A Valence Bond study of isocyanides' electronic structure

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VB Workshop - July 2012

Plan

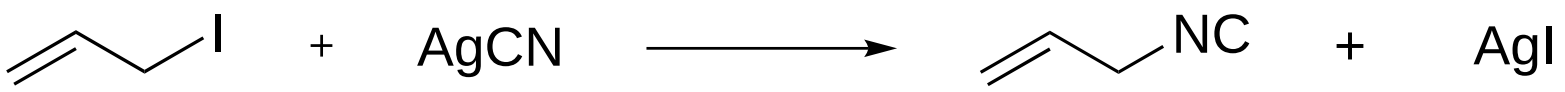
1 Isocyanides in chemistry
- Presentation
- Isocyanides' reactivity
- Representing isocyanides
- Studies of the -NC bond

2 Application of VB to RNC
- Mesomeric forms
- Methodology
- Effect of the substituent
- Importance of structures
- Isocyanides' nucleophilicity

3 XMVB 2.0

4 Conclusion

First isocyanides synthesis by Lieke (1859)



- Lieke synthesis :
  - Expensive and toxic method
  - Reduced applications
- Other synthesis developed at the end of the 20^{th} century.

Why did isocyanides remain marginal for decades ?

Isocyanides' smell

- "*It has a penetrating, extremely unpleasant odour ; the opening of a flask of allyl [iso]cyanide is enough to foul up the air in a room for several days.*" W. Lieke.

- "*It is true that many potential workers in this field have been turned away by the odour.*" I. Ugi.

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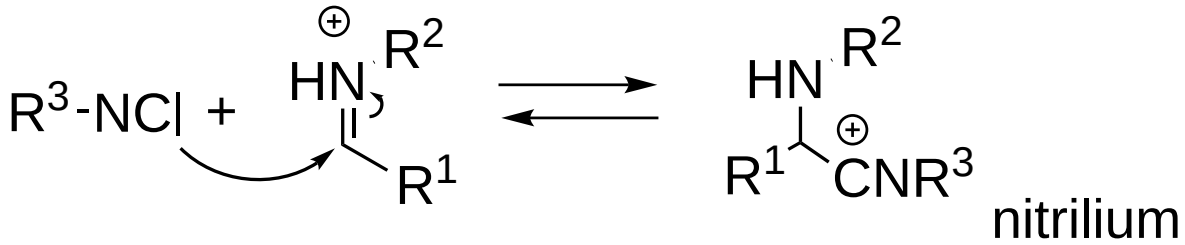
Isocyanides' toxicity

Bayer industry showed in the 60's that oral and subcutaneous doses of 0.5-5 kg/kg of most isocyanides can be tolerated by mice.

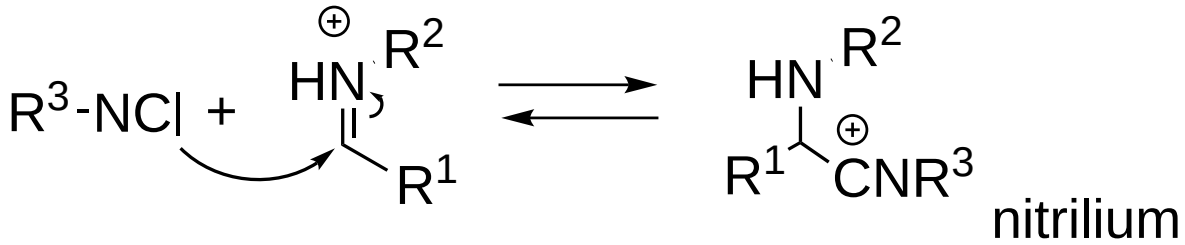
Reactivity of isocyanides

Isocyanide as a nucleophile

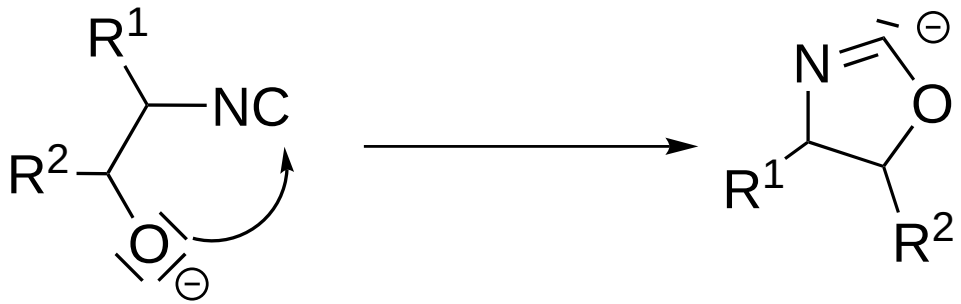


Reactivity of isocyanides

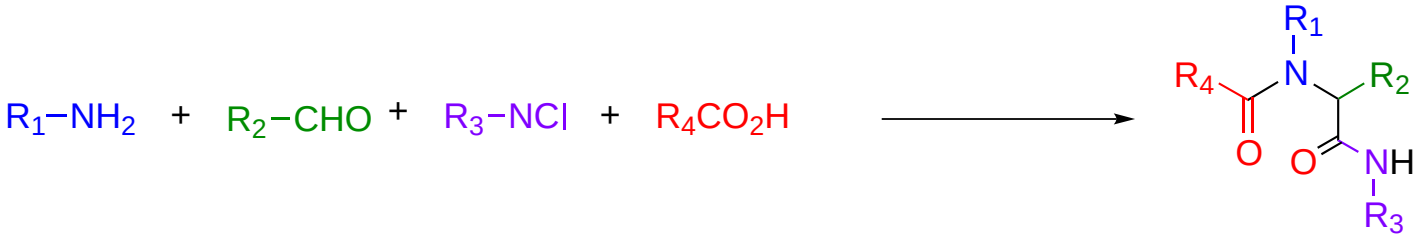
Isocyanide as a nucleophile



Isocyanide as an electrophile



Isocyanides in MCR : the Ugi coupling



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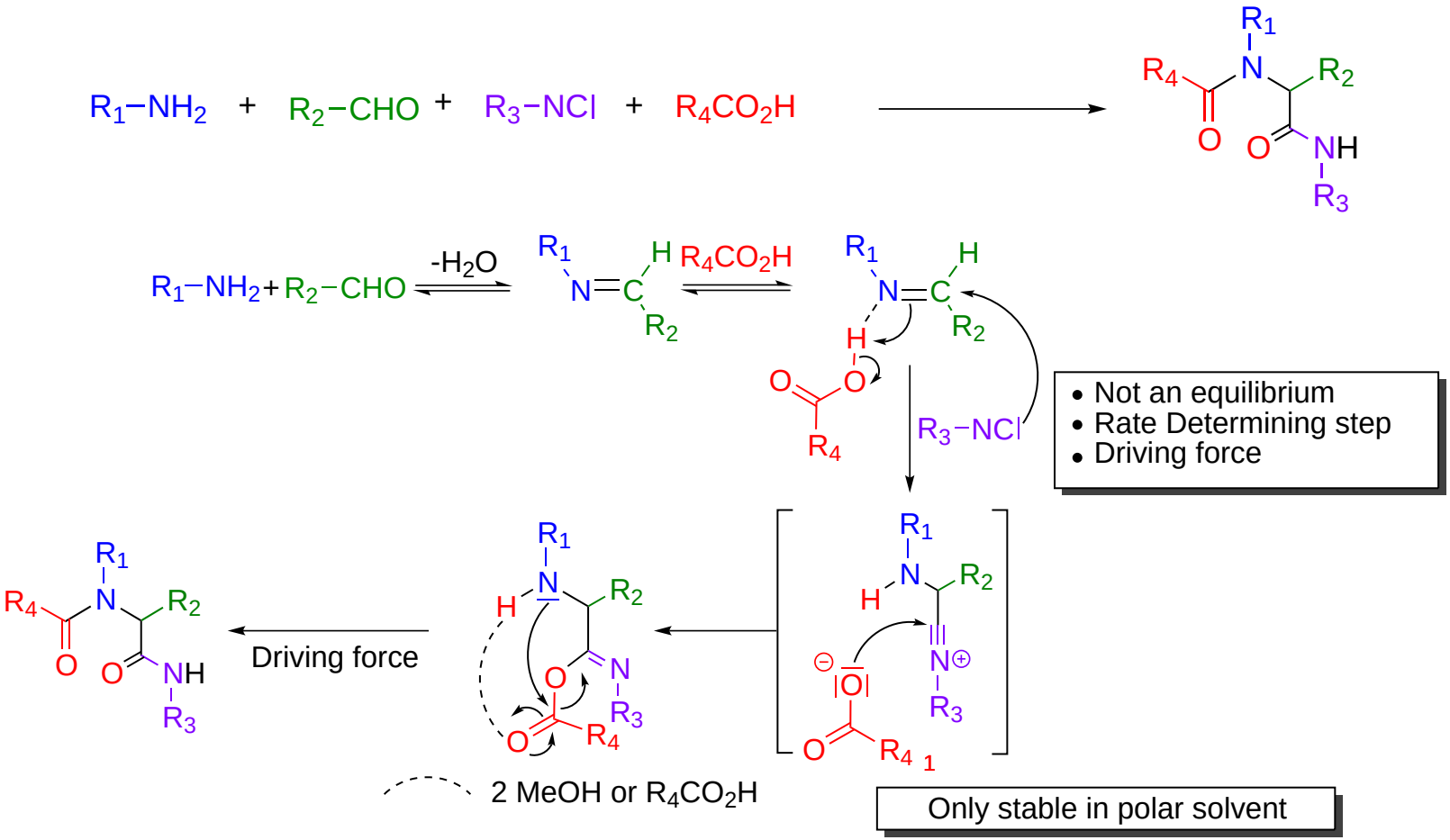
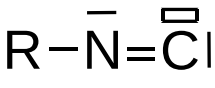


J. Org. Chem., **2012**, 77 (3), 1361-1366

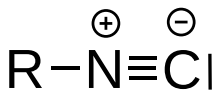
Lewis structures usually accepted

Carbene representation



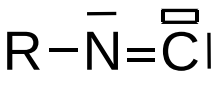
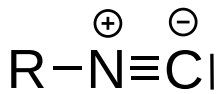
(Nef - 1892)

Zwitterionic representation



(Lindemann and Wiegrebe - 1930)

Lewis structures usually accepted

Carbene representation	***Zwitterionic representation***
	
(Nef - 1892)	(Lindemann and Wiegrebe - 1930)

Experimental facts

- Linear R-N-C linkage observed by electron diffraction.
- C-N stretching band around 2130 cm^{-1} and slow variation with the solvent.
- Isoeletronic with CO.

Zwitterionic mesomeric form
more used by organic chemists.

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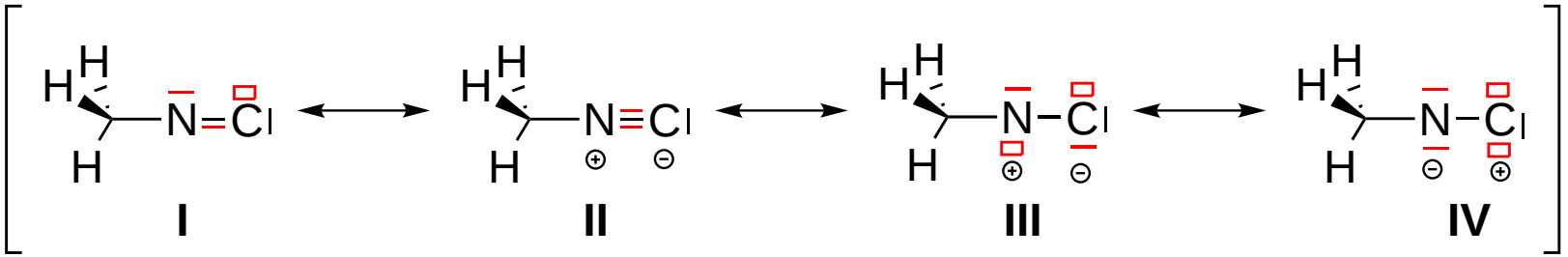
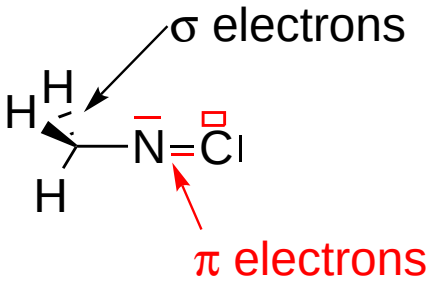
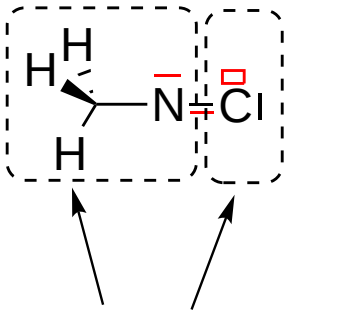
Mesomeric forms for MeNC

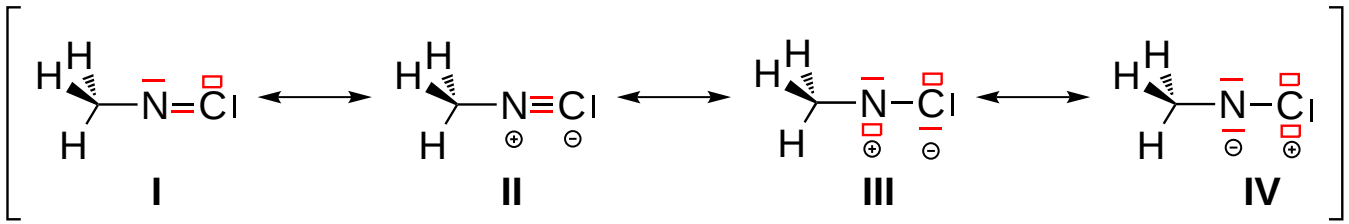
How to write the VB wave function for MeNC?







Effect of the VB method

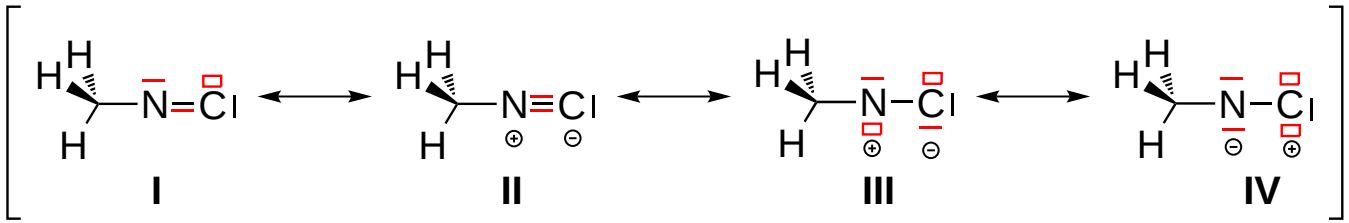


Weight in percent of each structure

R-NC	I	II	III	IV	Energy (kcal.mol^{-1})
MeNC$^{a}_{vbscf}$	56.8	27.9	8.4	6.9	16.1
MeNC$^{a}_{bovb}$	51.5	28.1	8.8	11.6	0
MeNC$^{b}_{bovb}$	49.8	29.9	9.6	10.7	-

Geometries optimized in MP2/6-311^{++}G**.
^{a} : Basis set for VB calculations : 6-31G*.
^{b} : Basis set for VB calculations : 6-31^{+}G*.

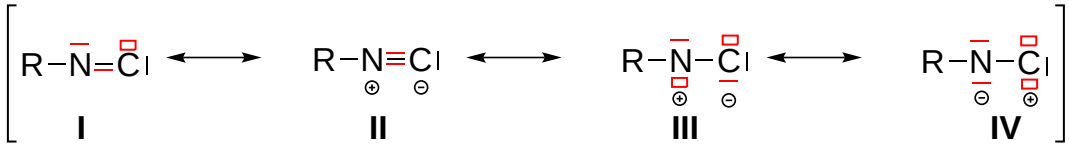
Effect of the solvation



R-NC	I	II	III	IV
MeNC	51.5	28.1	8.8	11.6
$MeNC_{PCM(H_2O)}$	49.5	31.0	9.7	9.8
$MeNC_{PCM(CH_2Cl_2)}$	49.8	30.6	9.6	10.0
MeNC...H-OH	50.4	29.8	9.3	10.5
MeNC...H-$CHCl_2$	50.7	29.3	9.3	10.7

Geometries optimized in MP2/6-311^{++}G**.
All VB calculations are done in BOVB/6-31G*.
Weight in percent of each structure.

Effect of the substituent



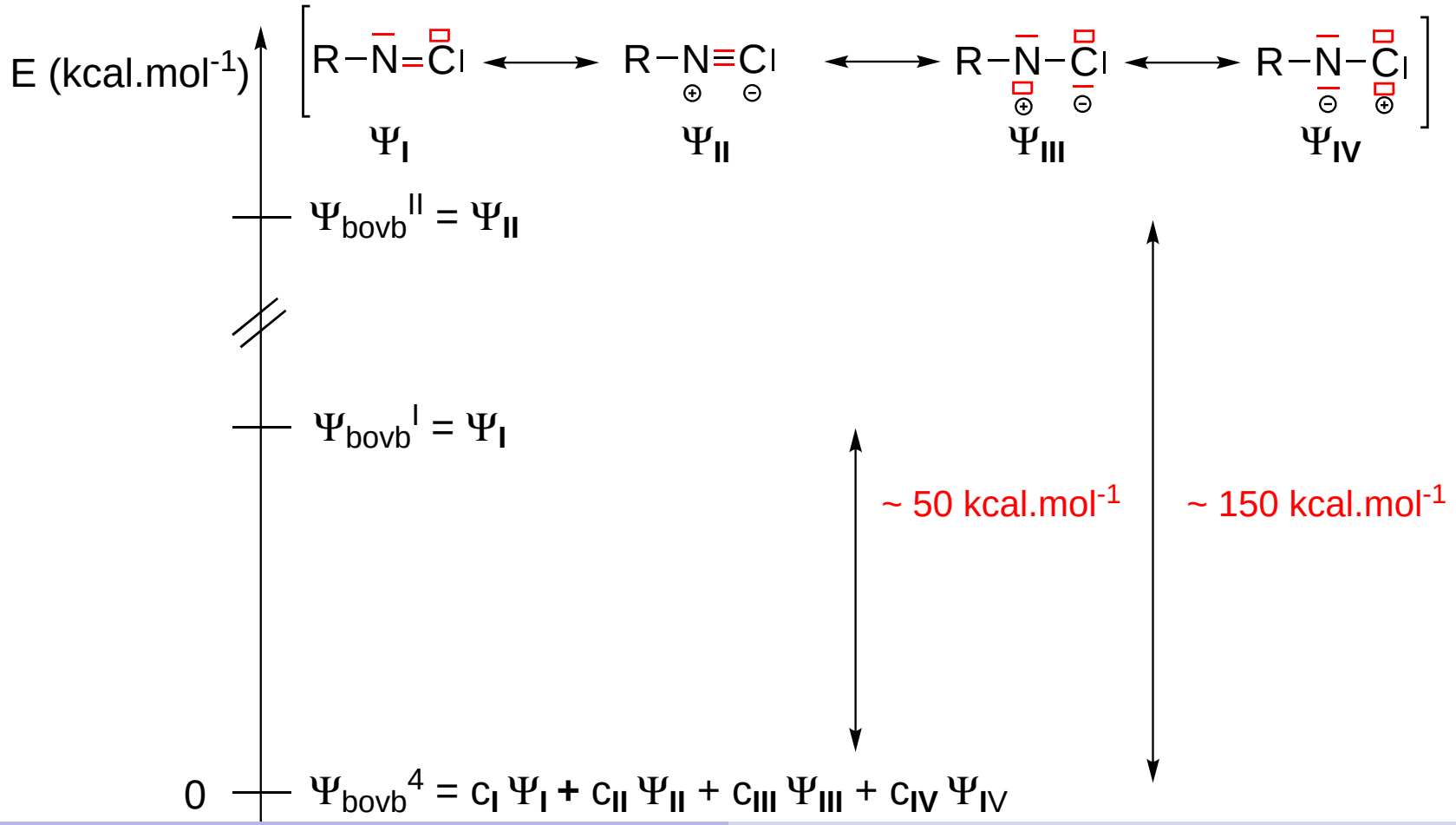
R-NC	I	II	III	IV
MeNC	51.5	28.1	8.8	11.6
EtNC	51.1	28.4	8.9	11.6
***i*-PrNC**	50.9	28.6	9.0	11.5
***t*-BuNC**	50.1	29.4	9.4	11.1
$PhCH_2NC$	50.9	28.3	9.0	11.9
CH_2=CHNC	52.0	27.4	8.6	12.0
CF_3NC	54.8	23.8	7.5	14.6
$MeSO_2CH_2NC$	54.5	26.5	8.0	11.0

Geometries optimized in MP2/6-311^{++}G**.
All VB calculations are done in BOVB/6-31G*.

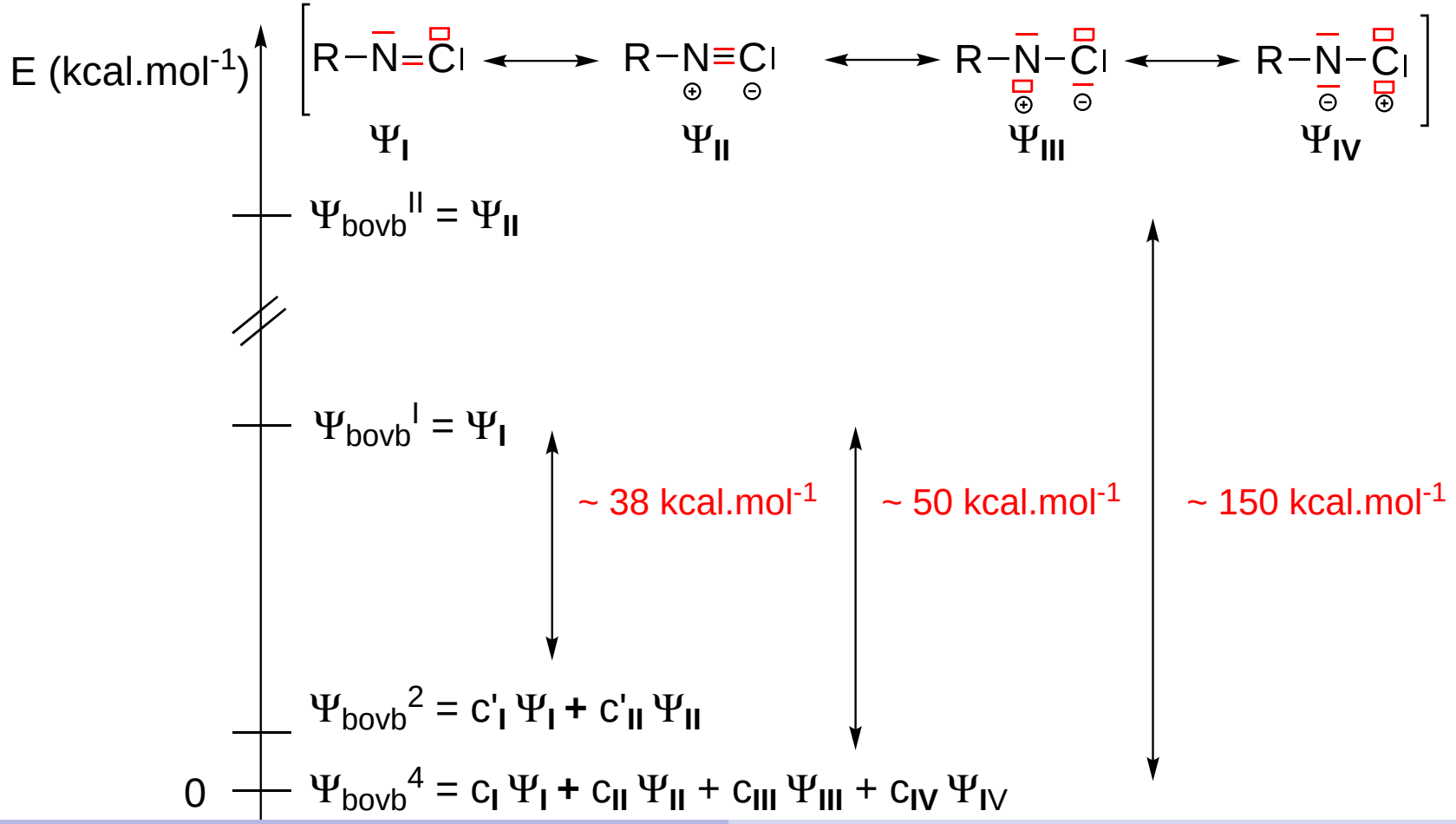
Preliminary results

- Unexpected major mesomeric form : the carben one (50-55%).
- **III** et **IV** can be considered as exotic mesomeric forms.
- No significant effect of the solvation.
- Variation with the substituent.
- The carben form explains the reactivity of isocyanides but...not all experimental facts.

Influence of structures to correctly describe the wave function ?



Are all structures useful to correctly describe the wave function ?



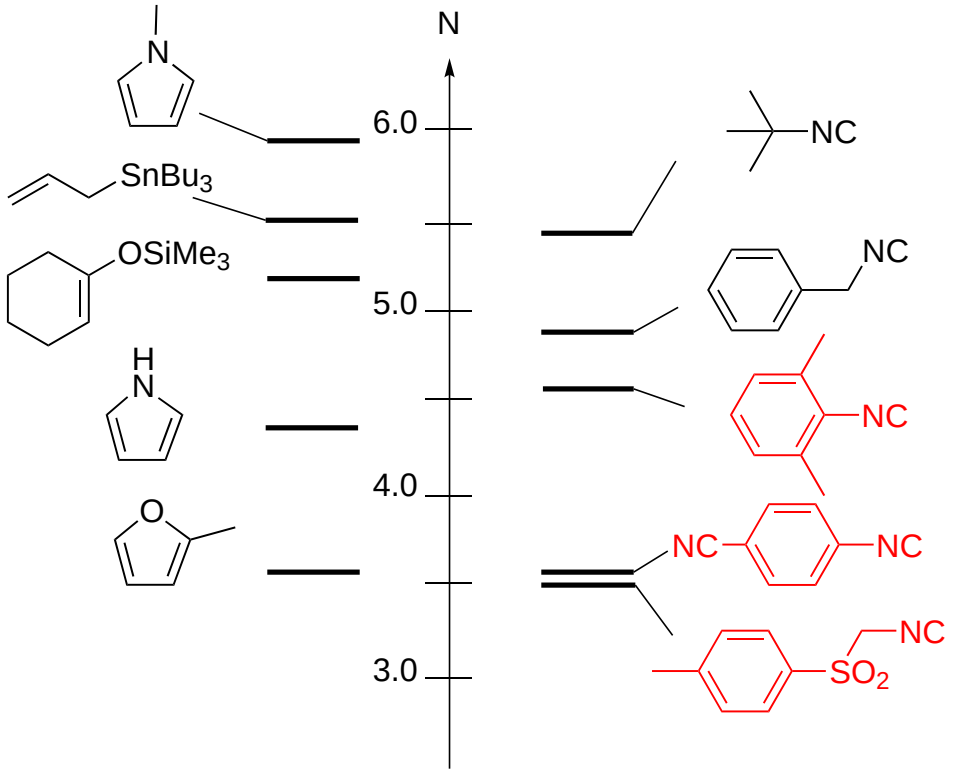
Conclusion

- The carben form is not enough to correctly describe the RNC structure.
- Strong stabilization of the zwitterionic form II due to the donation of the π lone pair of the nitrogen. Explain :
  - the linear geometry.
  - the C-N stretching band around 2130 cm^{-1}.

New J. Chem., **2012**, 36, 1137-1140

- Can VB be helpful to deeply understand isocyanides' reactivity ?

Isocyanides' nucleophilicity



Mayr, H. & al, *Angew. Chem. Int. Ed.*, **2007**, 46, 3563-3566.

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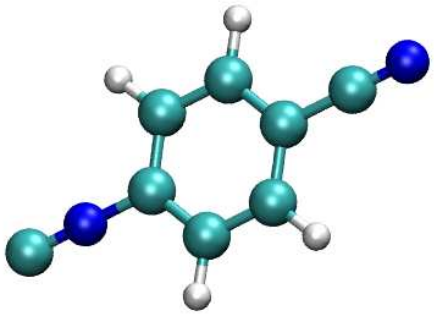
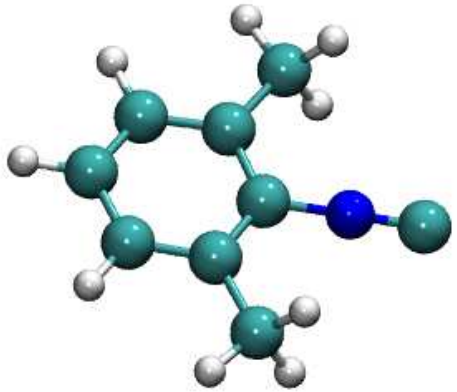
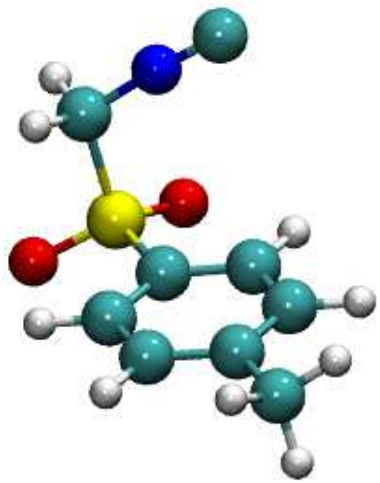




R-NC	Nb of (heavy) atoms	Nb of electrons	Nb of basis functions	Number of basis structures	Time
4-CNPhNC$_{vbscf}$	14 (10)	66	158	20	45 min
4-CNPhNC$_{bovb}$	14 (10)	66	202	6	4h47
PhMe$_2$NC$_{vbscf}$	17 (10)	70	168	20	1h25
PhMe$_2$NC$_{bovb}$	17 (10)	70	214	6	7h30

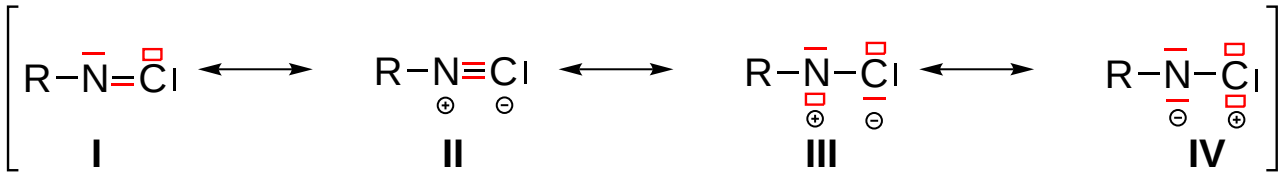
Xeon Woodcrest 3.0 GHz
Geometries optimized in MP2/6-311^{++}G**. Basis set for VB calculations : 6-31G*
Inputs are available for tutorials : /home/vbws_tutor /EXERCISES/MORE

Tosmic



R-NC	Nb of (heavy) atoms	Nb of electrons	Nb of basis functions	Number of basis structures	Time
Tosmic$_{vbscf}$	22 (13)	102	217	6	9h40
Tosmic$_{VB-QMC}$	22 (13)	102	217	6	1h48
Tosmic$_{bovb}$	22 (13)	102	310	6	50h

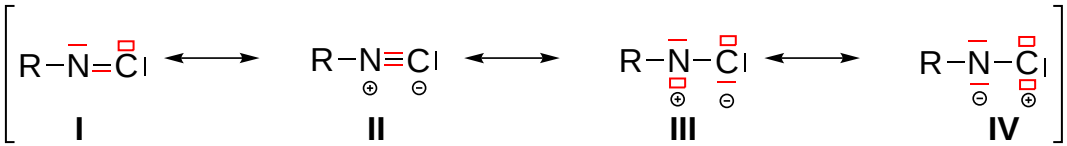
VBSCF & BOVB : AMD magny-cours 2.3 Ghz
VB-QMC : Blue Gene/P (2048 proc.)
Geometries optimized in MP2/6-311^{++}G**. Basis set for VB calculations : 6-31G*

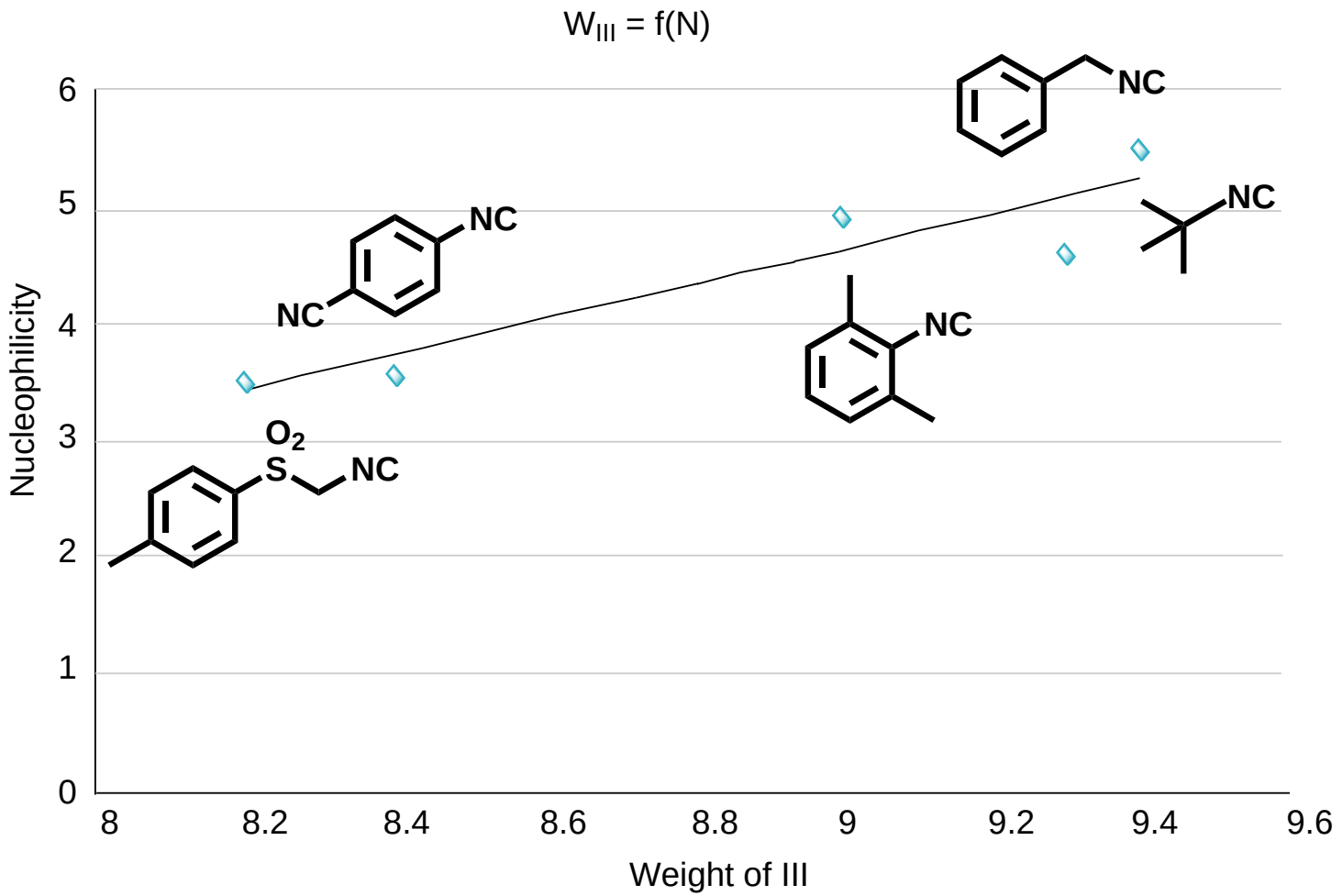


Weight in percent of each structure in BOVB

R-NC	**I**	**II**	**III**	**IV**	**N** (Experimental)
t-**BuNC**	50.1	29.4	9.4	11.1	5.47
PhCH$_2$NC	50.9	28.3	9.0	11,9	4.90
PhMe$_2$NC	50.2	29.2	9.3	11.3	4.59
pCNPhNC	52.0	26.3	8.4	13.3	3.57
Tosmic	52.5	26.2	8.2	13.1	3.50

Geometries optimized in MP2/6-311^{++}G**.
Basis set : 6-31G*.


I
II
III
IV


W_III = f(N)
Nucleophilicity
Weight of III
0
1
2
3
4
5
6
8
8.2
8.4
8.6
8.8
9
9.2
9.4
9.6
NC
NC
NC
NC
O2
S
NC

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- The carben form is the major mesomeric form but the zwitterion form is necessary to correctly describe isocyanides.

- Besides mesomeric form III is exotic, one can explain the nucleophilicity of isocyanides.

Acknowledgments

- Paul Fleurat-Lessard and Benoît Braïda
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