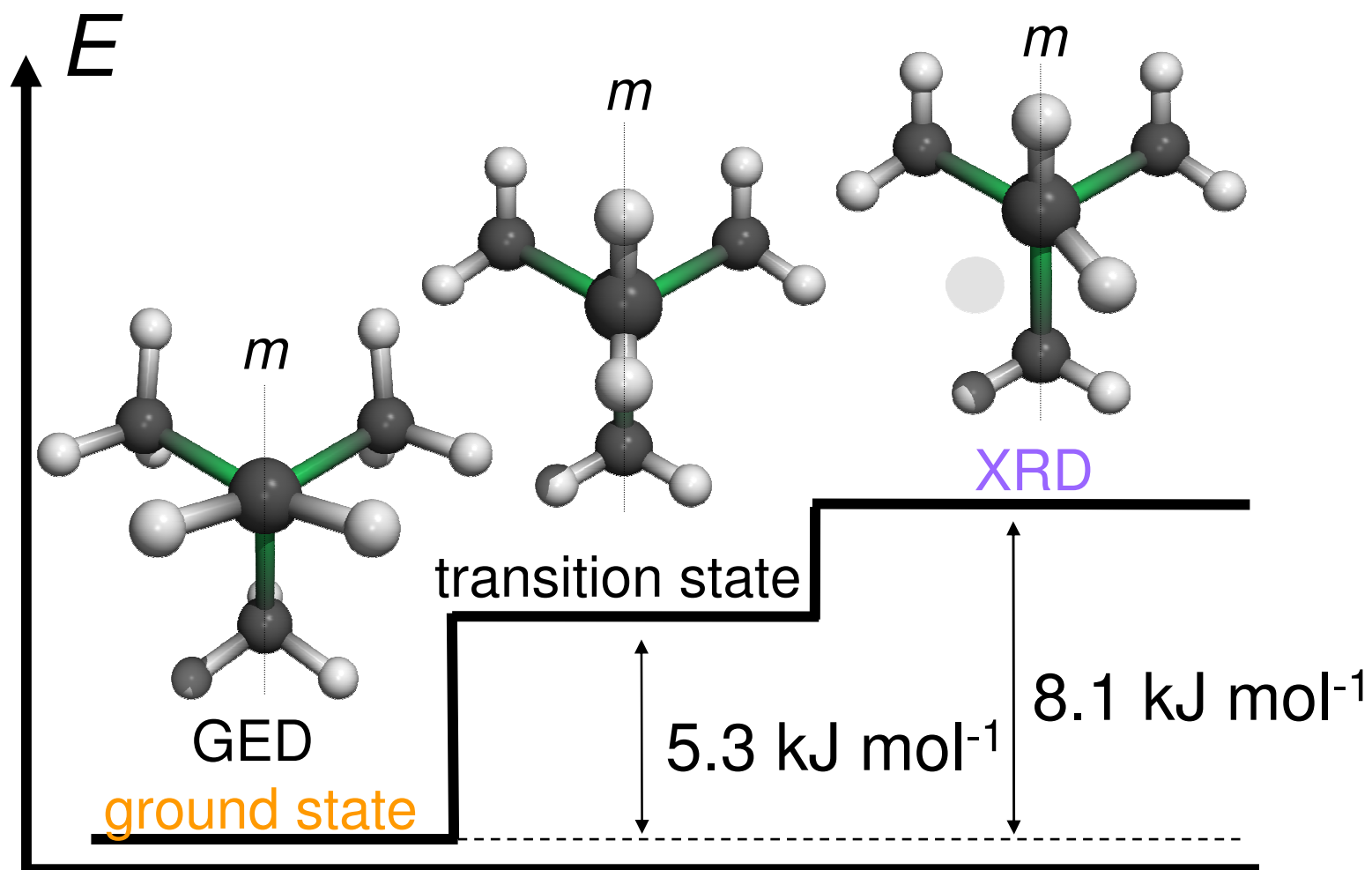
# Me<sub>3</sub>P=CH<sub>2</sub> in the gas phase

GED /

MP2/6-311G\*\*

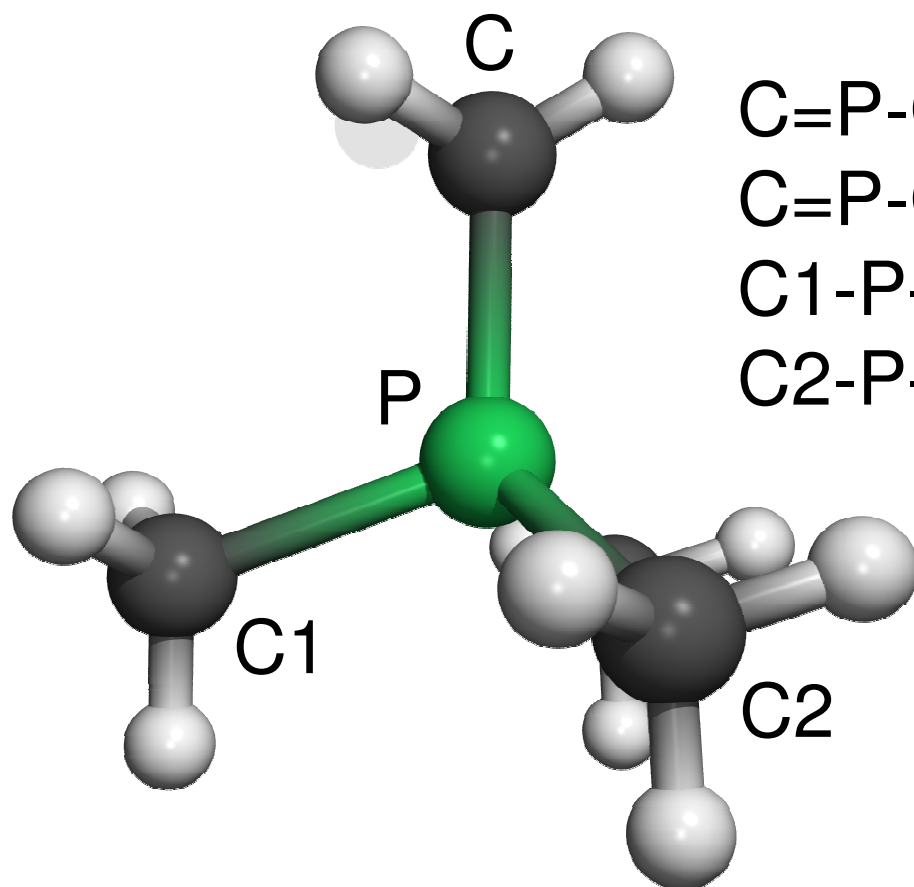


## Me<sub>3</sub>P=CH<sub>2</sub> in different phases



## Me<sub>3</sub>P=CH<sub>2</sub> - solid state geometry

The molecular solid-state geometry is close to that of the calculated transition state of rotation of the CH<sub>2</sub> unit about the P=C bond.



C=P-C1  
C=P-C2  
C1-P-C2  
C2-P-C2'

XRD

110.6(2)°  
115.6(1)°  
105.6(1)°  
102.9(2)°

TS

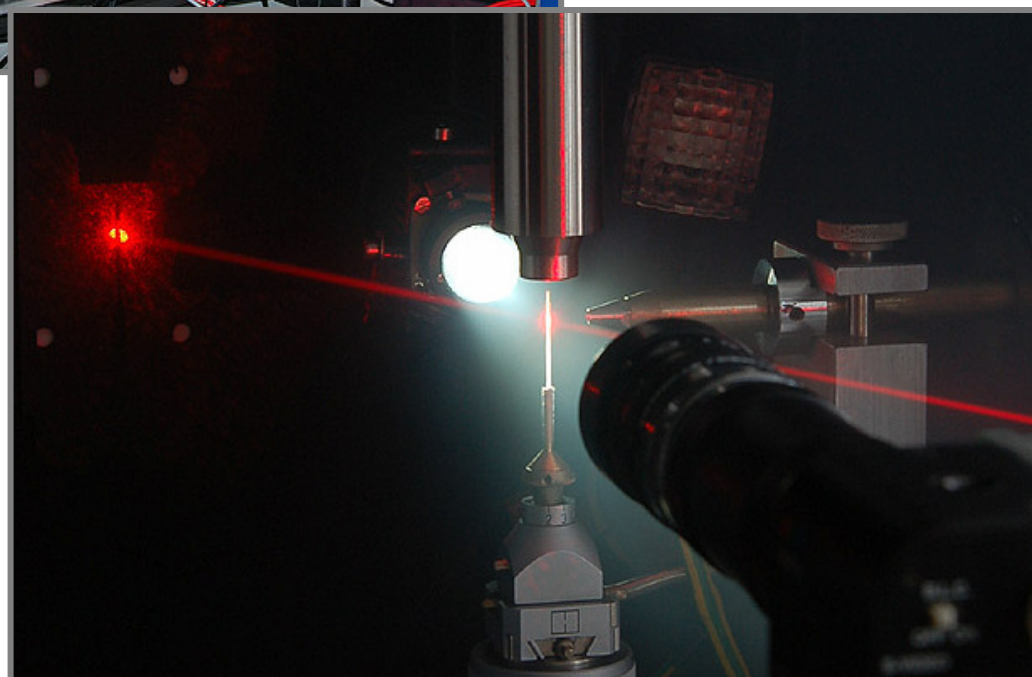
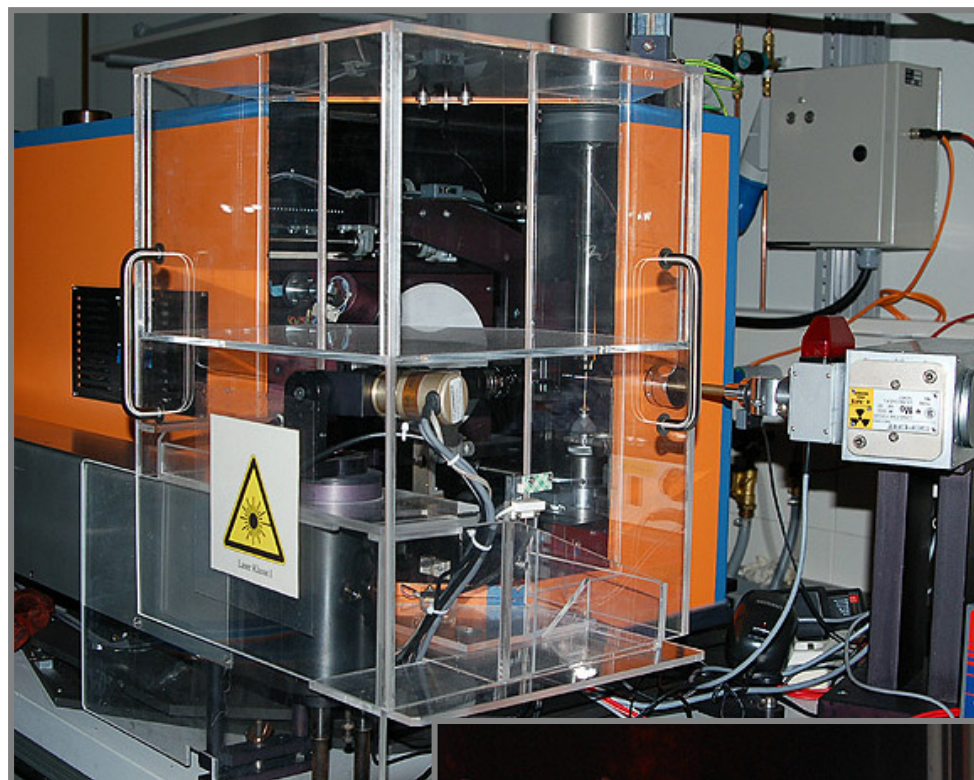
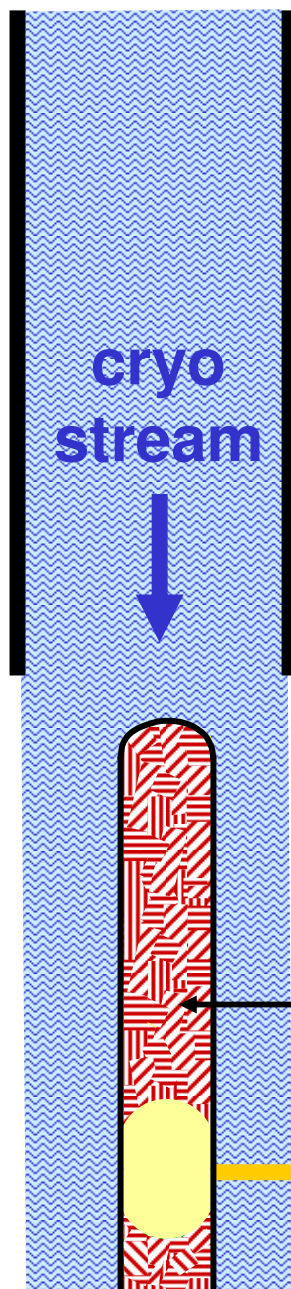
MP2/6-311G\*\*

110.3°  
117.5°  
104.8°  
100.5°

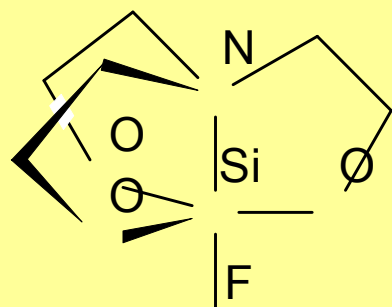
compare gas:  
C=P-C:  
122.4(7)°

# In situ crystallisation

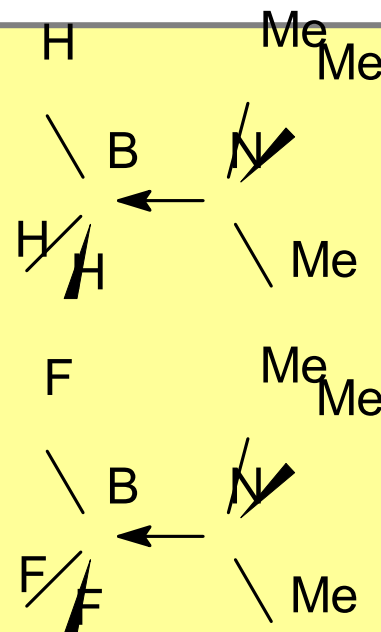
## OHCD Optical Heating Crystallisation Device



## Gas versus solid – dative bonds



$r(\text{Si-N}) / \text{\AA}$   
solid 2.042(1)  
gas 2.324(14)

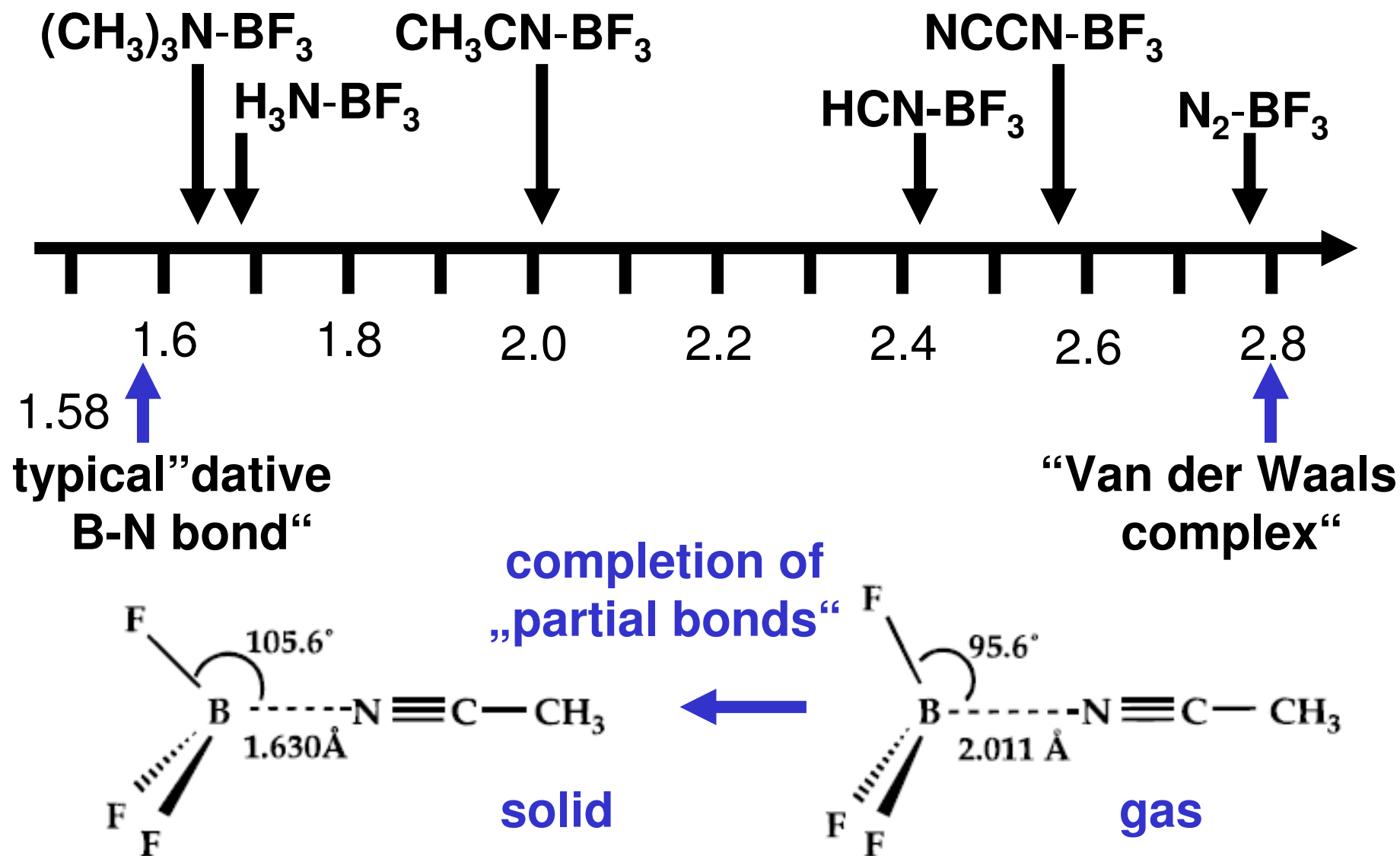


$r(\text{B-N}) / \text{\AA}$   
solid gas  
1.564 1.672

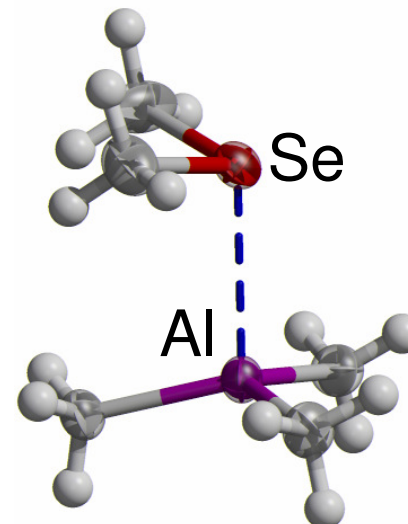
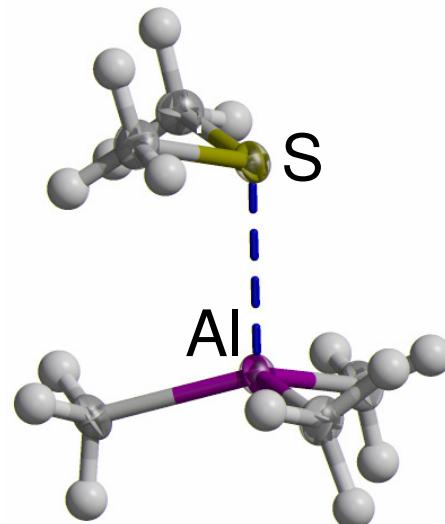
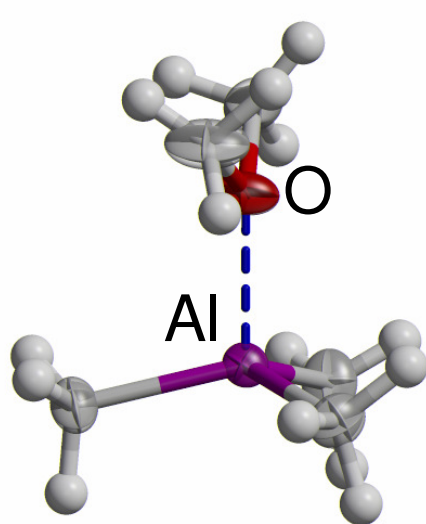
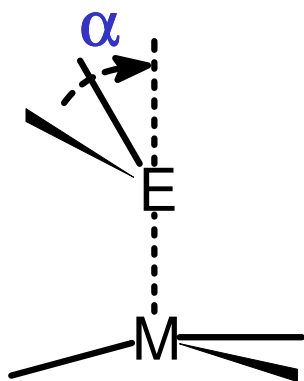
1.58 1.669



## Gas-phase values for B-N interactions of BF<sub>3</sub>



# Me<sub>2</sub>E-AlMe<sub>3</sub>-Adducts



**Al-E**  
[Å]

**1.940(2)**  
*2.014(14)<sup>a</sup>*

**2.461(av)**  
*2.55(2)<sup>b</sup>*

**2.605(av)**

**α**

**12.5(1)°**  
*5.1(43)°<sup>a</sup>*

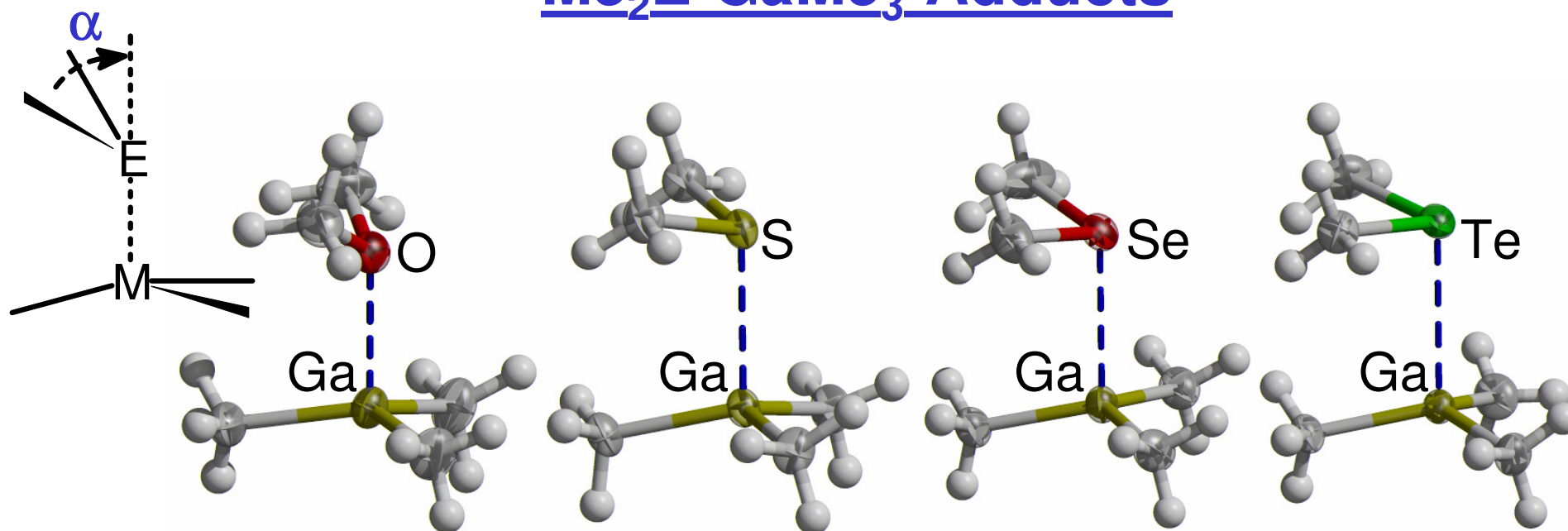
**69.2(av)°**  
*31(5)°<sup>b</sup>*

**73.6(av)°**

*GED: a) Haaland, Samdal, Stokkeland, Weidlein, 1977*

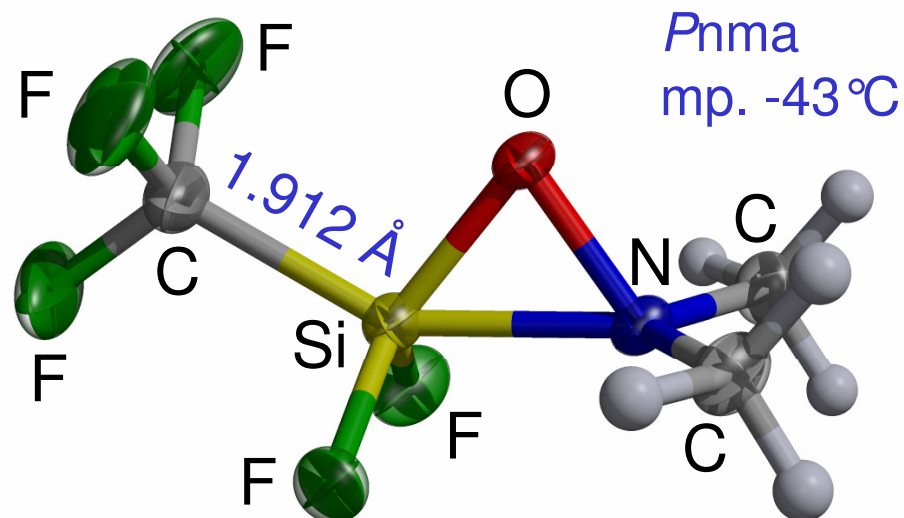
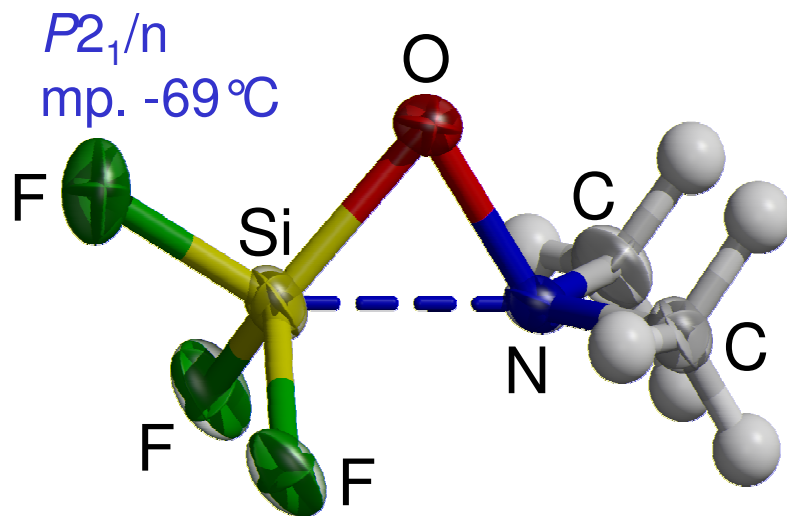
*b) Fernholt, Haaland, Hargittai, Seip, Weidlein, 1981*

## Me<sub>2</sub>E-GaMe<sub>3</sub>-Adducts



<b>Ga-E</b> [Å]	<b>2.155(2)</b> <i>2.045(21)</i>	<b>2.530(av)</b>	<b>2.654(av)</b>	<b>2.828(2)</b>
<b><math>\alpha</math></b>	<b>38.6(1)°</b> <i>7(112)°</i>	<b>69.6(av)°</b>	<b>74.0(av)°</b>	<b>79.8(2)°</b>

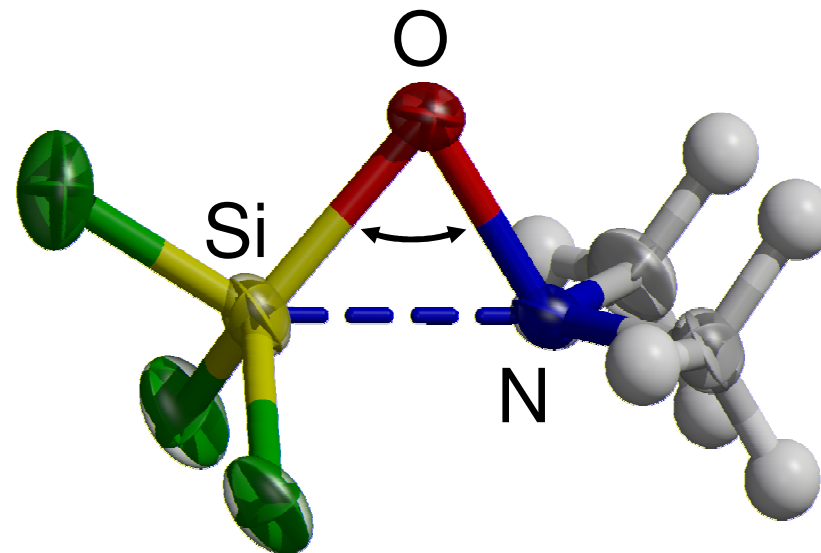
# $F_3SiONMe_2$ / $(F_3C)F_2SiONMe_2$



	Å, °	XRD solid	GED gas
$F_3SiONMe_2^a)$	$\angle SiON$ $d(Si \cdots N)$	77.1(1) 1.963(1)	94.3(9) 2.273(17)
$F_3CF_2SiONMe_2^b)$	$\angle SiON$ $d(Si \cdots N)$	74.1(1) 1.904(2)	79.4(6) 2.011(17)

## F<sub>3</sub>SiONMe<sub>2</sub> - calculations

Methode	<SiON
<b>GED</b>	<b>94.3(9)°</b>
HF/TZVPP	106.6°
MP2/6-311G**	93.8°
MP2/pVQZ	88.1°
MP2/TZVPP	86.5°
MP2/TZVP	83.6°
PBE/TZVPP	87.3°
B3LYP/TZVPP	102.5°
B3LYP/6-311++G**	105.4°
BP/TZVPP	93.1°
BP/TZVP	86.2°



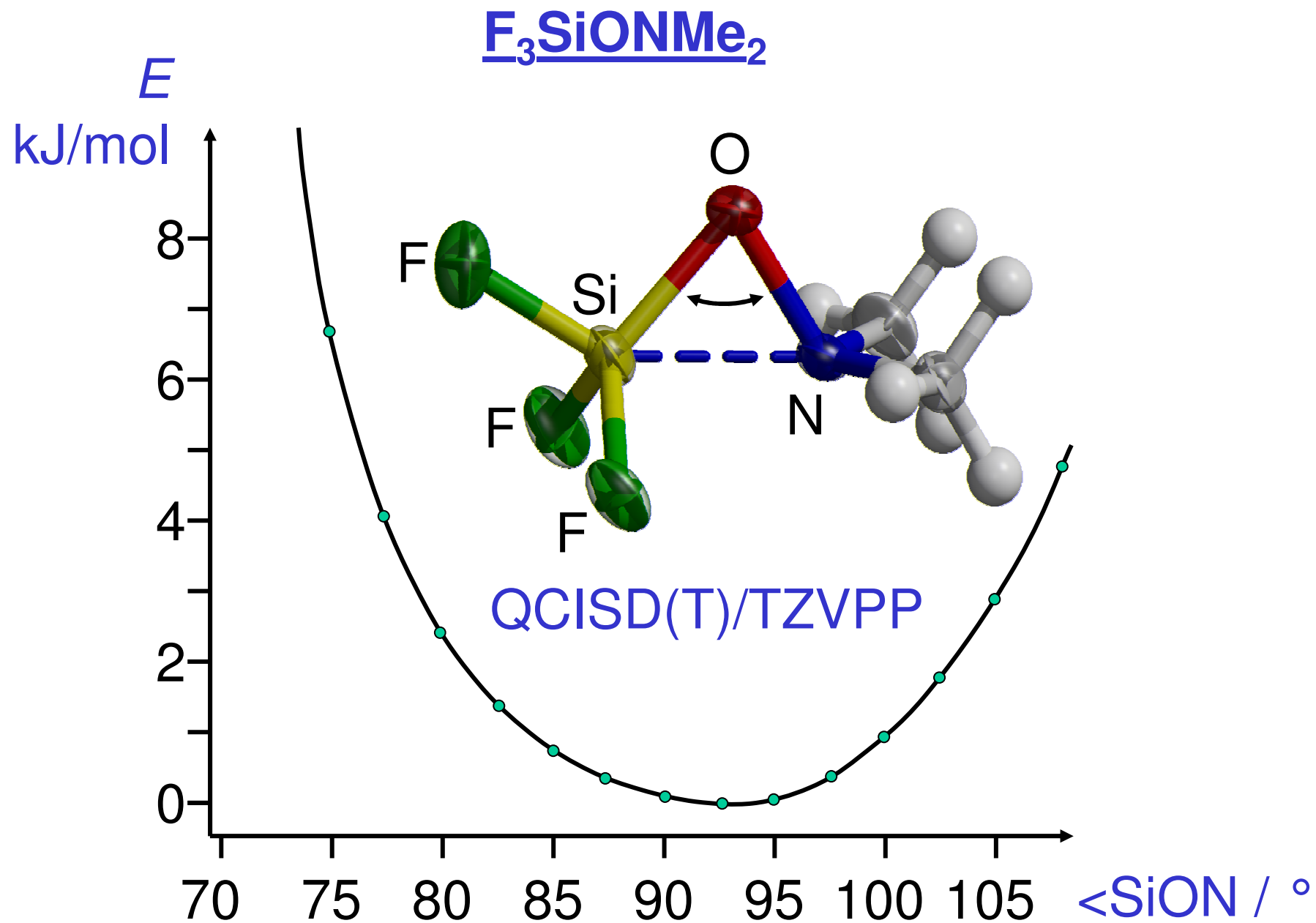


TABLE V. Results for problematic geometry parameters with common functionals, B2-PLYP and SCS-MP2. If not noted otherwise, the def2-TZVPP basis sets have been used.

Parameter	Ref.	Deviation (Expt. – Theor.)				
		PBE	TPSS	B3-LYP	B2-PLYP	SCS-MP2
( <i>N,N</i> -dimethylaminoxy)trifluorosilane: $r(\text{Ni-Si})$ (pm)	227.3 <sup>a</sup>	2.5	12.8	–17.8	–10.5	1.5 <sup>b</sup>
[Ar–NO] <sup>+</sup> : $r(\text{Ar-N})$ (pm)	299.8 <sup>c</sup>	40.0	39.0	28.7	17.4	–3.0
[2.2]metacyclophane: $r(\text{C8-C16})$ (pm)	263.3 <sup>d</sup>	0.3	1.4	–2.7	0.4	2.1 <sup>b</sup>
Lithium dimer: $r(\text{Li-Li})$ (pm)	267.3 <sup>e</sup>	–6.6	–8.5	–4.0	–4.6	–7.6
Sodium dimer: $r(\text{Na-Na})$ (pm)	307.9 <sup>e</sup>	–1.4	–8.2	2.2	1.9	–1.6
Potassium dimer: $r(\text{K-K})$ (pm)	392.2 <sup>f</sup>	–7.8	–17.2	–5.2	–3.0	–4.1
[HCN–BF <sub>3</sub> ]: $r(\text{N-B})$ (pm)	247.3 <sup>g</sup>	2.6 <sup>h</sup>	16.9 <sup>h</sup>	–8.8 <sup>h</sup>	0.1 <sup>h</sup>	5.4 <sup>h</sup>
Styrene: $\theta(\text{C2C1C7C8})$ (deg)	28.0 <sup>i</sup>	26.1	26.2	25.9	23.0	12.6

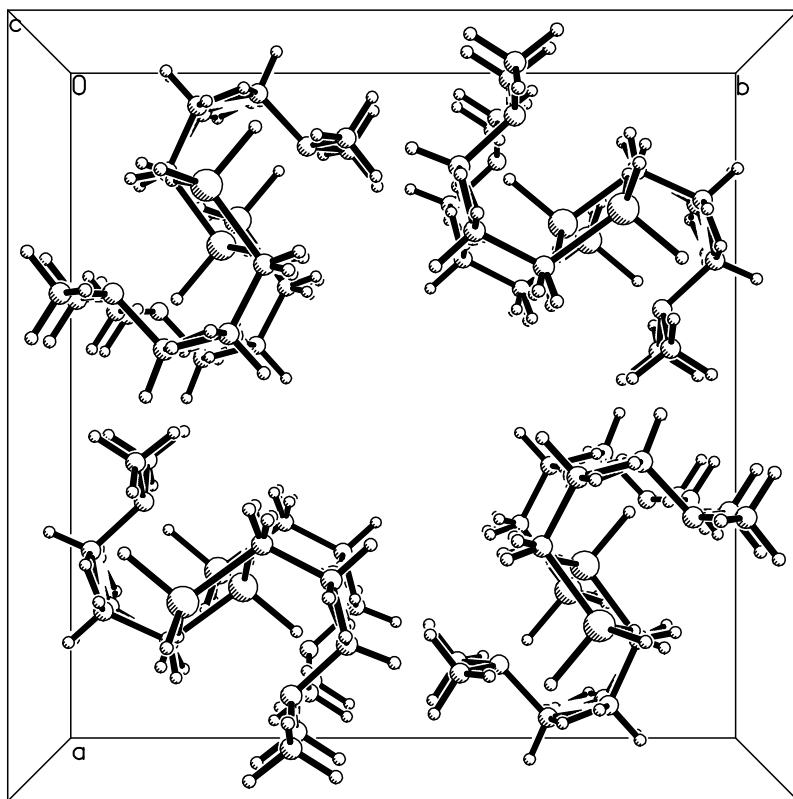
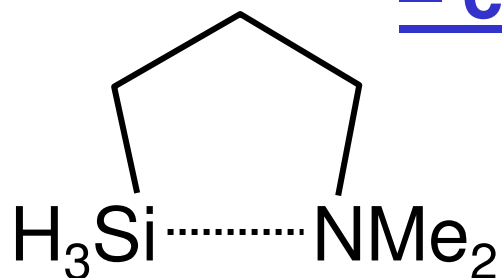
<sup>a</sup>Experimental data taken from Ref. 54.

<sup>b</sup>cc-pVTZ basis taken from Ref. Ref. 42.

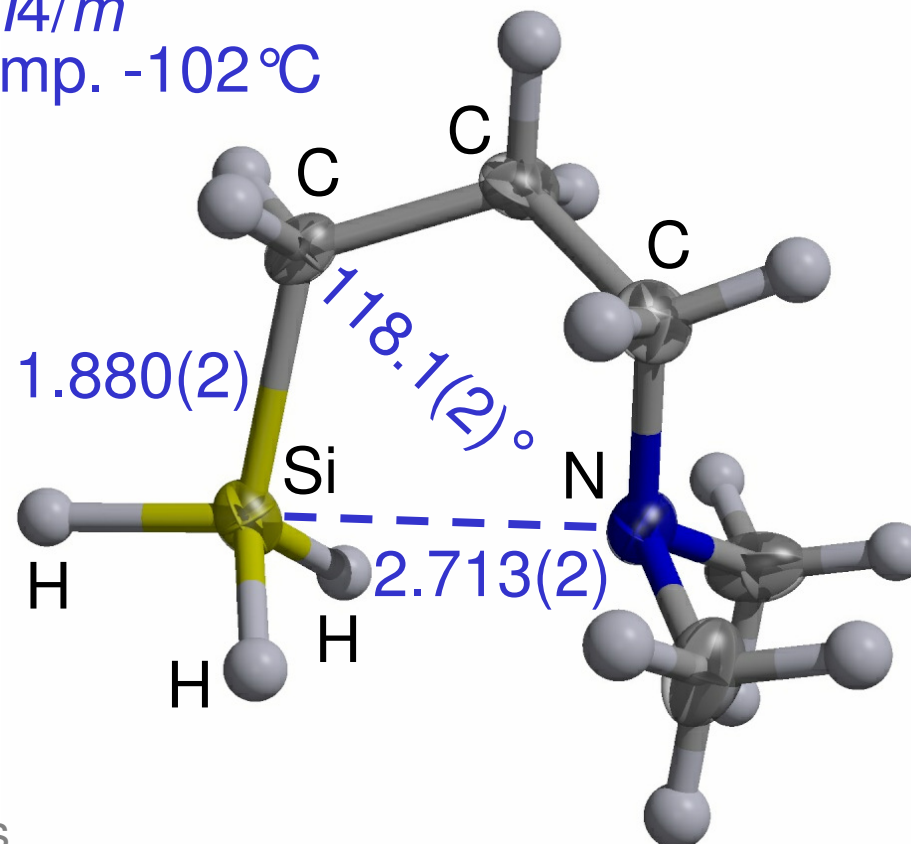


# $\text{H}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ – crystal structure

Michael  
Hagemann

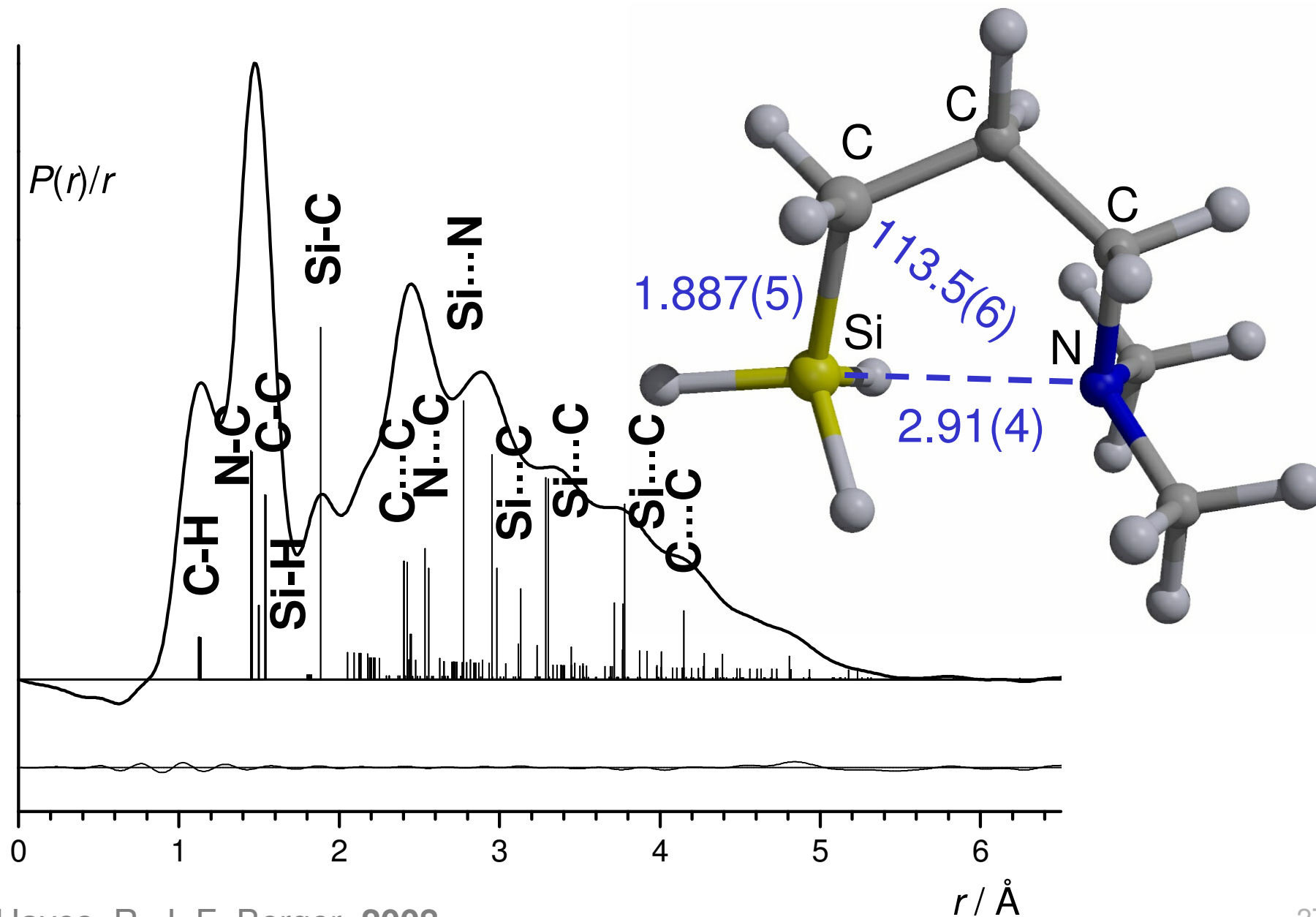


$I4/m$   
mp.  $-102^\circ\text{C}$



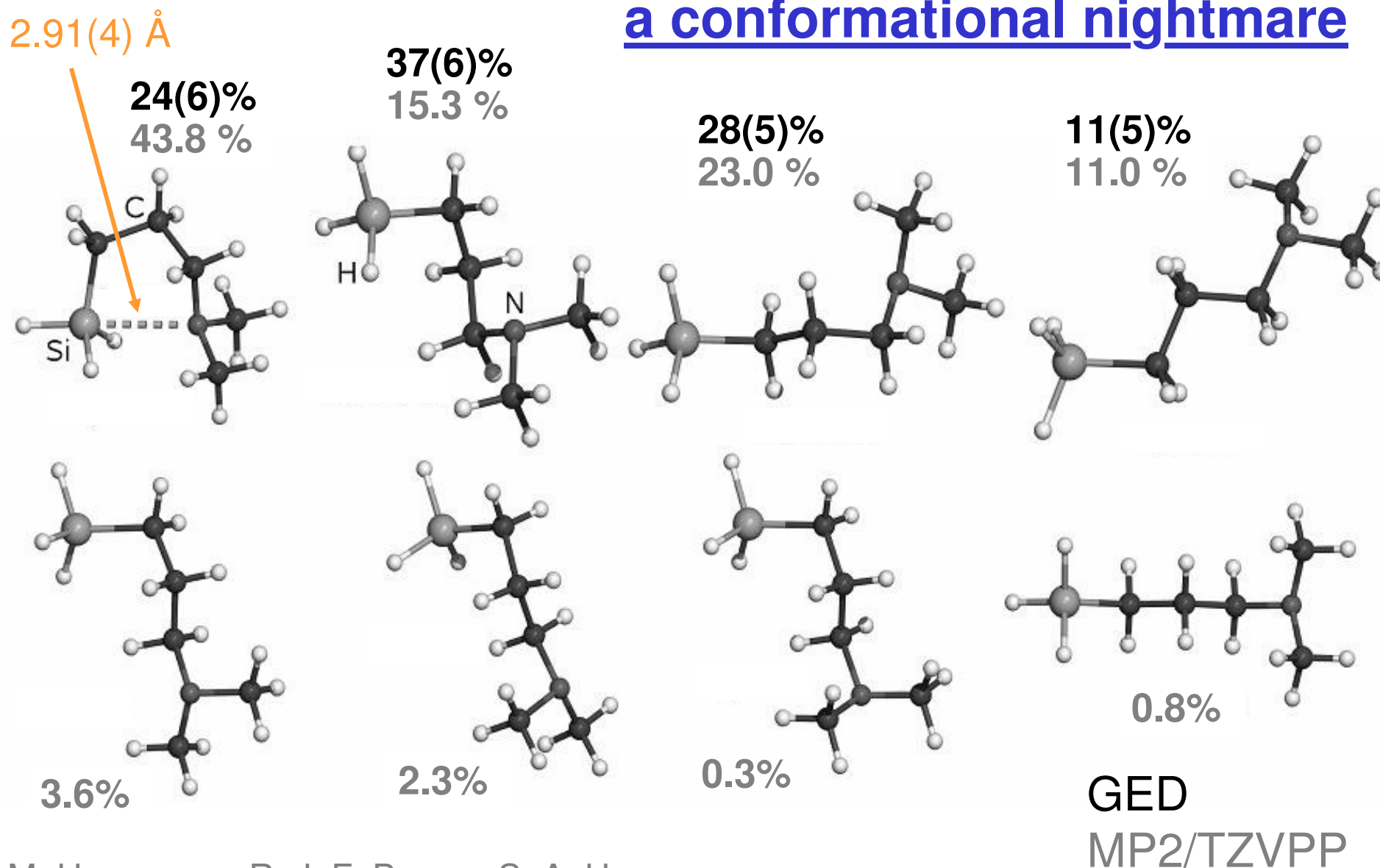
M. Hagemann, R. J. F. Berger, S. A. Hayes,  
H.-G. Stammler, N. W. Mitzel, *Chem. Eur. J.* **2008**, *14*, 11027

# $\text{H}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ – gas phase structure



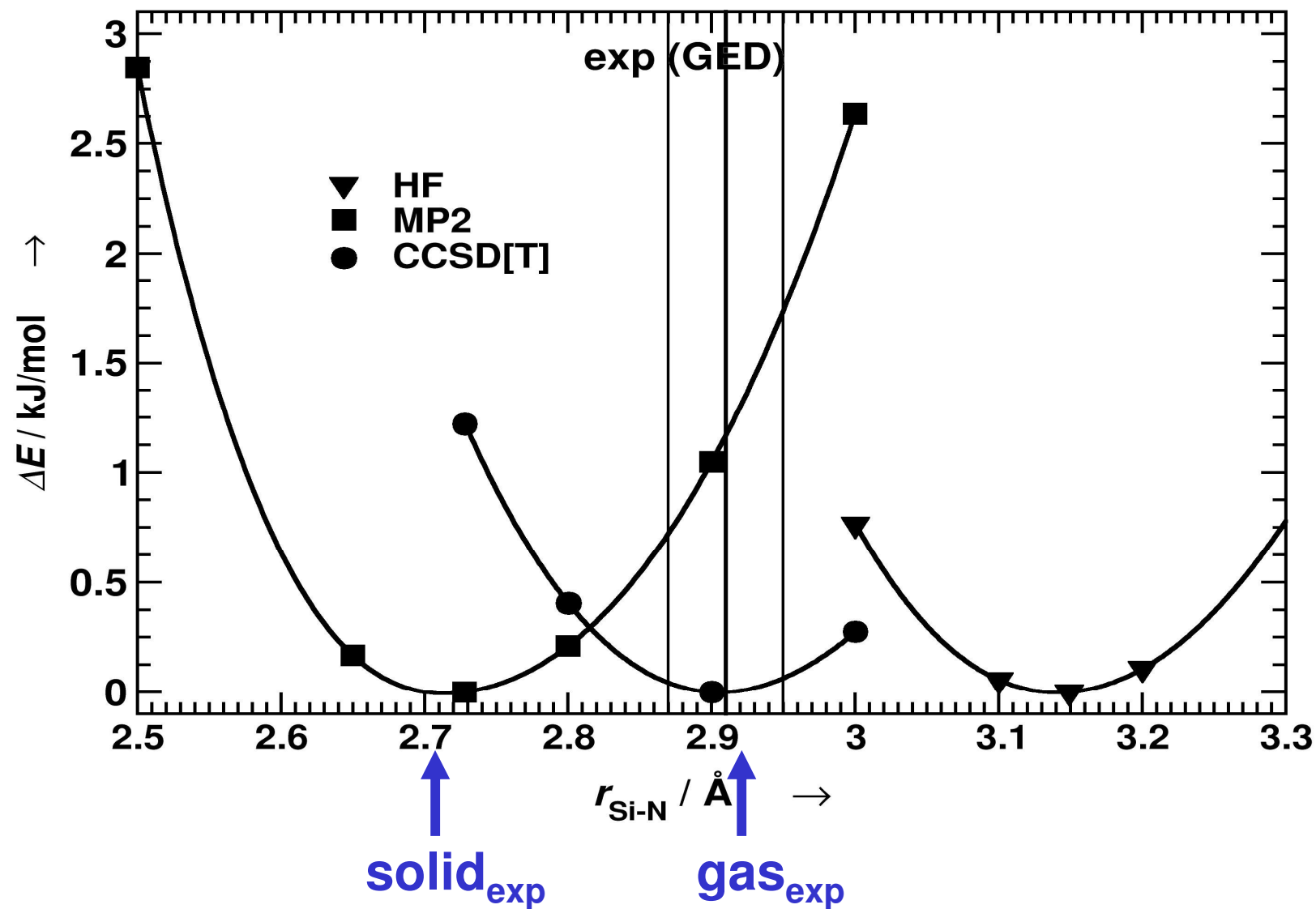
# H<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> – gas phase

## a conformational nightmare

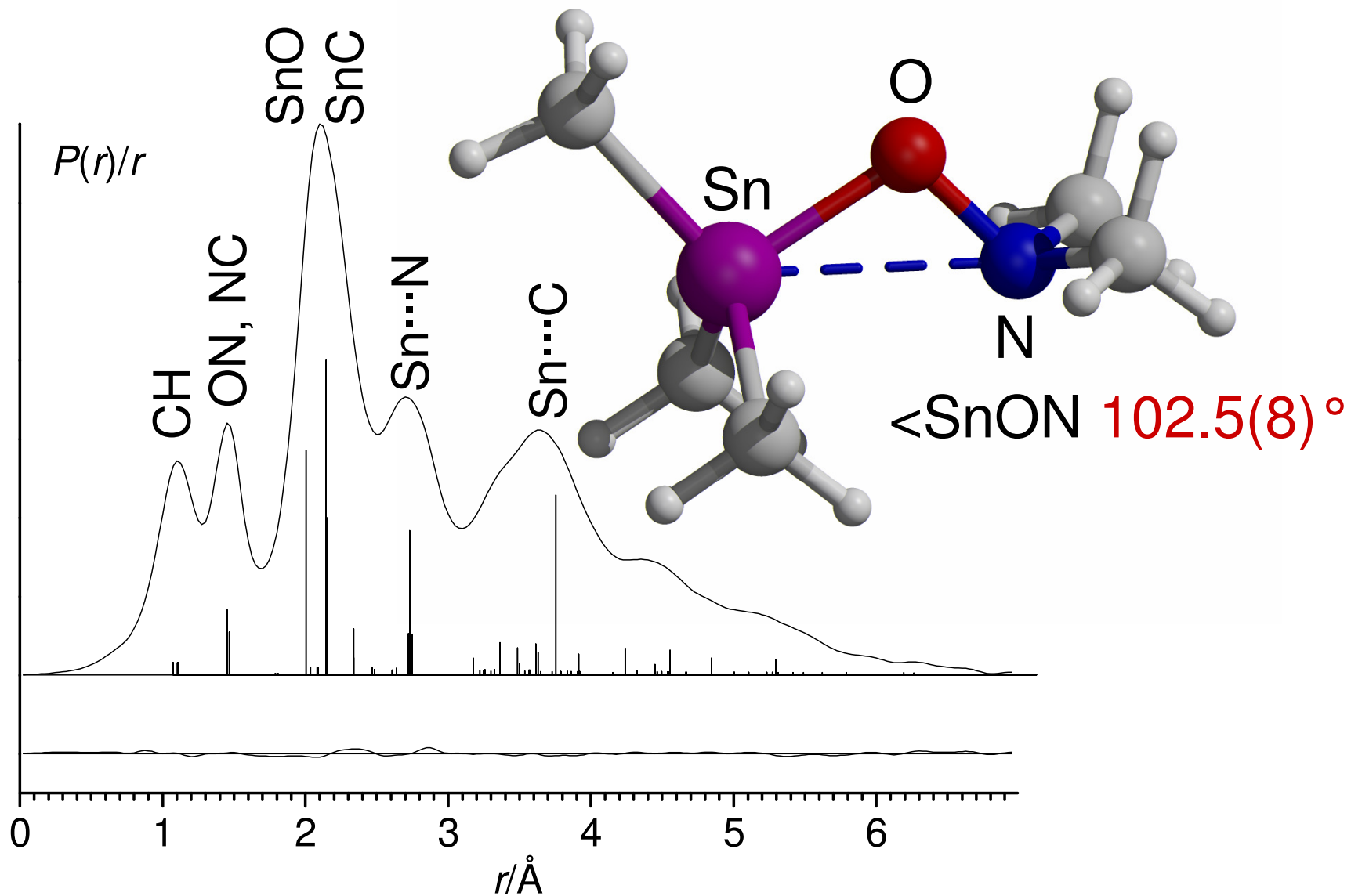


M. Hagemann, R. J. F. Berger, S. A. Hayes,  
H.-G. Stammler, N. W. Mitzel, *Chem. Eur. J.* **2008**, *14*, 11027

## H<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> – calculations



## Me<sub>3</sub>SnONMe<sub>2</sub> GED





**GED** → **XRD**  
 gas → solid

$P2/n$   
 Smp.  
 $-85^\circ\text{C}$

**<SnON**

$102.5(8) \rightarrow 101.5(4)^\circ$

**<OSnC**

$99.6(10) \rightarrow$   
 $99.7(4)^\circ$

**<OSnC'**

$108.1(6) \rightarrow$   
 $118.1(\text{av})^\circ$

$\text{Sn} \cdots \text{N}: 2.745(9) \text{ \AA}$   
 $\text{Sn} \cdots \text{O}': 2.998(10) \text{ \AA}$

U. Losehand, N.W. Mitzel, A. Richard-  
 Son, *Organometallics* **1999**, 18, 2610

# Ir(phpy)<sub>3</sub>

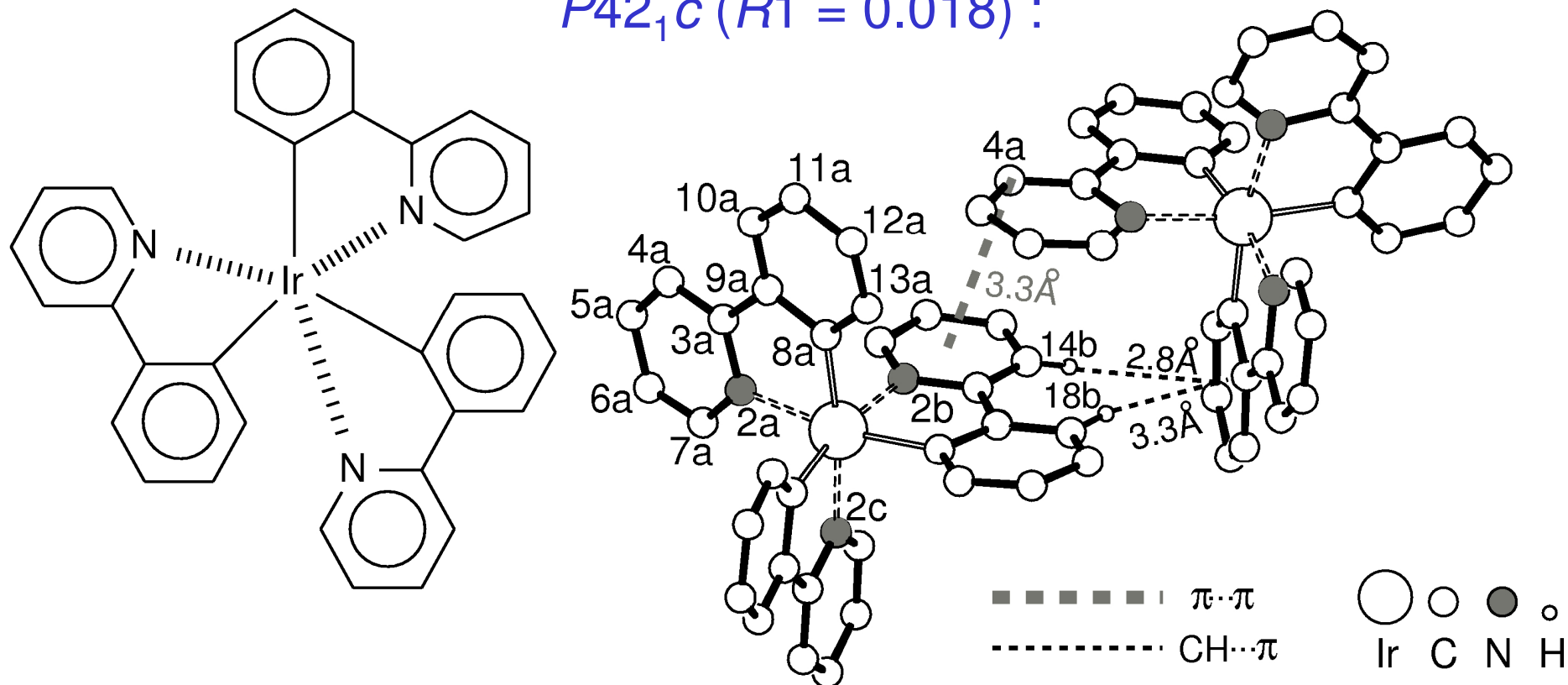
Earlier XRD structure (twinned,  $P\bar{3}$ )

J. Breu, H. Yersin,

*Chem. Mater.* **2005**, 17, 1745

new modification

$P\bar{4}2_1c$  ( $R1 = 0.018$ ) :



strong green phosphorescence  
used in organic light emitting diodes (OLED)

R. J. F. Berger, B. Neumann,  
H.-G. Stammler, N. W. Mitzel, *Eur. J. Inorg. Chem.* **2010**, 1613



# Ir(phpy)<sub>3</sub>

GED:

$r(\text{Ir-C})$  2.033(6) Å

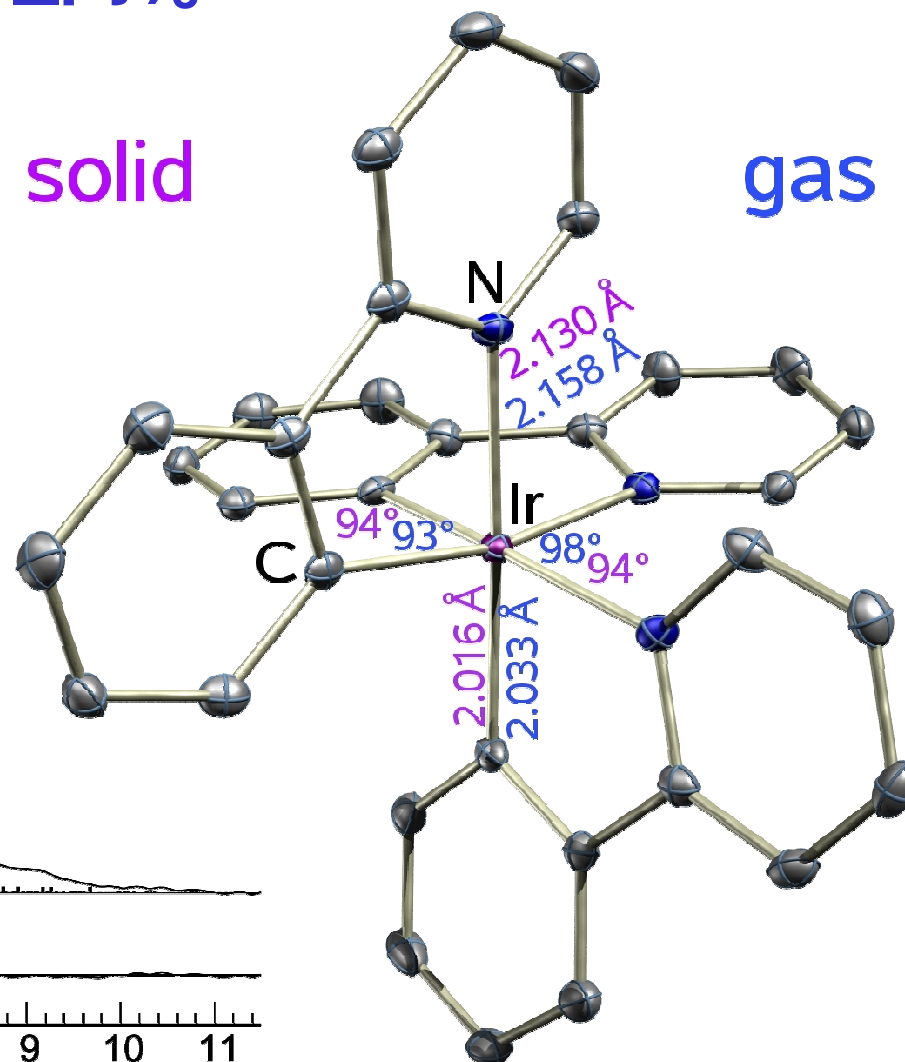
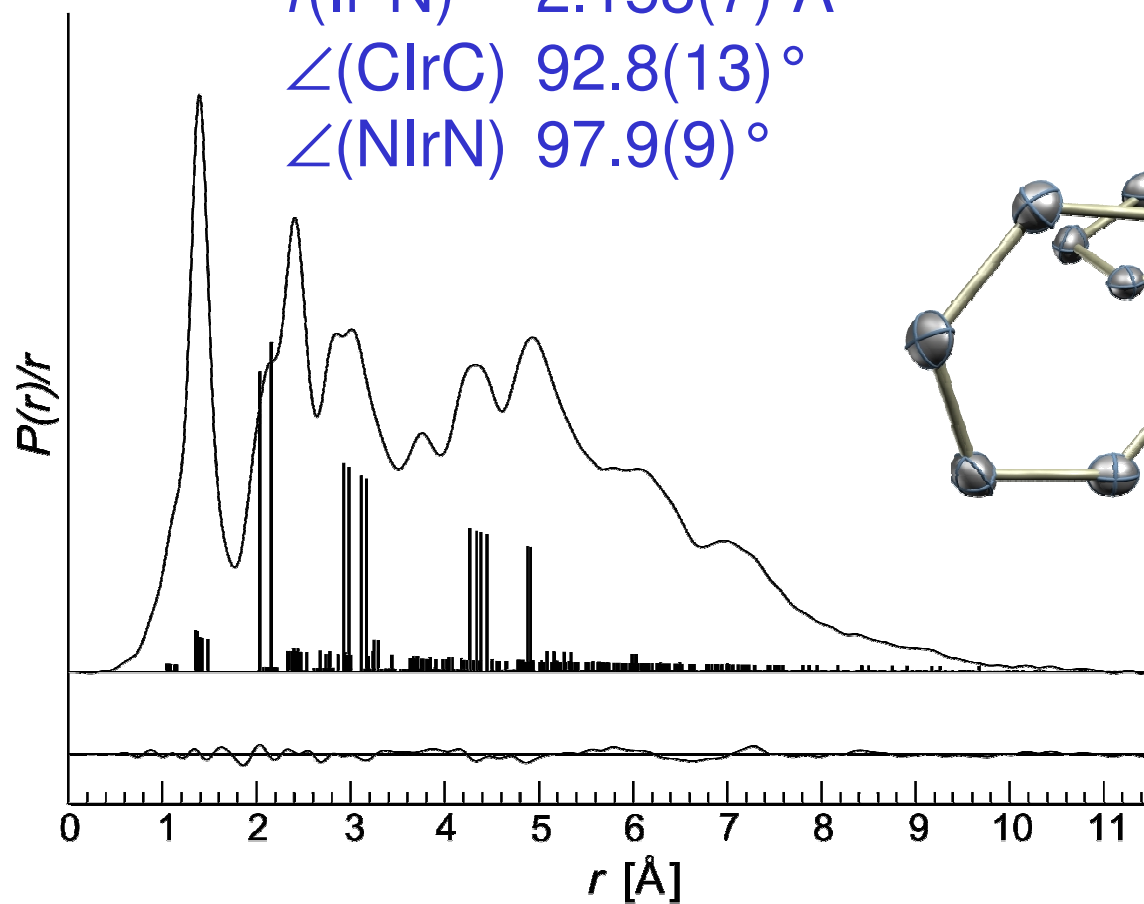
$r(\text{Ir-N})$  2.158(7) Å

$\angle(\text{C Ir C})$  92.8(13)°

$\angle(\text{N Ir N})$  97.9(9)°

solid

gas



R. J. F. Berger, B. Neumann,  
H.-G. Stammler, N. W. Mitzel, *Eur. J. Inorg. Chem.* **2010**, 1613

## Conclusions

Where are large structural differences between solid state and gas phase to be expected?

### Gas phase

undercoordinate atoms

weak bonds broken

dative bonds

coordinative bonds

conformational possibilities

### Solid

aggregation

weak bonds formed

dative bonds strenghtened

coordinative bonds stronger

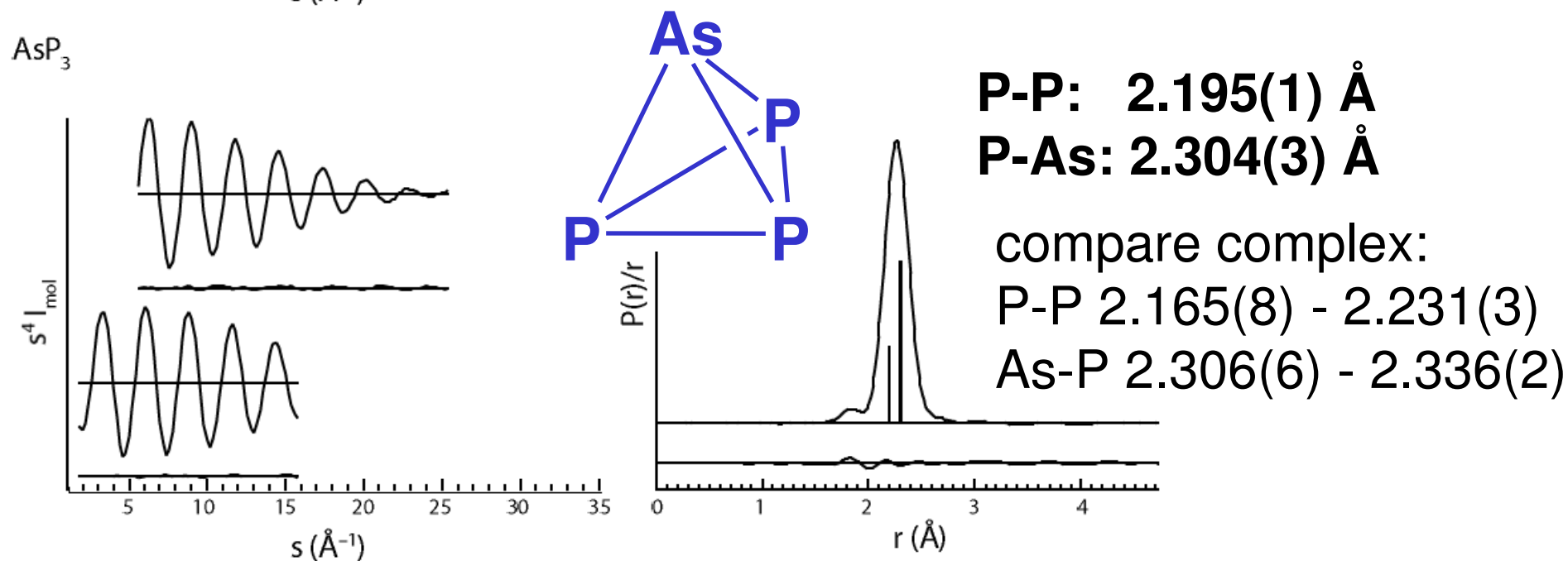
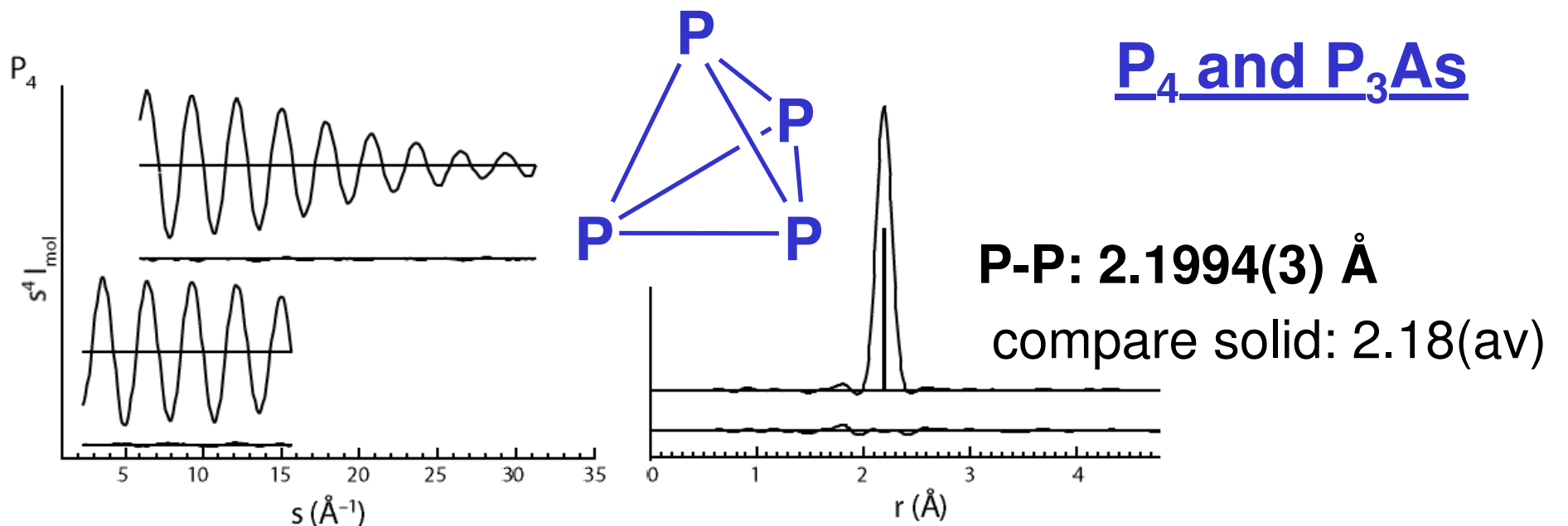
one conformation selected

Additional forces in the solid:

dipolar fields, steric repulsion, weak contacts

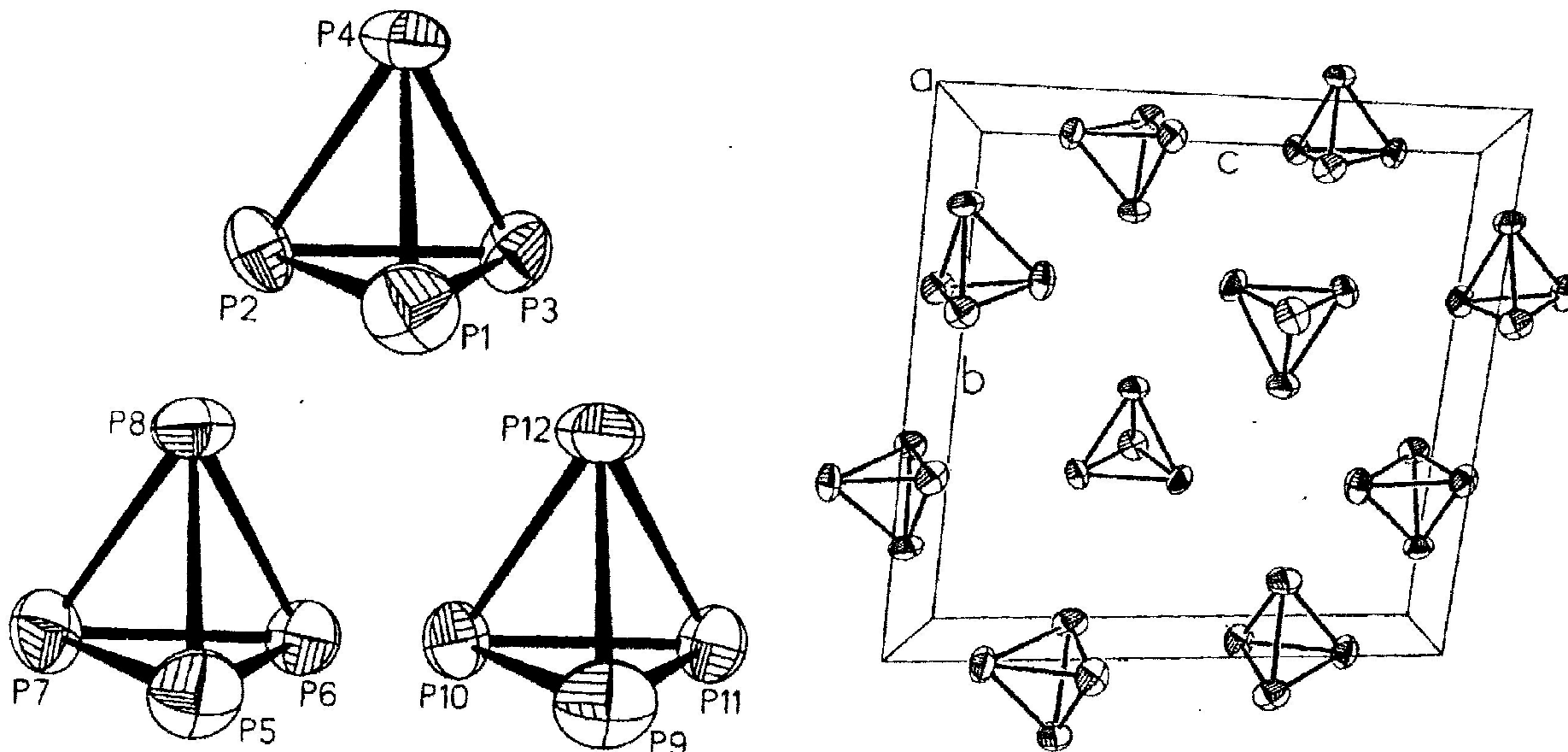
# Appendix

## P<sub>4</sub> and P<sub>3</sub>As



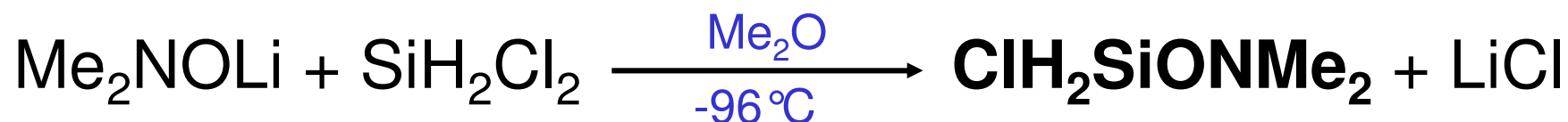
B. M. Cossairt, C. C. Cummins, A. R. Head, D. L. Lichtenberger, R. J. F. Berger, S. A. Hayes, N. W. Mitzel, G. Wu, *J. Am. Chem. Soc.* **2010**, 132, 8459.

## The P<sub>4</sub> molecule in the solid state

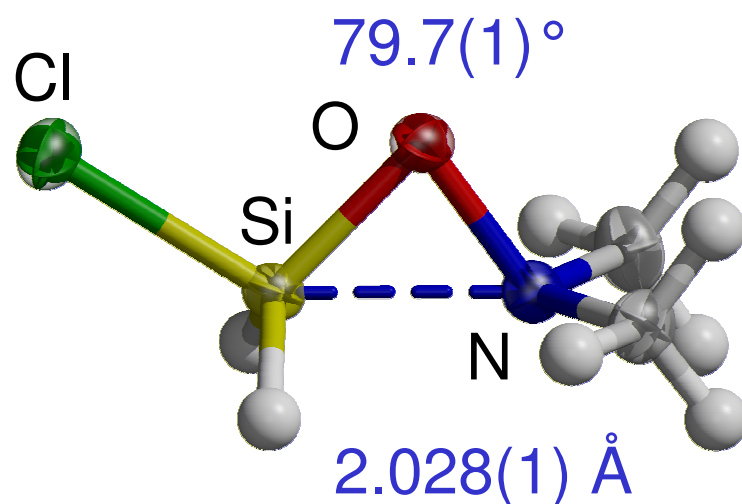


average value 2.182(5) Å (range 2.175(5) - 2.192(5) Å) as determined from 18 P-P bonds of 3 independent molecules)

## $\text{ClH}_2\text{SiONMe}_2$



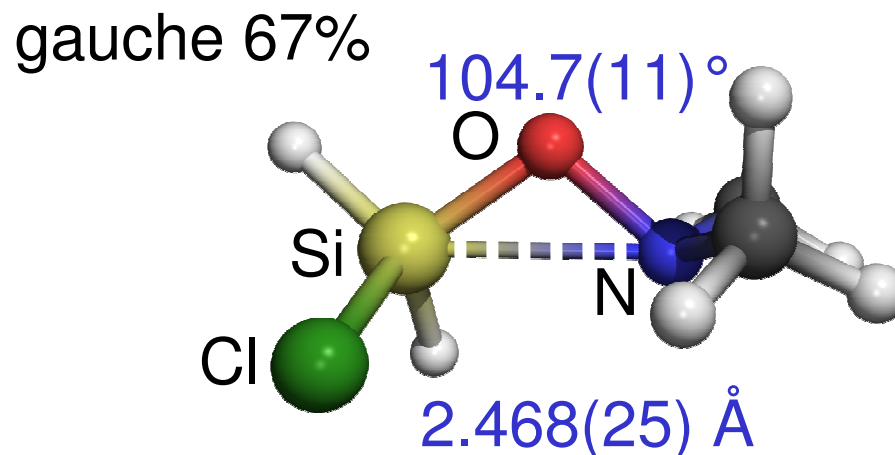
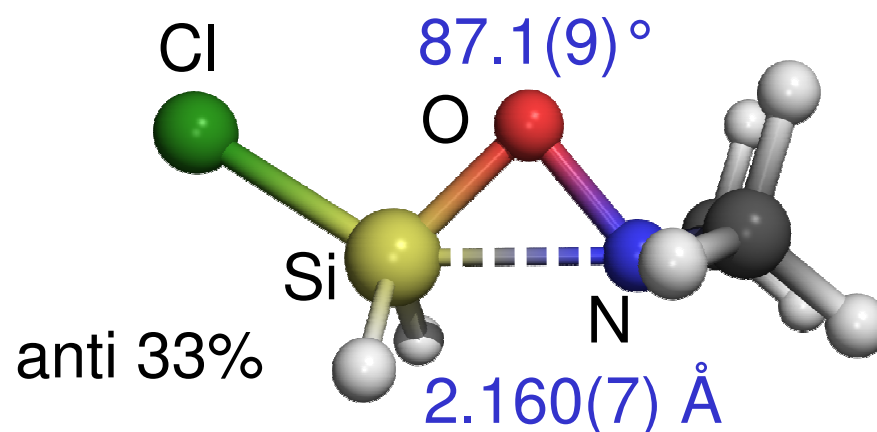
solid (XRD)



Fp.  $-55^\circ\text{C}$

$P\bar{1}$

gas phase (GED)



# Radial distribution curve for $\text{ClH}_2\text{SiONMe}_2$

