

# Теоретические основы органической ХИМИИ

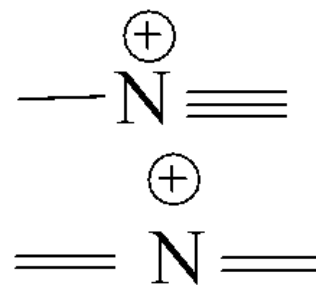
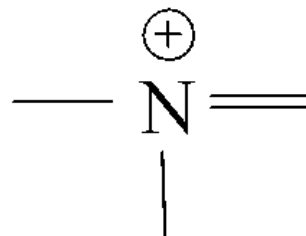
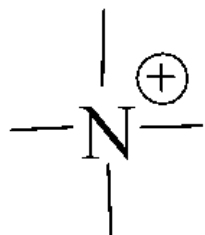
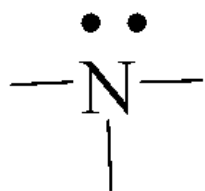
Азотцентрированные соединения.  
Теория гибридизации.

Лекция 5

(электронно-лекционный курс)

Проф. Бородкин Г.И.

# Теория гибридизации (N, J, F и др.)



$\angle \text{XNX} \quad 109^\circ$

$107^\circ$

$102^\circ$

$r_w^X \quad 2.0$

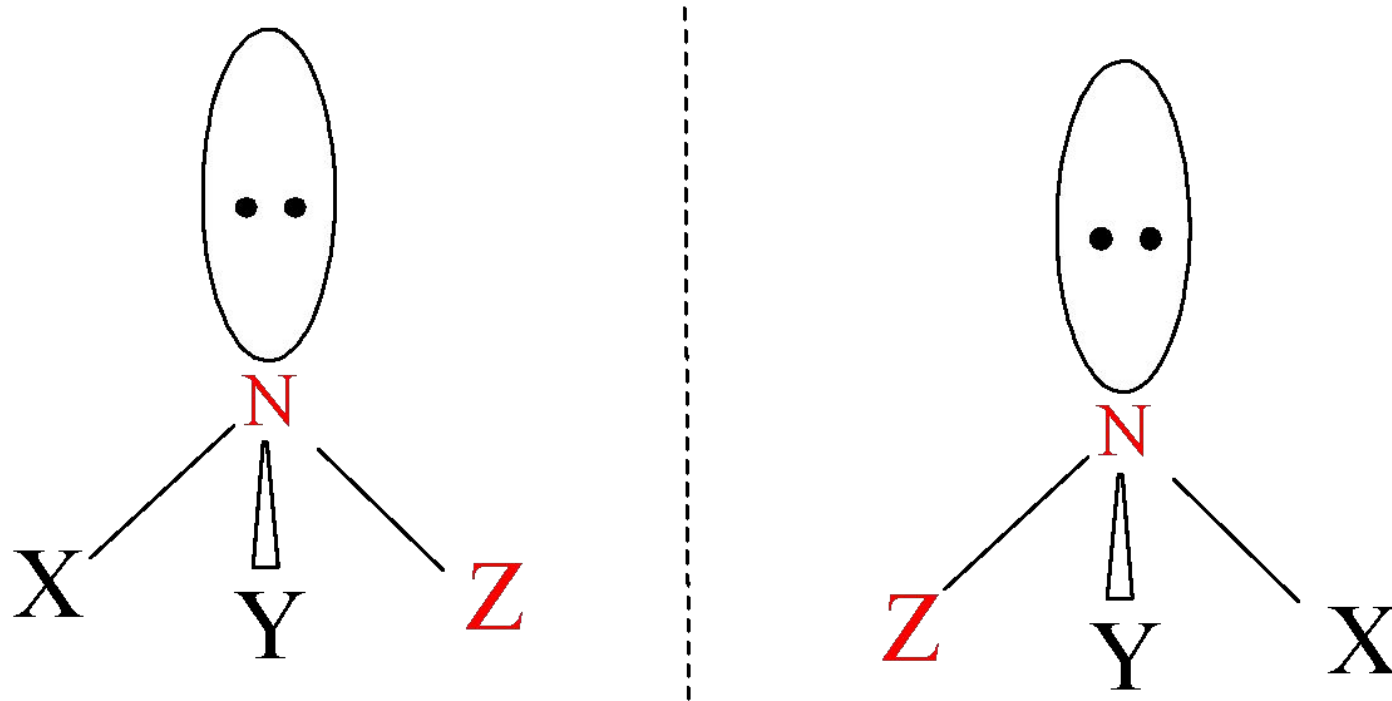
$1.2$

$1.35 \text{ \AA}$

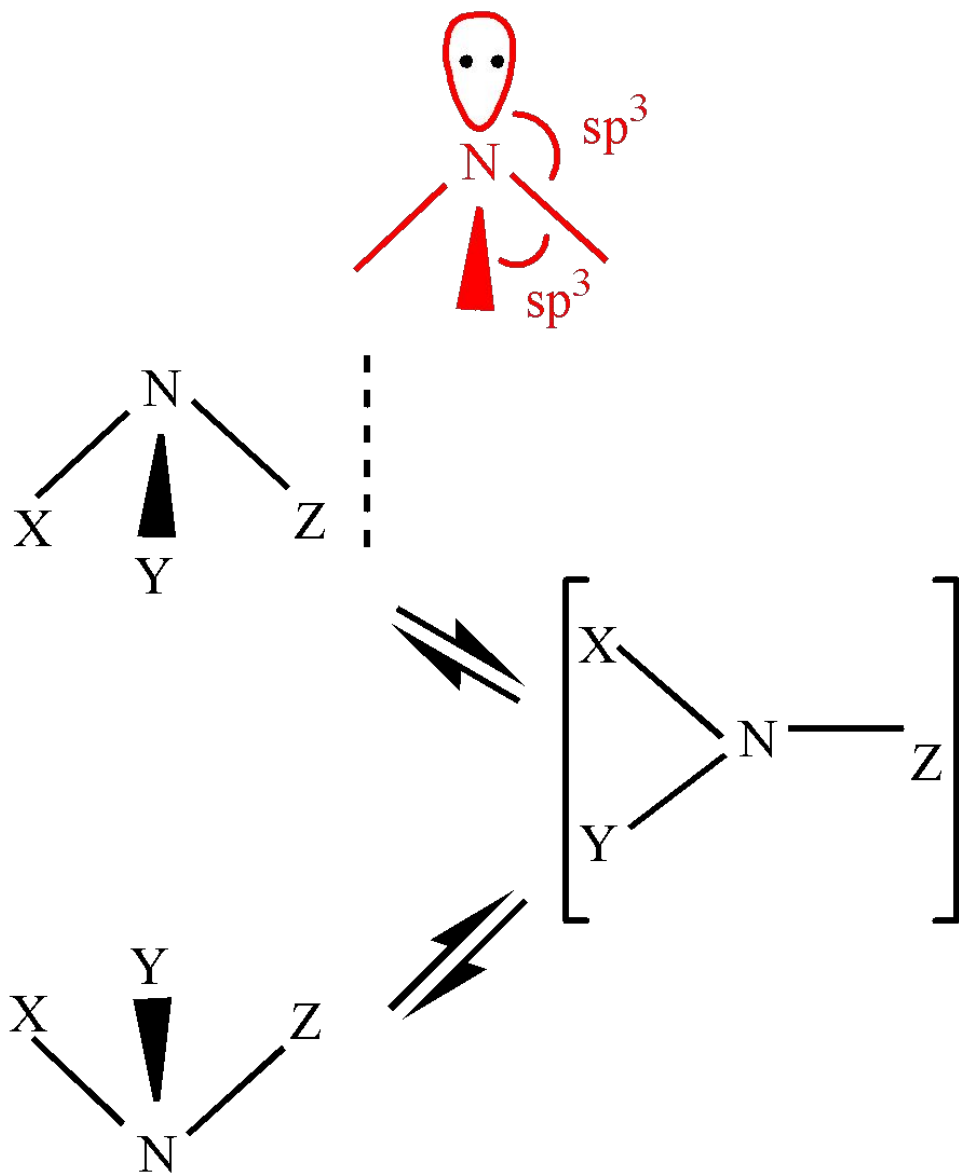
$r_F > r_H$

угол FNF < HNH

правило Бента



Оптическая изомерия ?



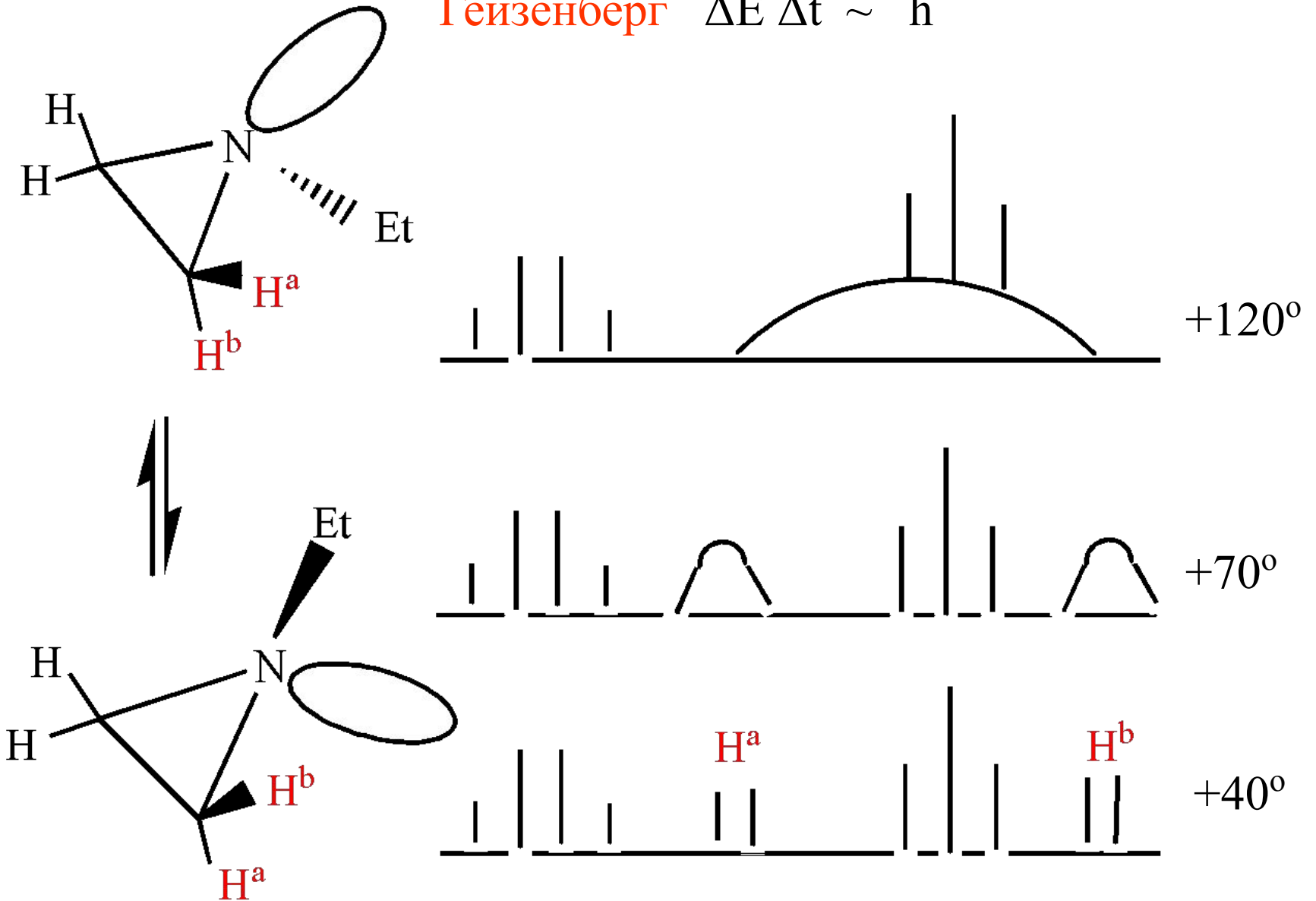
$\Delta G^\ddagger$   
инверс.  
(ккал/моль)

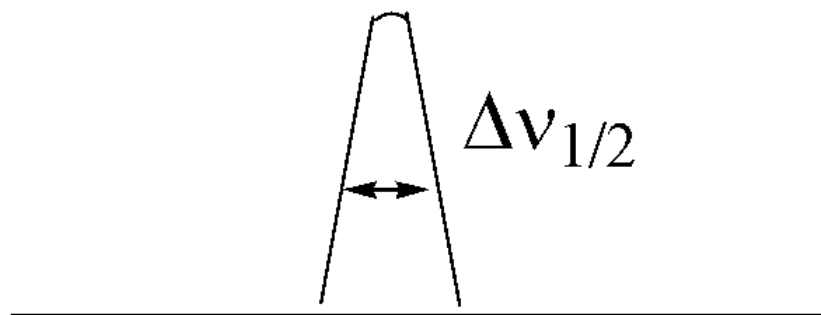
$\text{NH}_3$	5.8 (МВ)
$\text{MeNH}_2$	4.8 «-»
$\text{Me}_2\text{NH}$	4.4 «-»
$\text{Me}_3\text{N}$	7.5 (ИК)

$k_{25^\circ} (\text{NH}_3) 10^9 \text{ сек}^{-1}$

# Динамический ЯМР

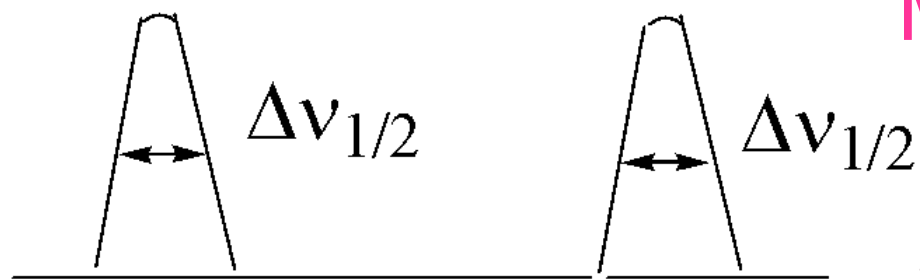
Гейзенберг  $\Delta E \Delta t \sim \hbar$





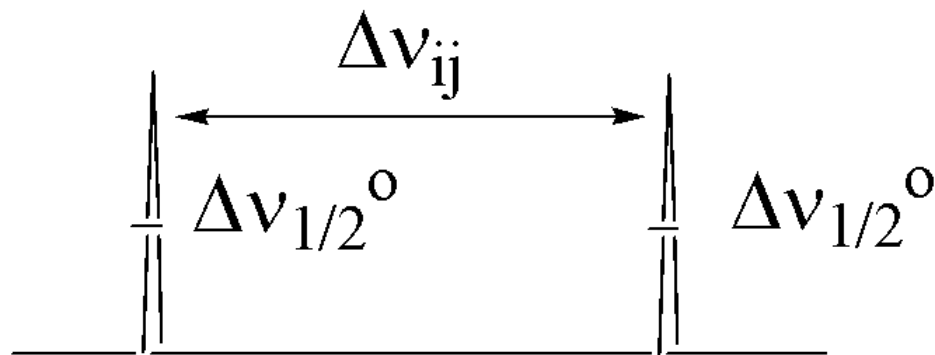
Быстрый обмен

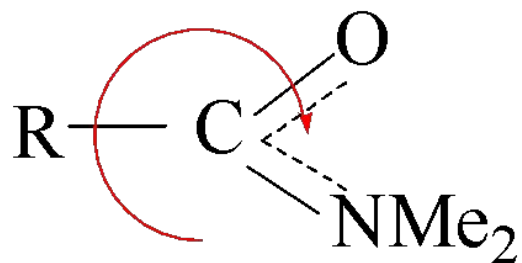
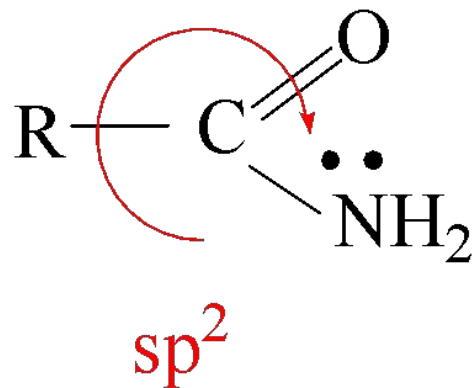
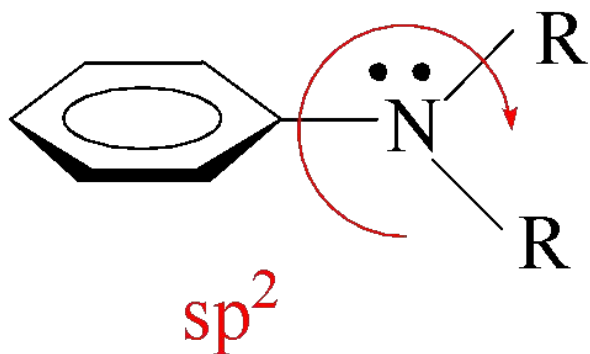
$$k = \frac{\pi \Delta\nu_{ij}^2}{2 (\Delta\nu_{1/2} - \Delta\nu_{1/2}^{\circ})}$$



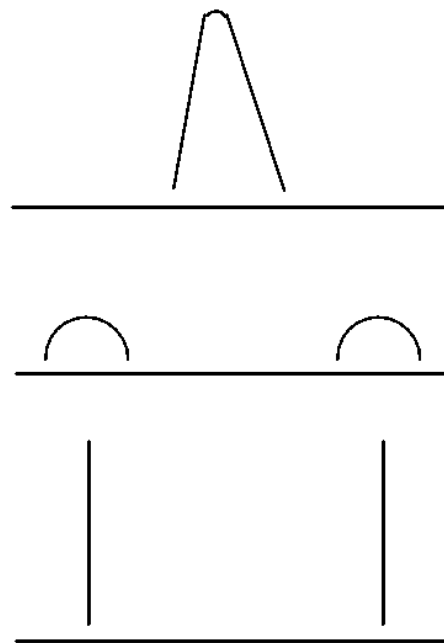
Медленный обмен

$$k = \pi (\Delta\nu_{1/2} - \Delta\nu_{1/2}^{\circ})$$





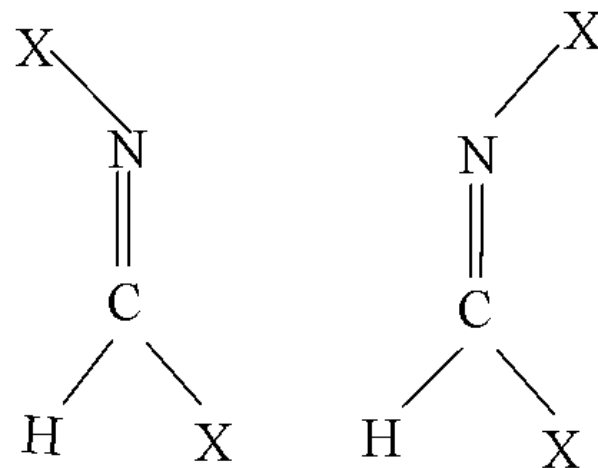
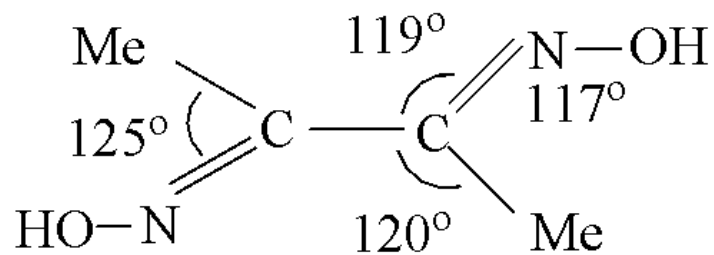
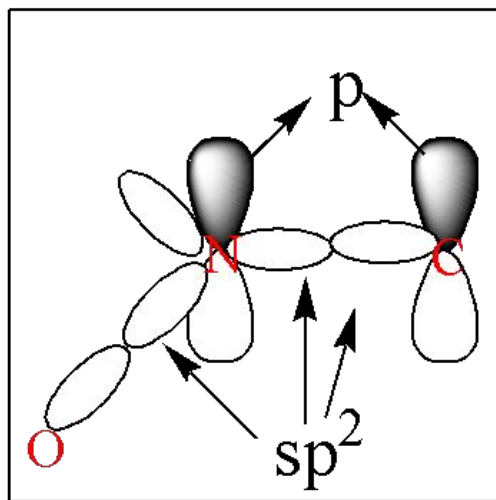
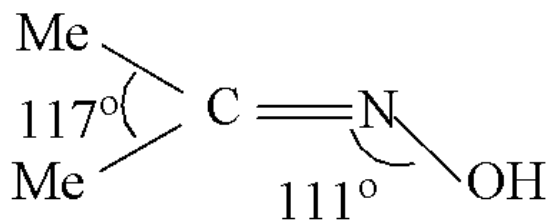
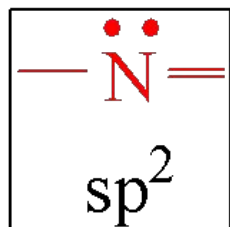
ПМР



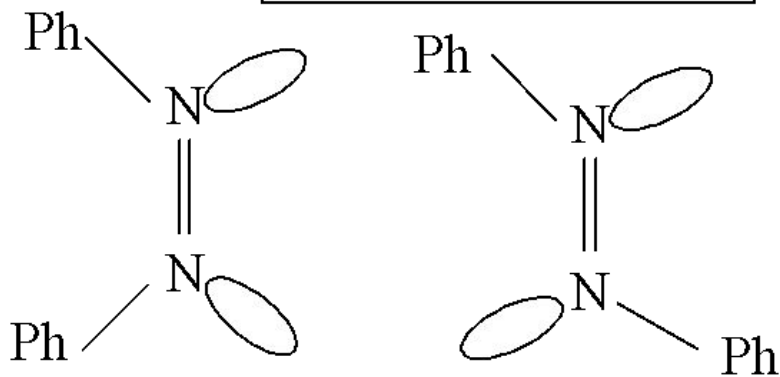
$\Delta G^\ddagger$ , ккал/моль

R	
H	21
Me	17
Ph	15

Физический или химический процесс ?



геометрические изомеры  
ОКСИМОВ

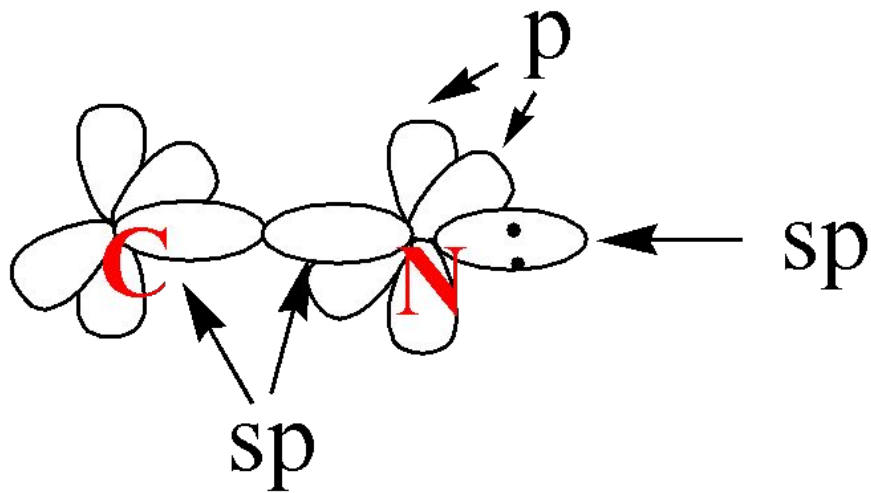
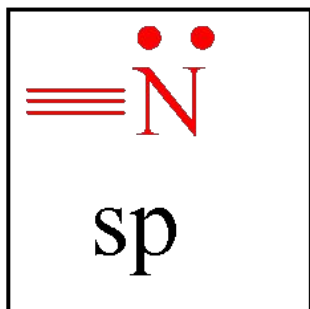


$\mu = 3 D$

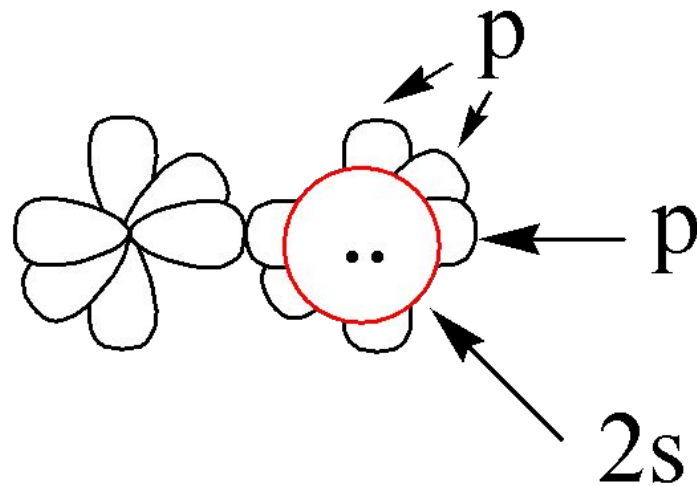
азобензол

$\mu = 0$

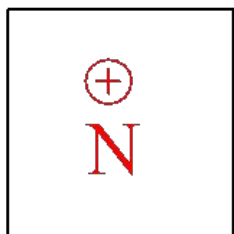




MeCN

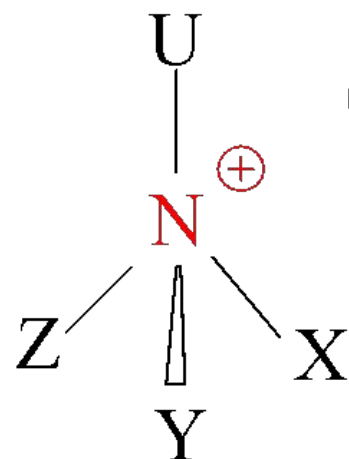
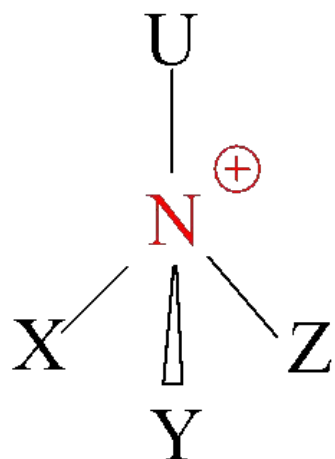


МЕНЕЕ ВЫГОДНА

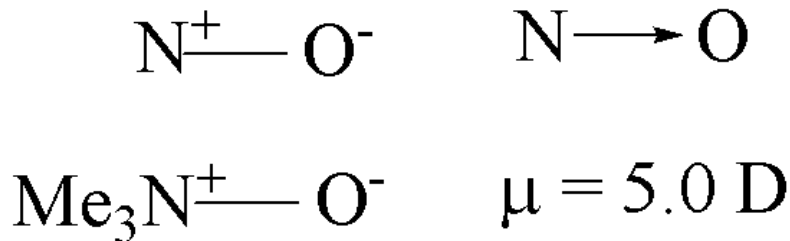
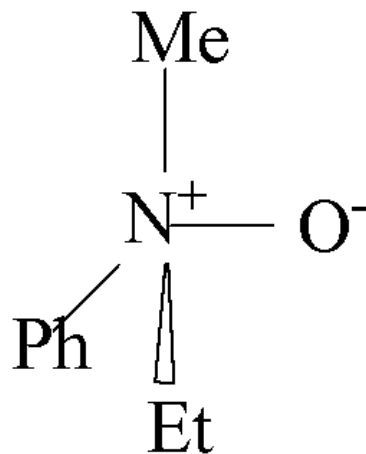


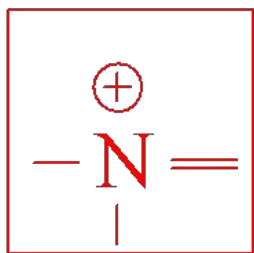
изоэлектронен C

Принцип  
изоэлектронности-  
изоэлектронности-  
изоэлектронности

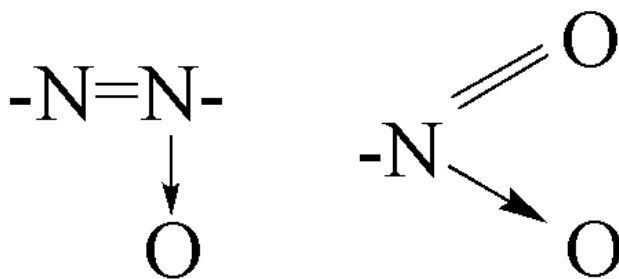


(1899 г. , Me, All, Bz, Ph)

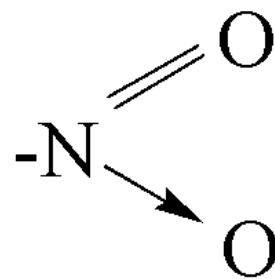




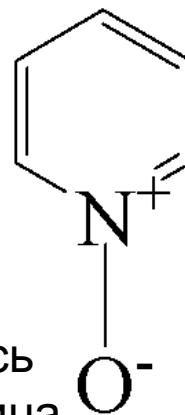
$sp^2$



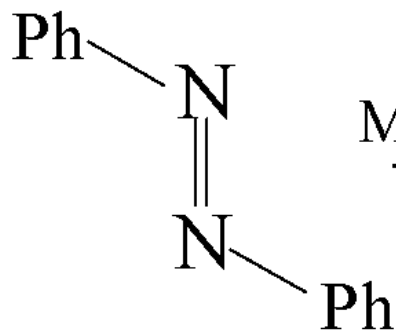
N-оксидная группа



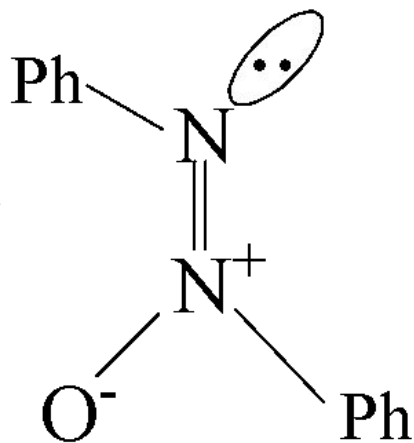
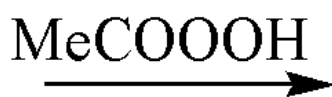
нитро



N-окись пиридина

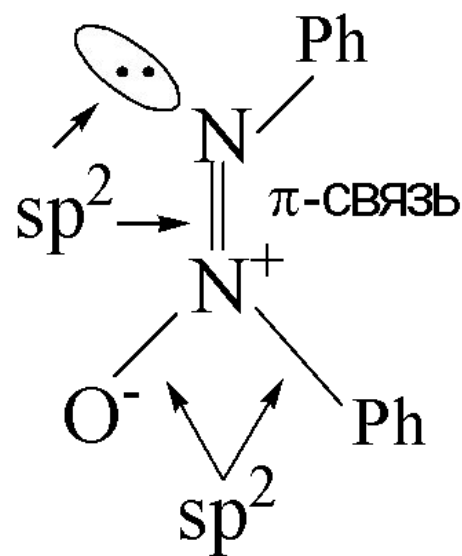


азобензол



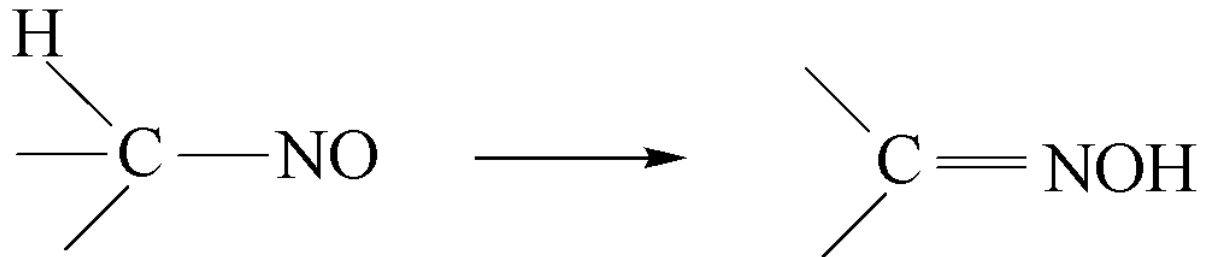
азоксибензол

$\mu = 1.7 \text{ D}$

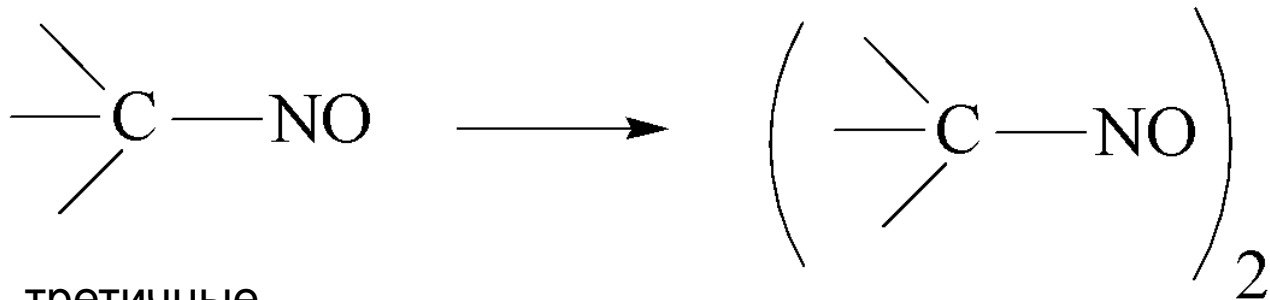


$\mu = 4.7 \text{ D}$

# Нитрозосоединения

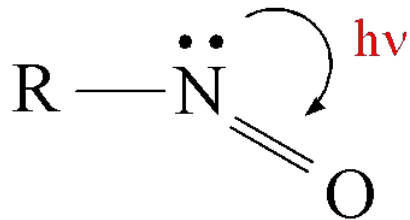


Первичные, вторичные



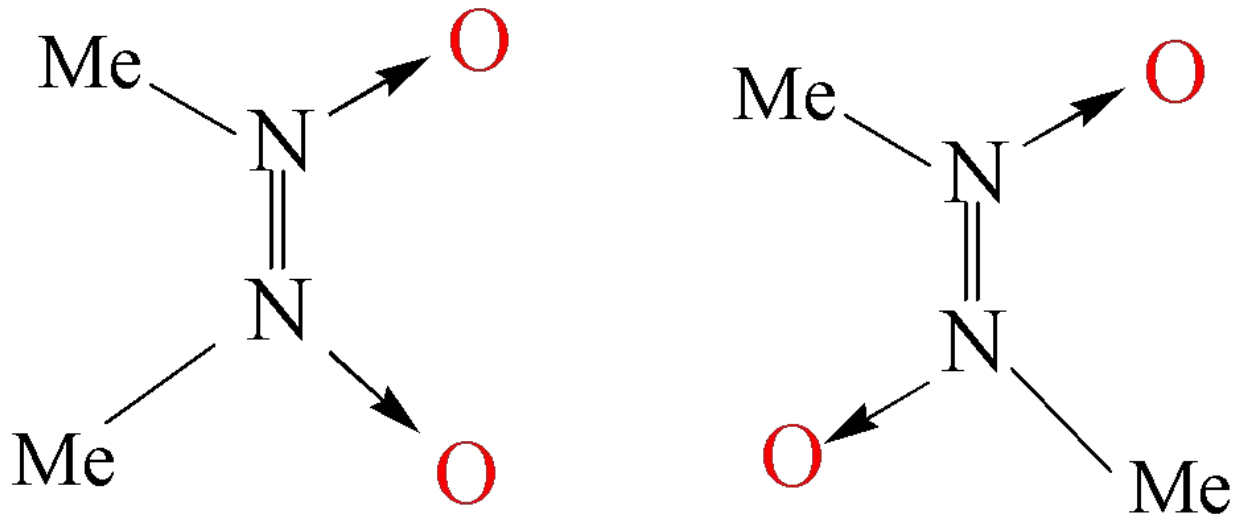
третичные

безцветны

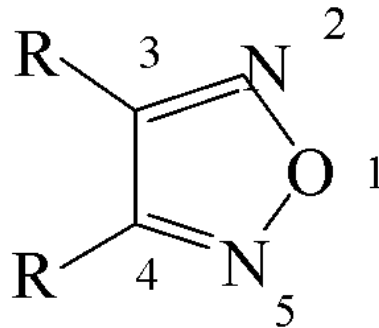
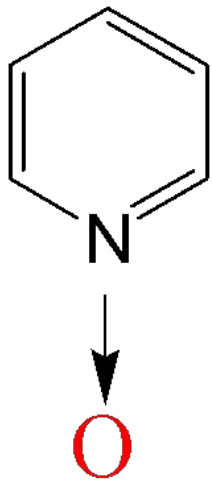


легкость  $n\text{-}\pi^*$  перехода  
голубая окраска, ArH - зеленая

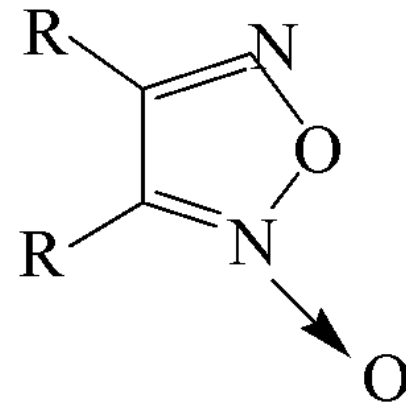
# Геометрическая изомерия диоксидов



## Гетероциклы

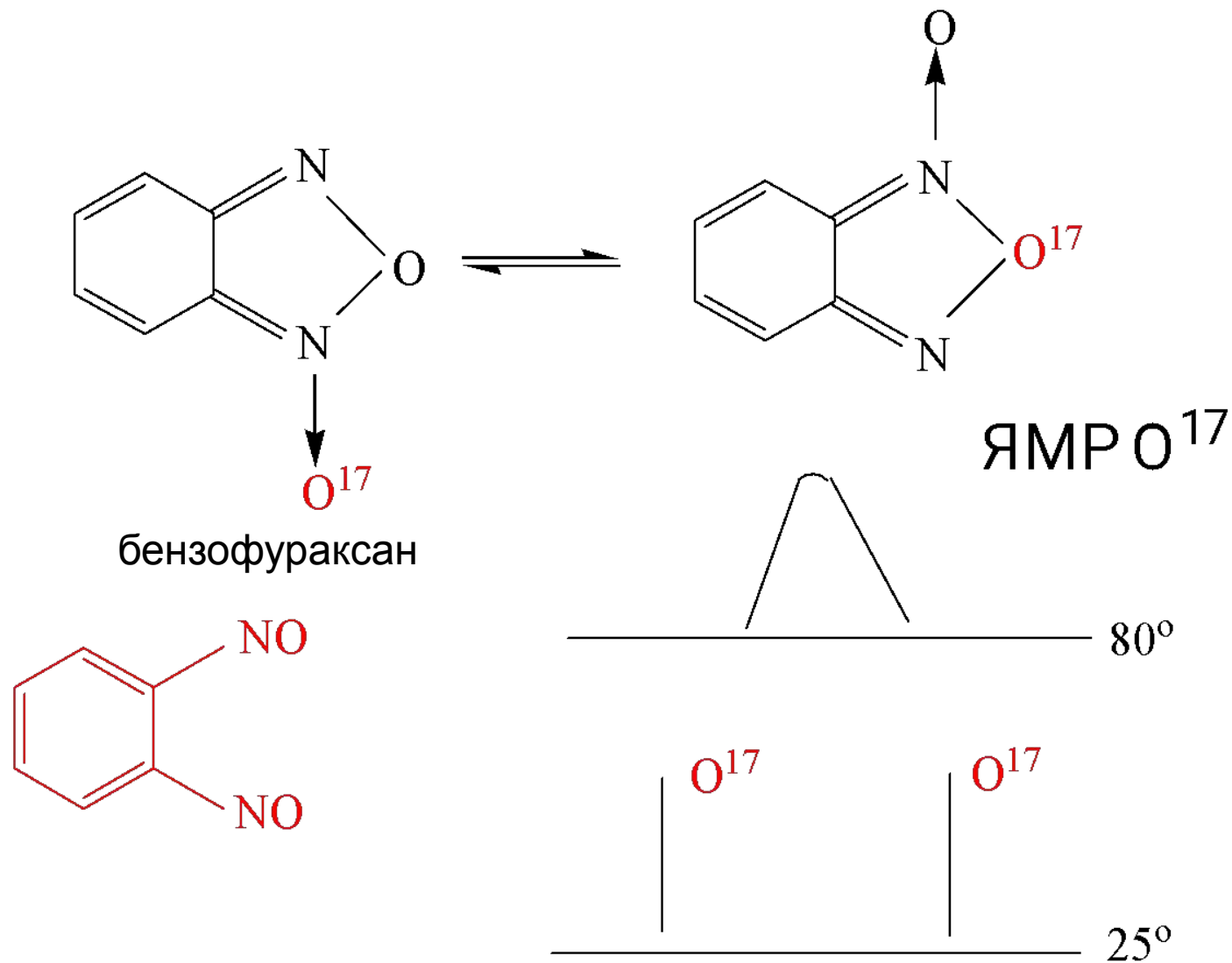


1,2,5-оксодиазол  
(фуразаны)

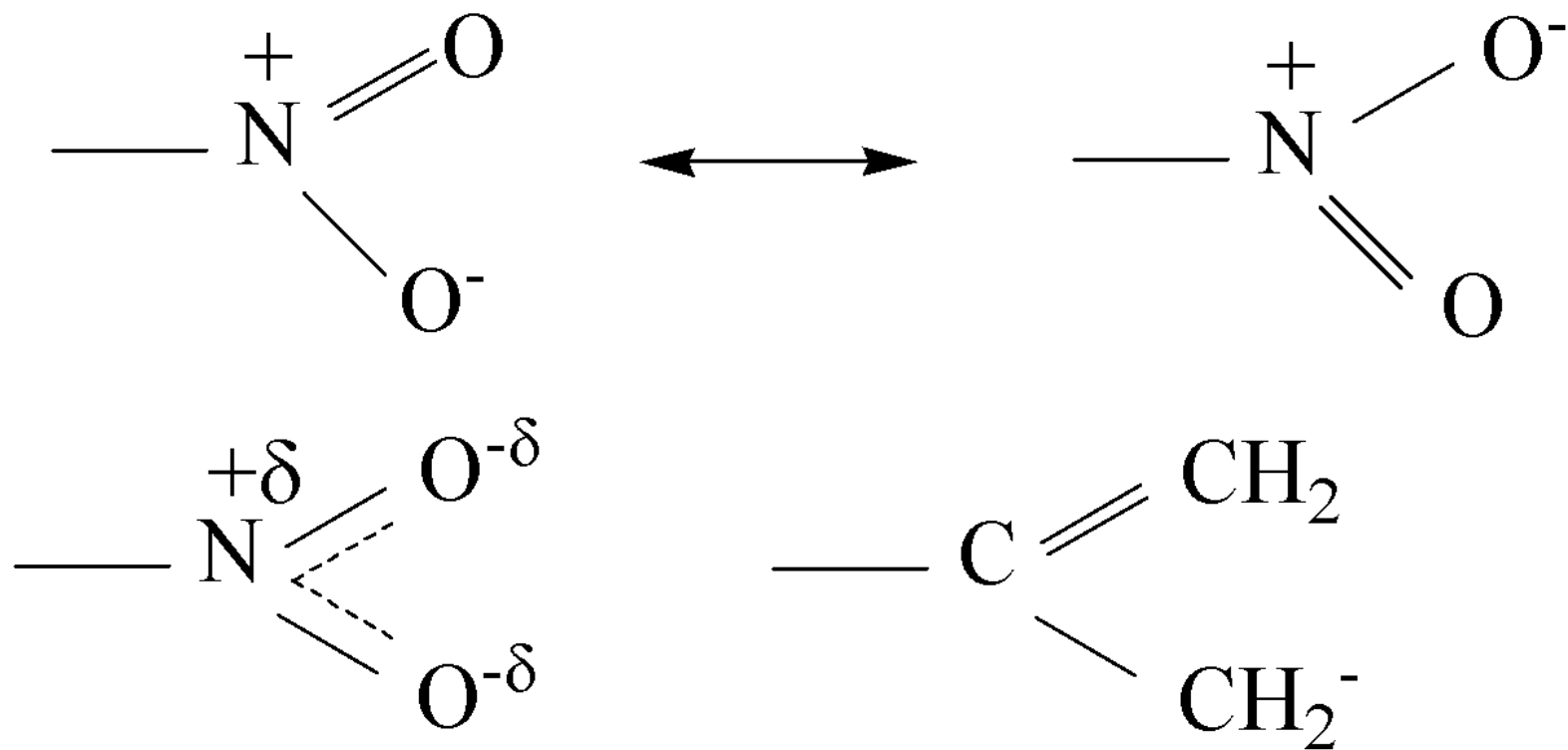


фуразаксаны

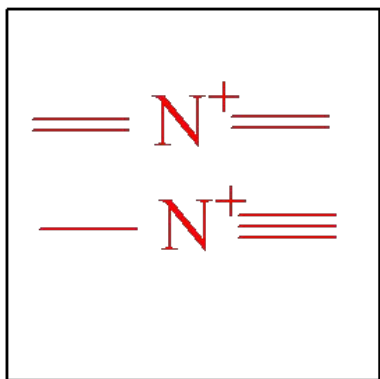
# Вырожденная перегруппировка



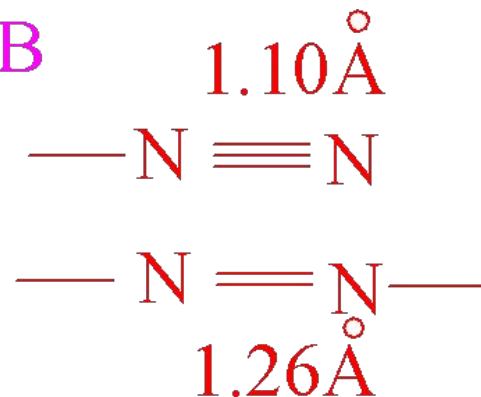
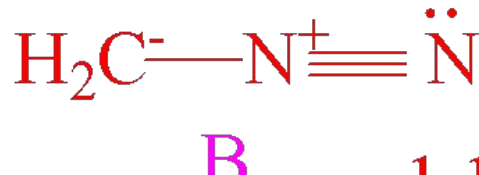
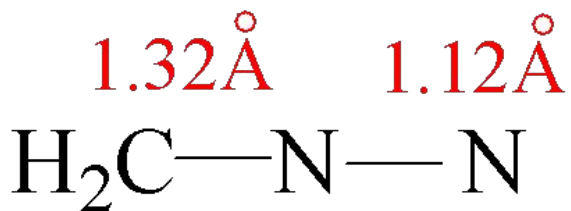
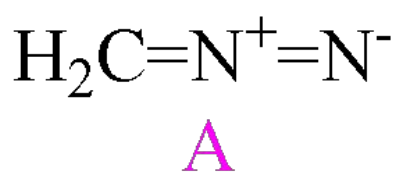
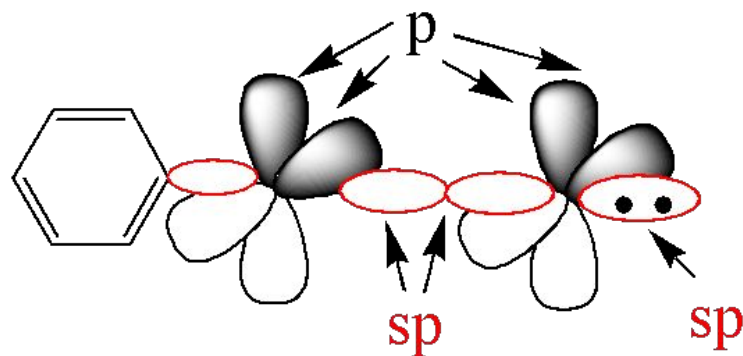
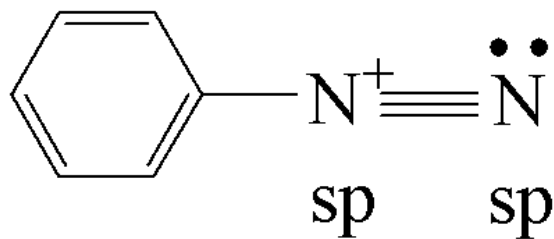
# Нитросоединения



$$\Delta E_{\pi} = 2\beta (1 - a_{\text{ot}}) = 2\beta \left(1 - \sqrt{\frac{1}{2}}\right)$$



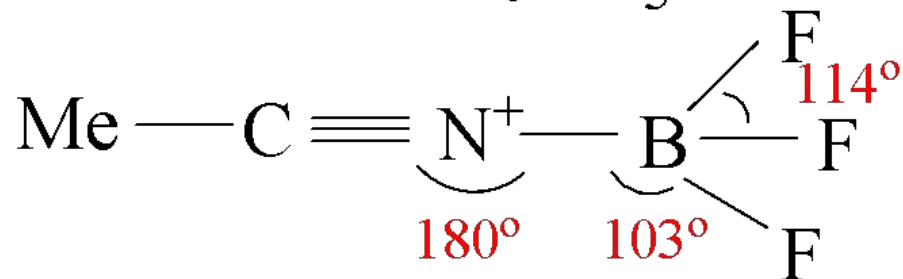
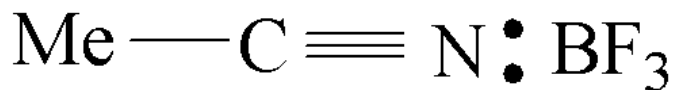
sp



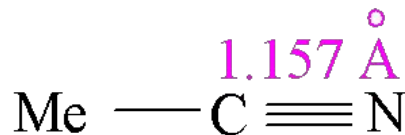
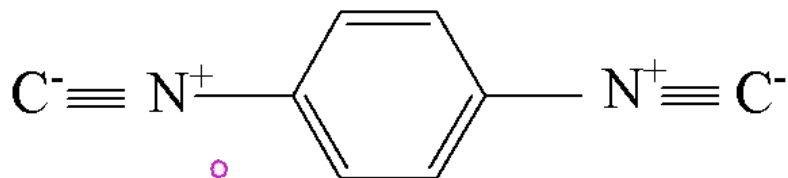
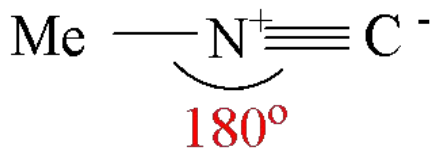
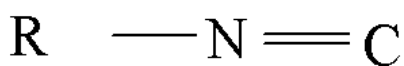
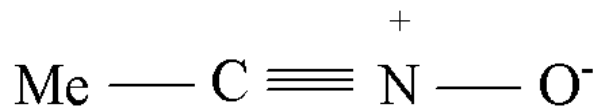
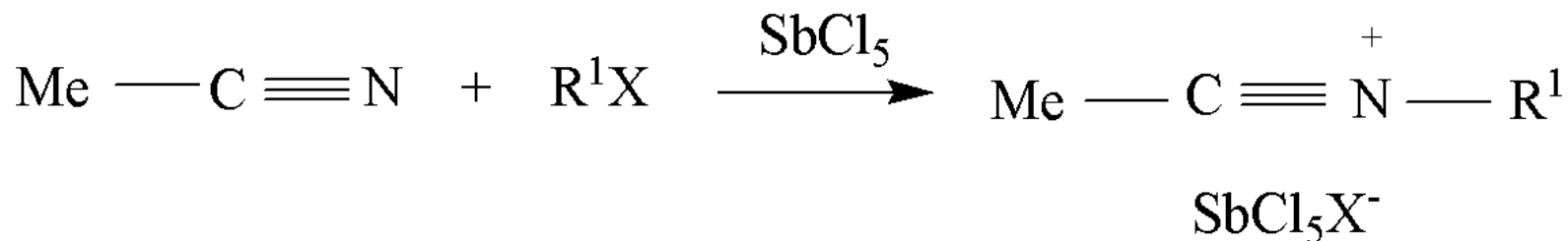
Микроволновая спектроскопия



# Соли нитрилов, окиси нитрилов, изонитрилы



Бент ?



$\mu = 0$