

Теоретические основы органической ХИМИИ

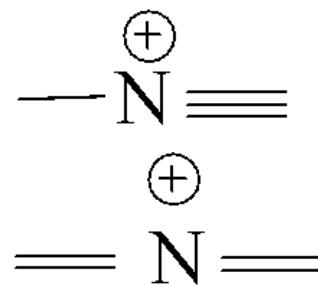
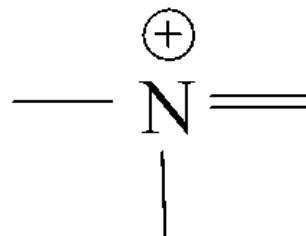
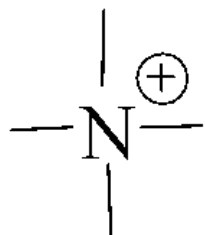
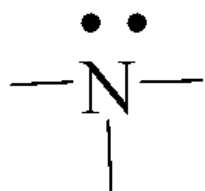
Азотцентрированные соединения.
Теория гибридизации.

Лекция 5

(электронно-лекционный курс)

Проф. Бородкин Г.И.

Теория гибридизации (N, J, F и др.)



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

107°

102°

$r_w^X \quad 2.0$

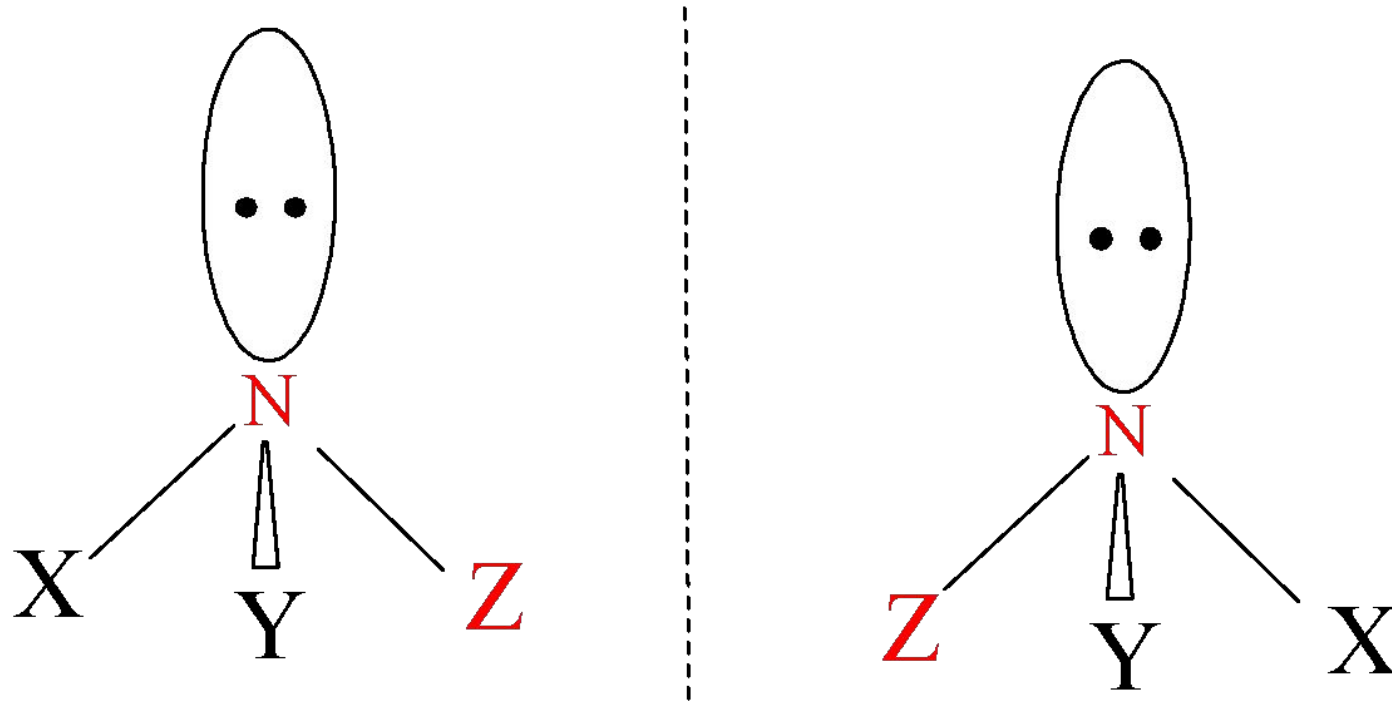
1.2

1.35 \AA

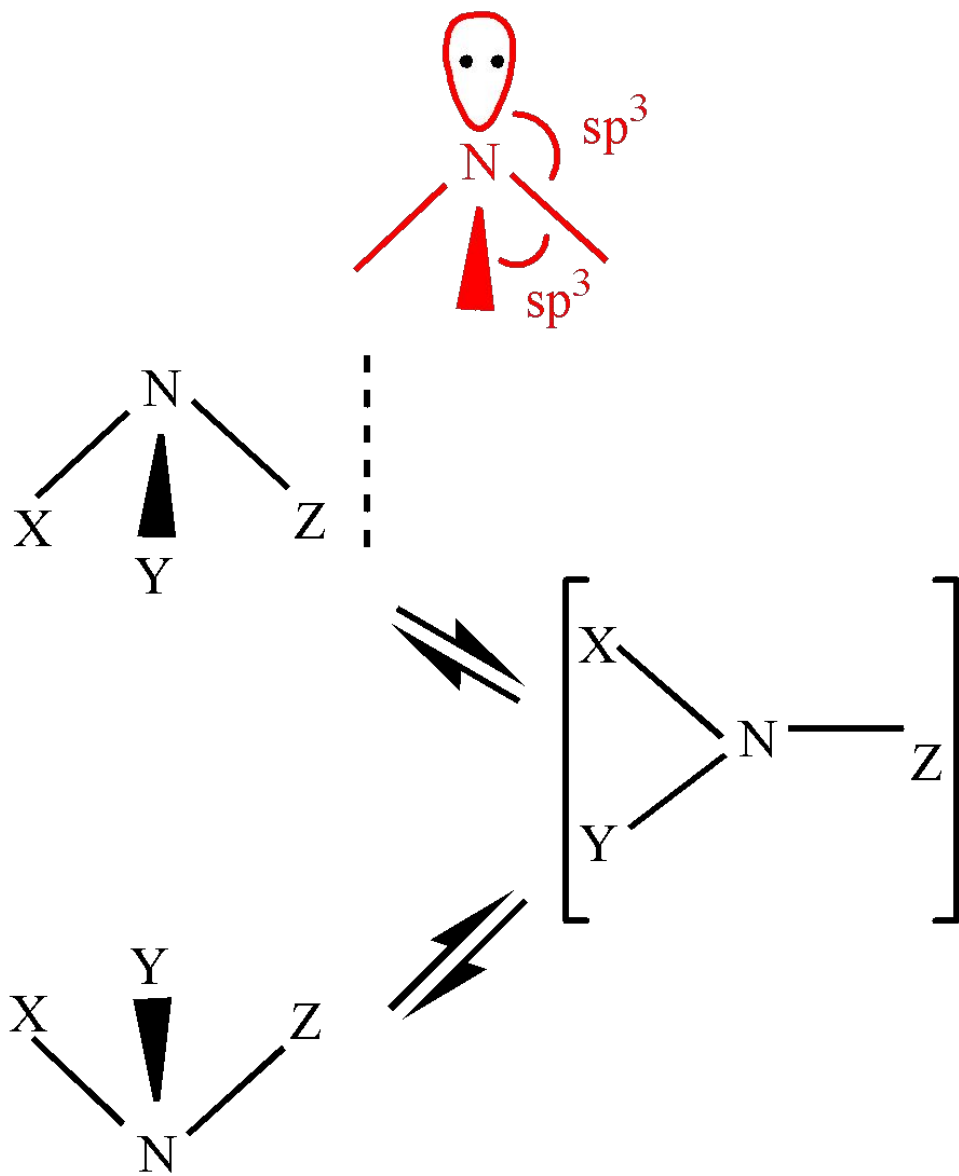
$r_F > r_H$

угол FNF < HNH

правило Бента



Оптическая изомерия ?



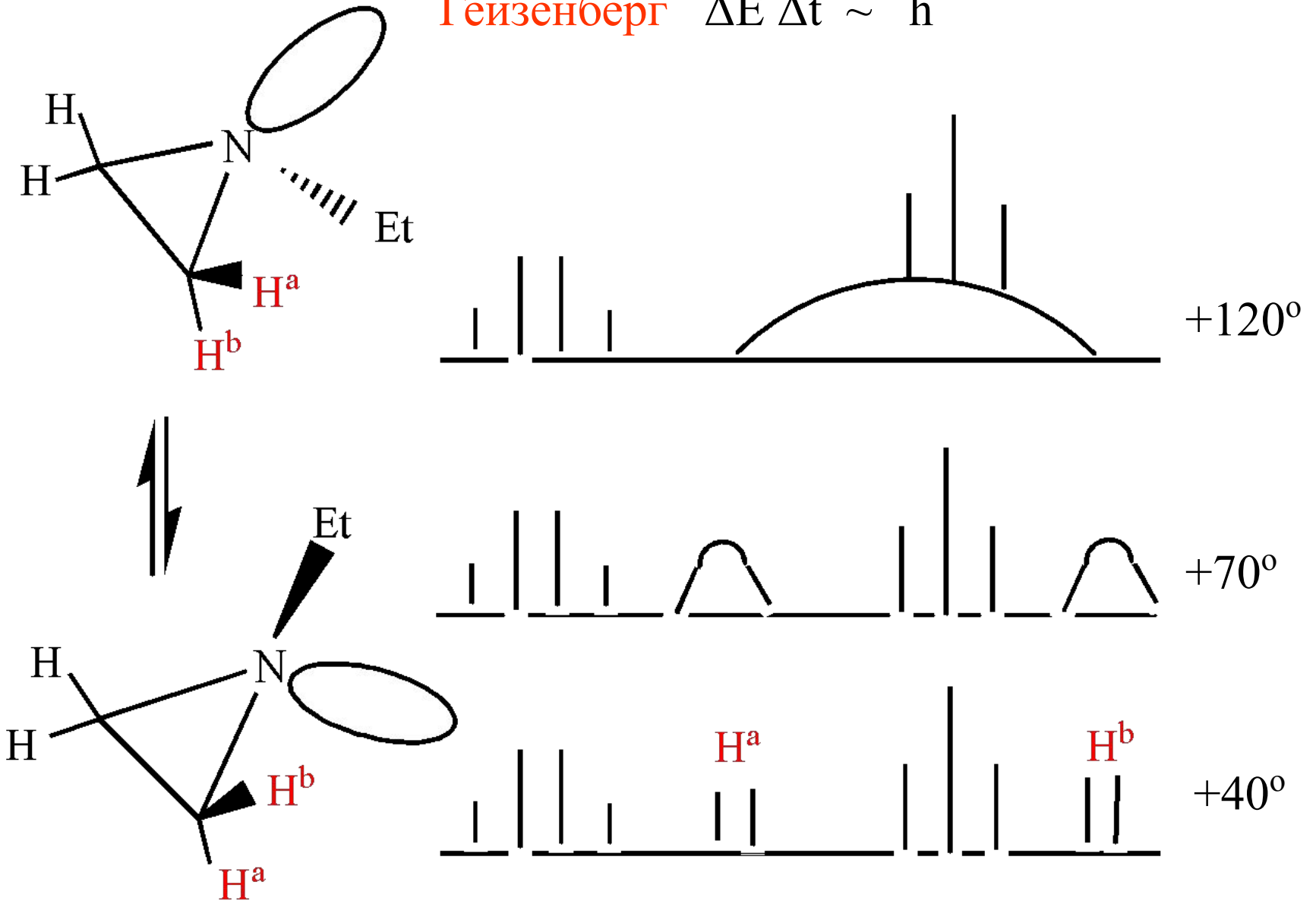
ΔG^\ddagger
инверс.
(ккал/моль)

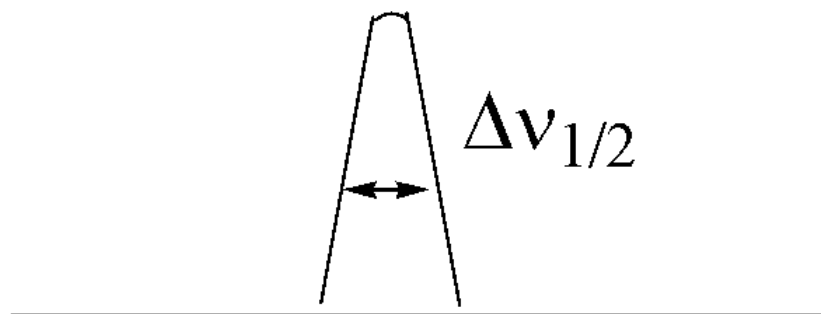
NH_3	5.8 (МВ)
MeNH_2	4.8 «-»
Me_2NH	4.4 «-»
Me_3N	7.5 (ИК)

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

Динамический ЯМР

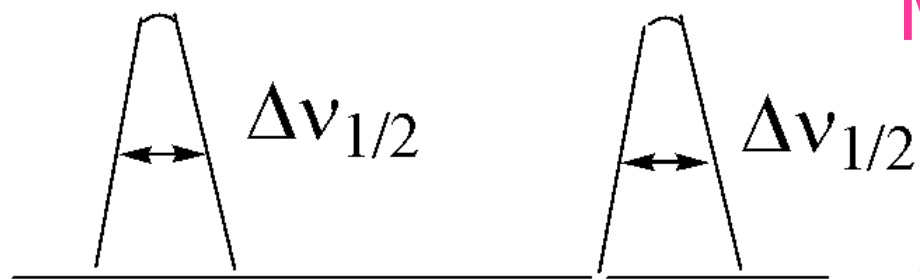
Гейзенберг $\Delta E \Delta t \sim \hbar$





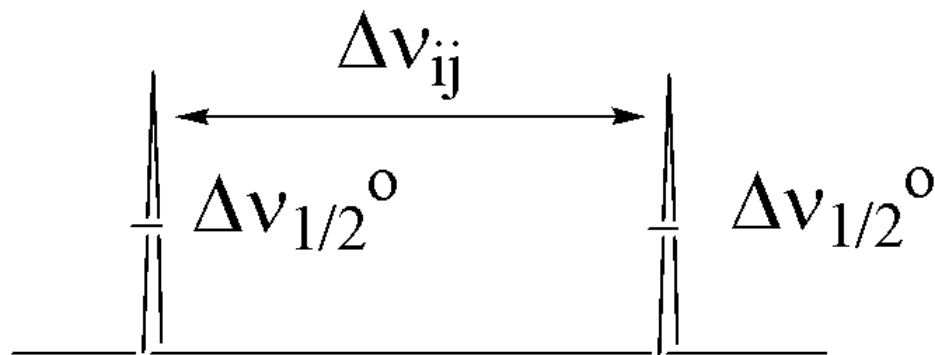
Быстрый обмен

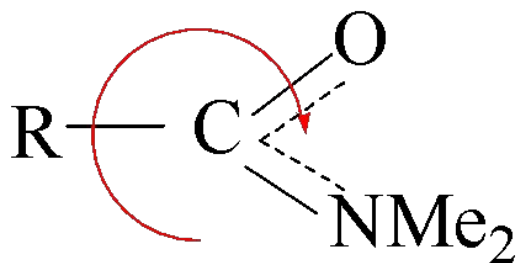
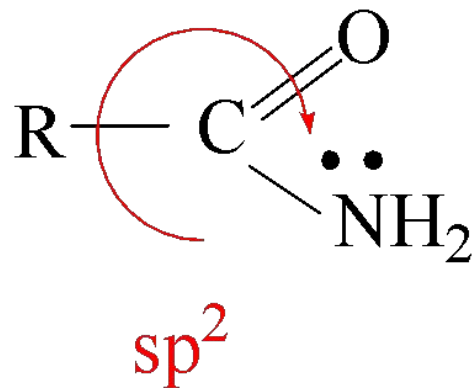
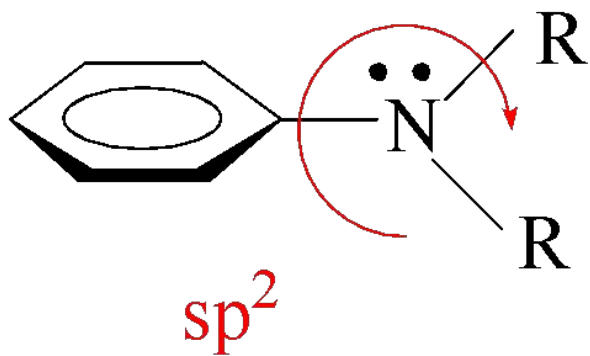
$$k = \frac{\pi \Delta\nu_{ij}^2}{2 (\Delta\nu_{1/2} - \Delta\nu_{1/2}^{\circ})}$$



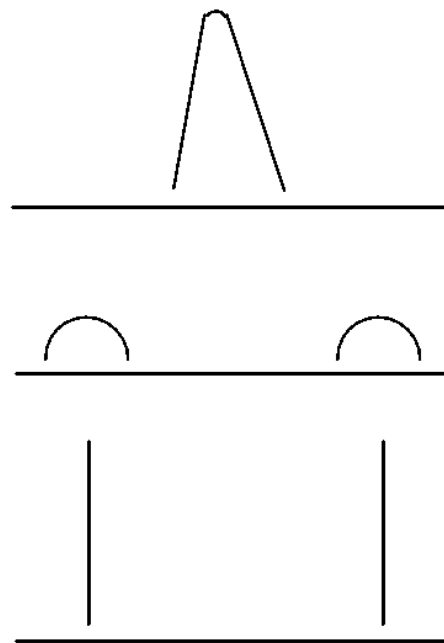
Медленный обмен

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





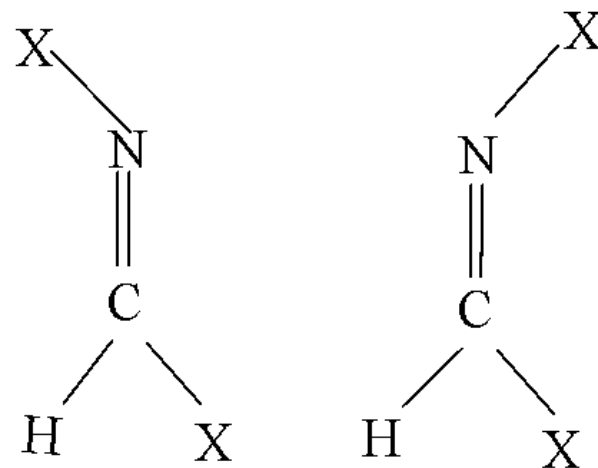
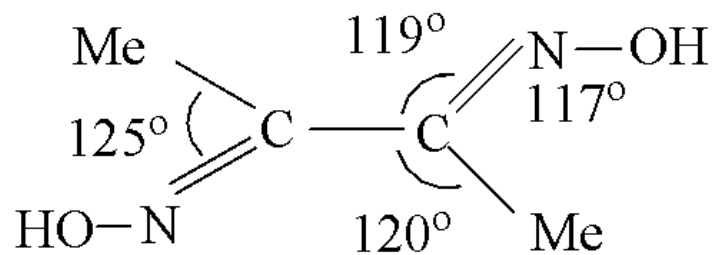
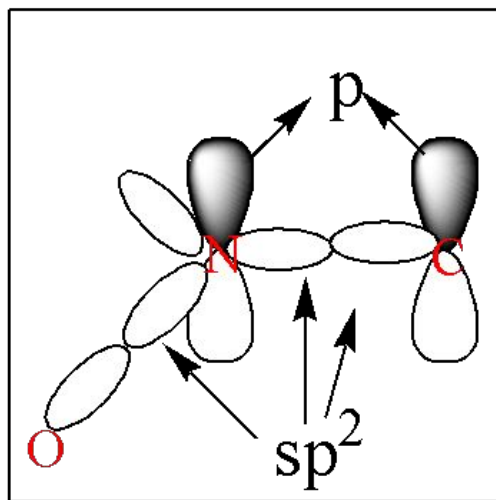
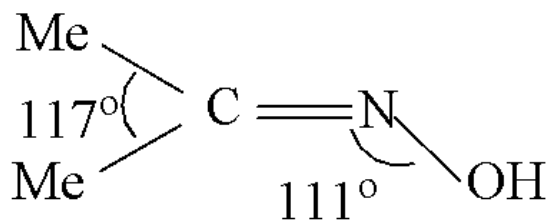
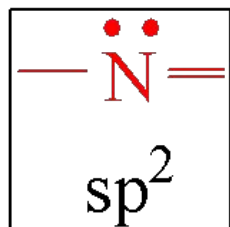
ПМР



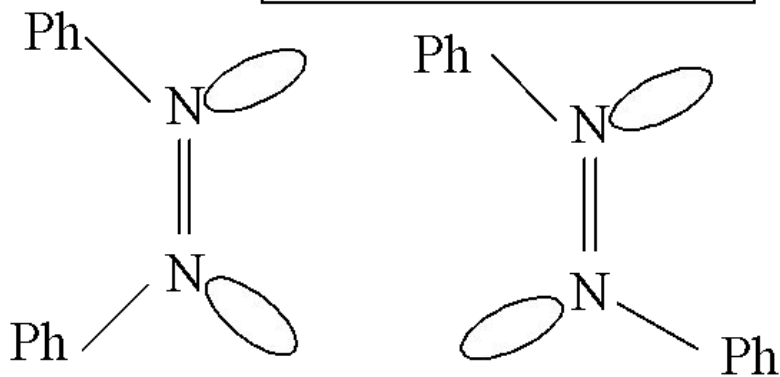
ΔG^\ddagger , ккал/моль

R	
H	21
Me	17
Ph	15

Физический или химический процесс ?



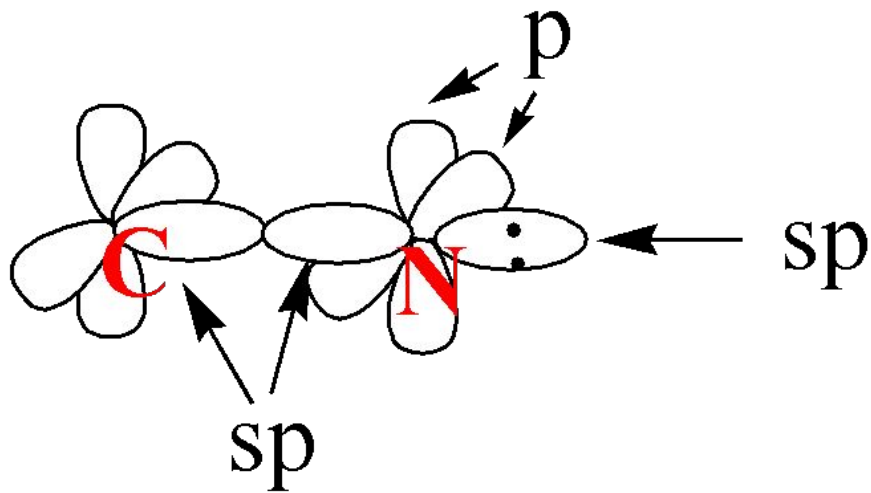
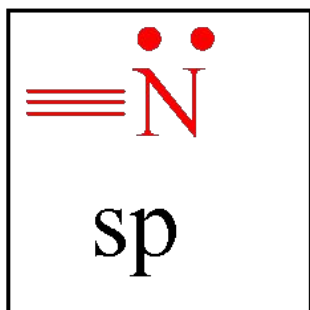
геометрические изомеры
ОКСИМОВ



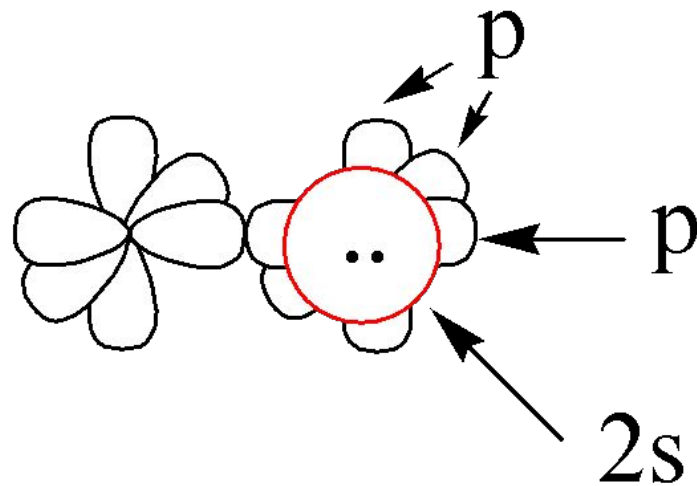
$\mu = 3 D$

азобензол

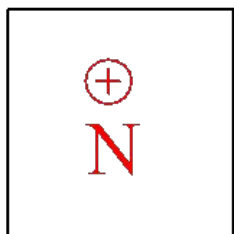
$\mu = 0$



MeCN

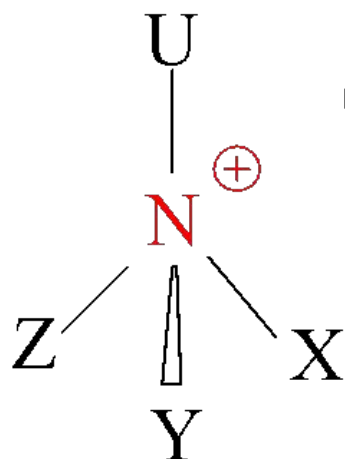
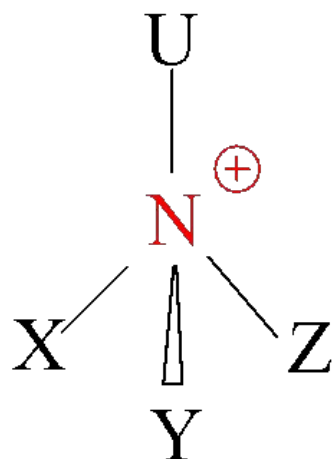


МЕНЕЕ ВЫГОДНА

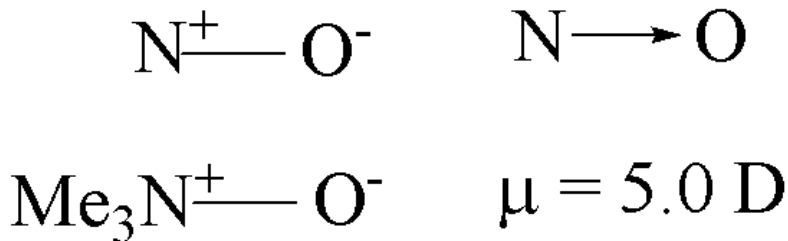
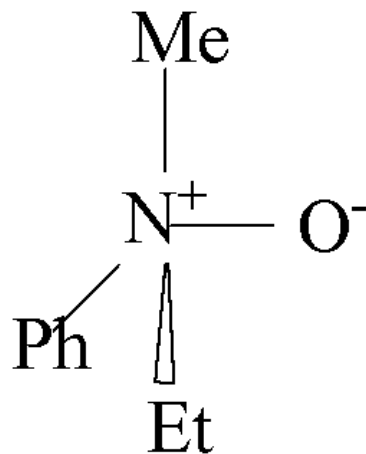


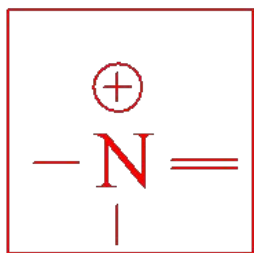
изоэлектронен C

Принцип
изоэлектронности-
изоэлектронности-
изоэлектронности

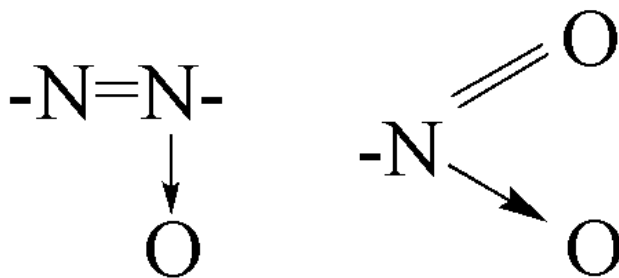


(1899 г. , Me, All, Bz, Ph)

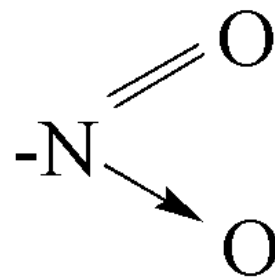




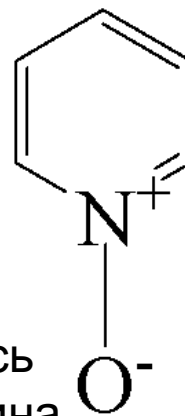
sp^2



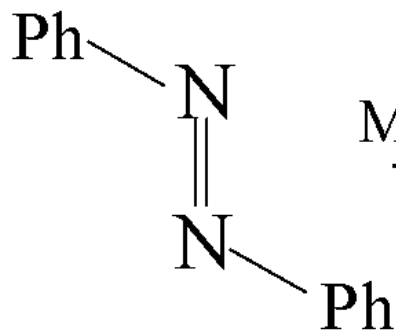
N-оксидная группа



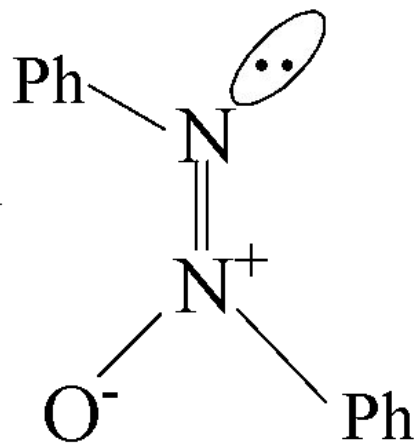
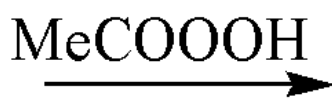
нитро



N-окись пиридина

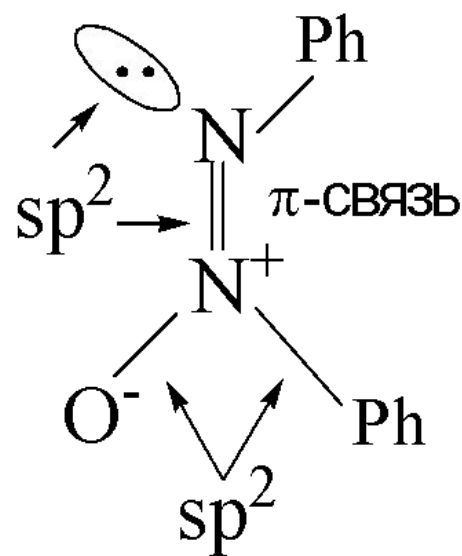


азобензол



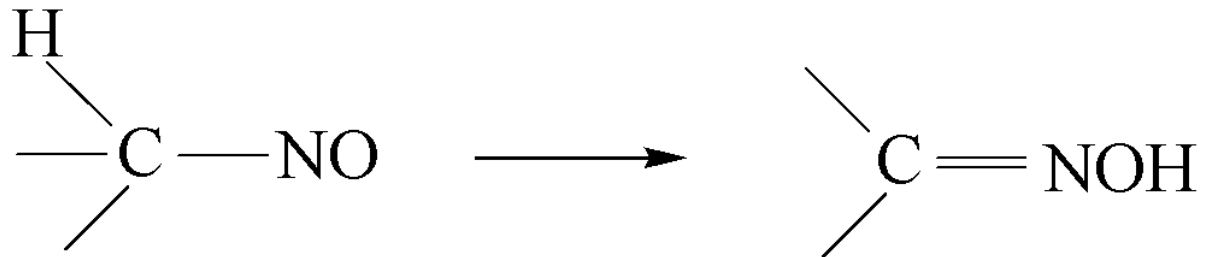
азоксибензол

$\mu = 1.7 \text{ D}$

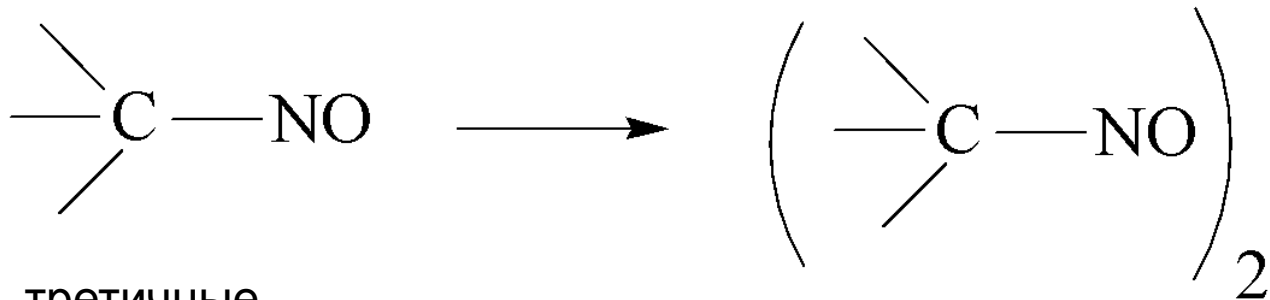


$\mu = 4.7 \text{ D}$

Нитрозосоединения

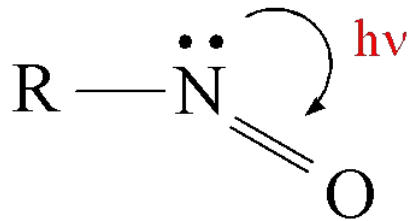


Первичные, вторичные



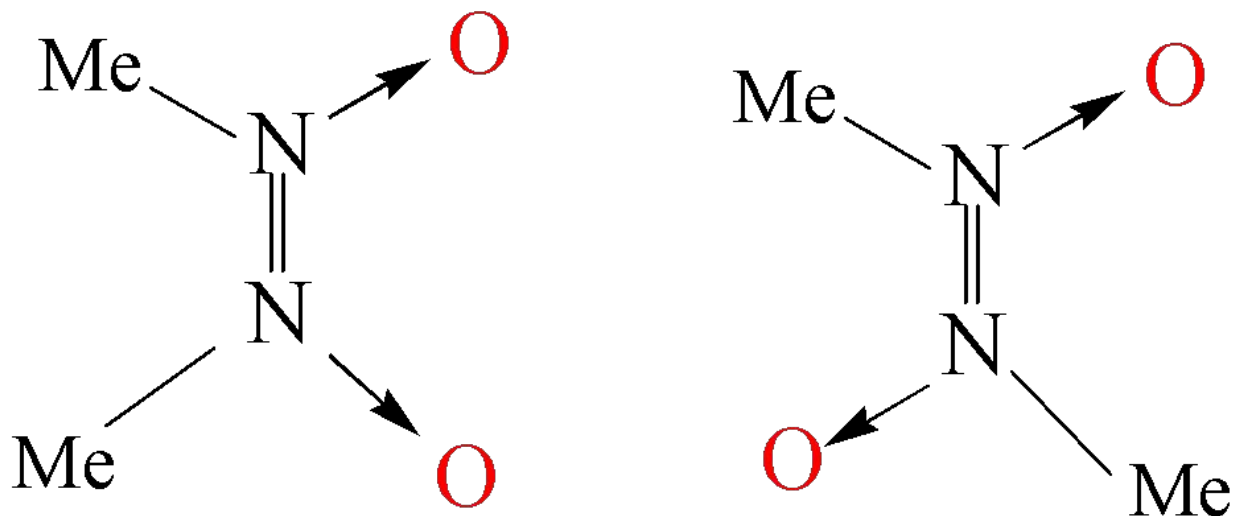
третичные

безцветны

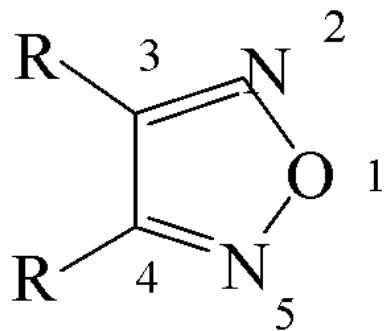
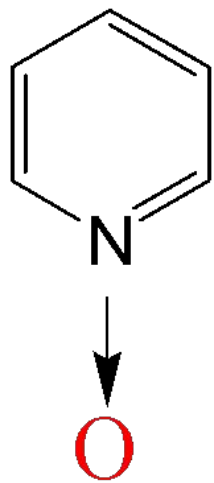


легкость $n\text{-}\pi^*$ перехода
голубая окраска, ArH - зеленая

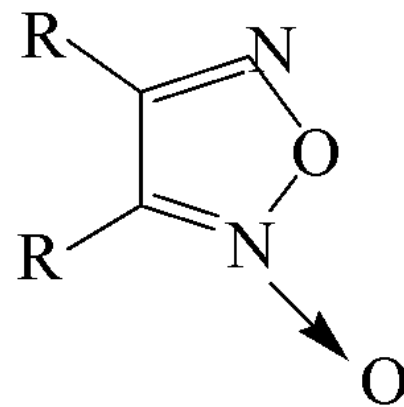
Геометрическая изомерия диоксидов



Гетероциклы

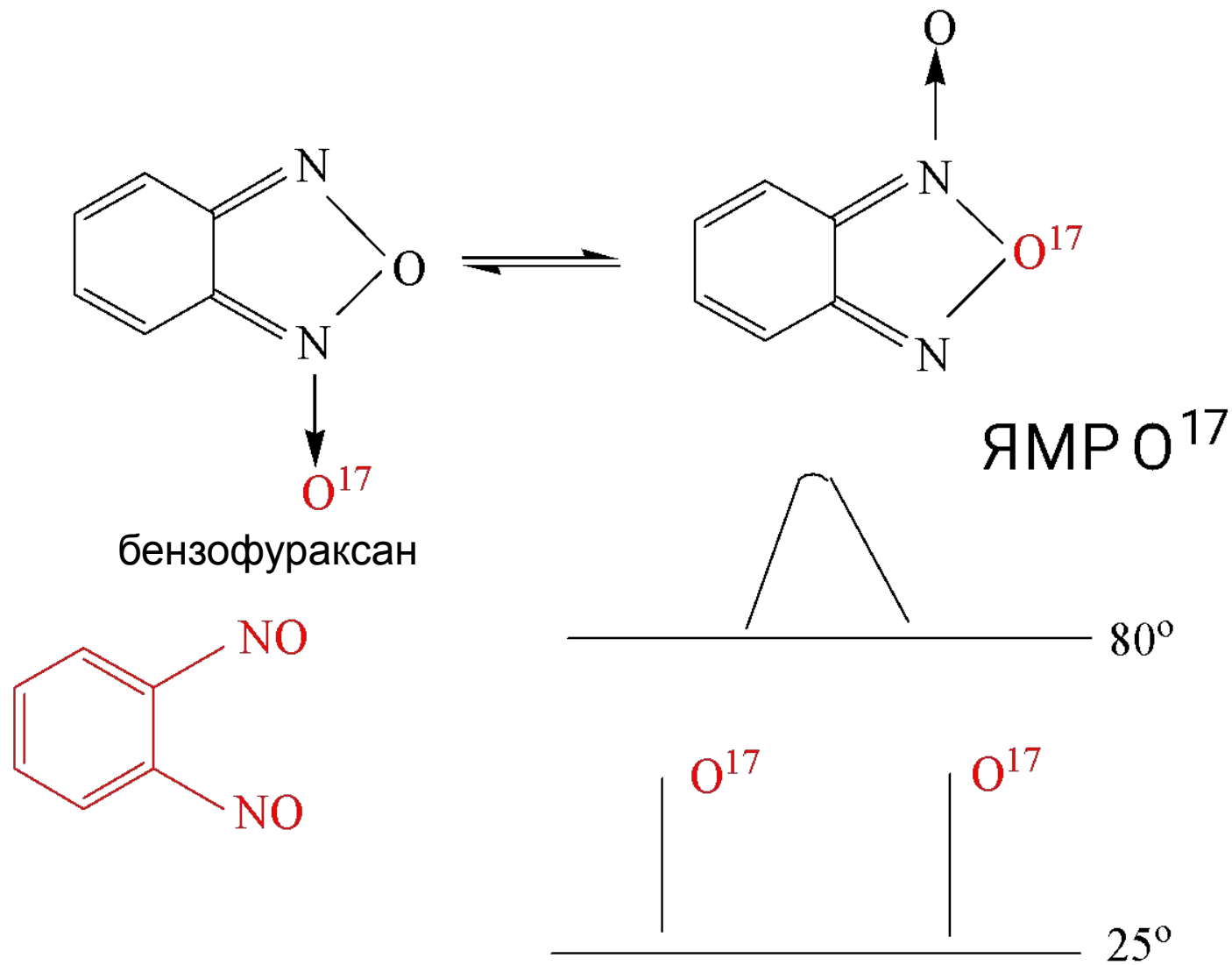


1,2,5-оксодиазол
(фуразаны)

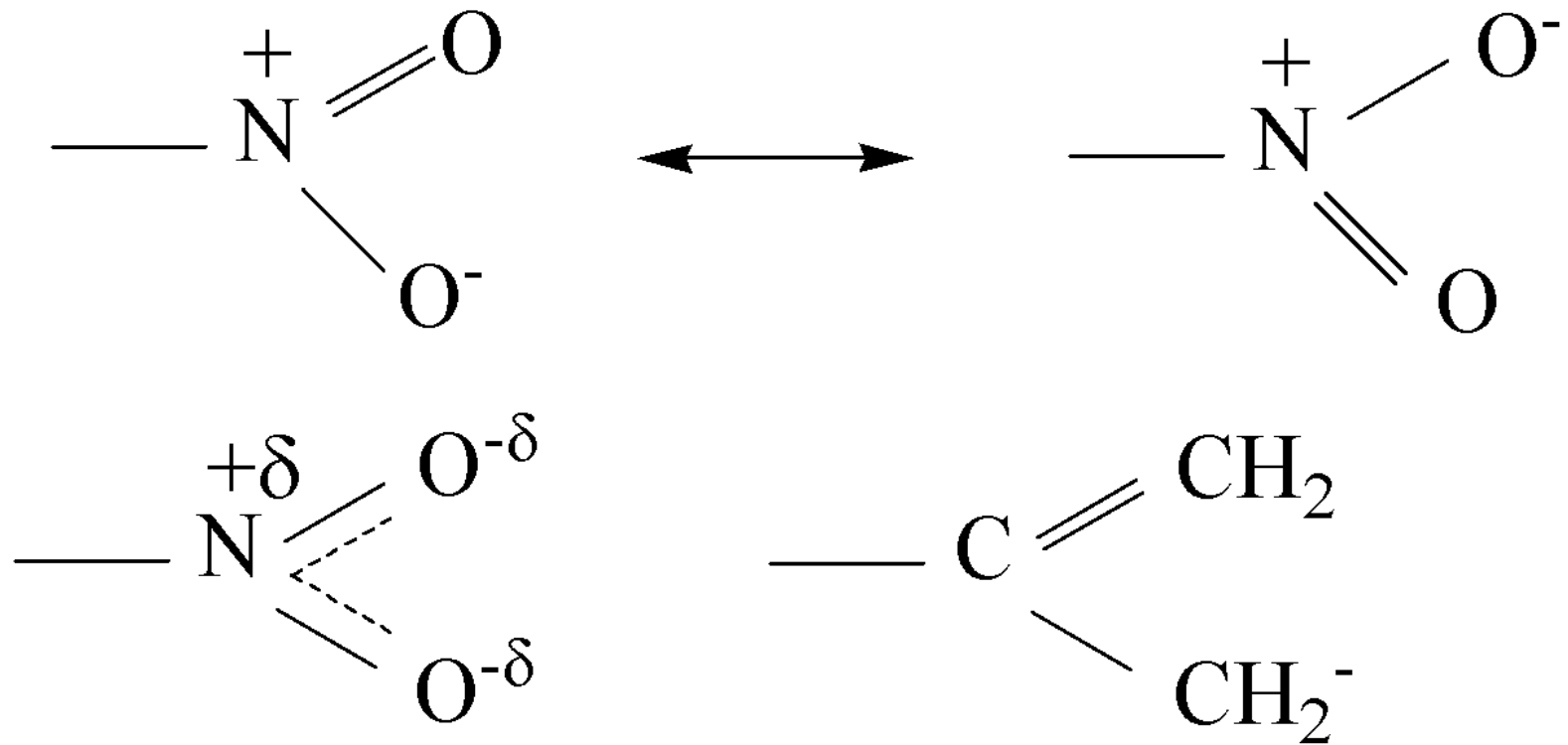


фуразаксаны

Вырожденная перегруппировка

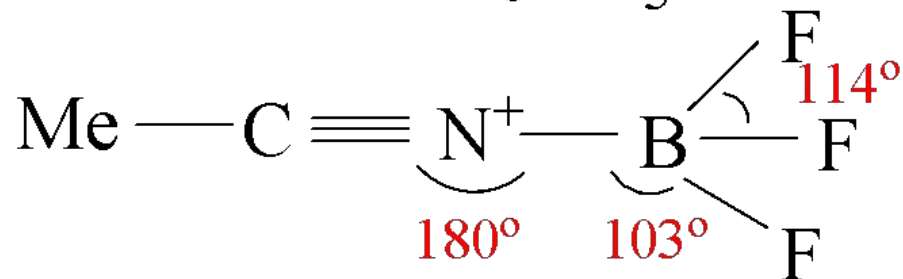
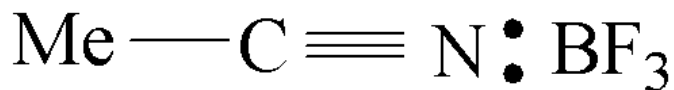


Нитросоединения

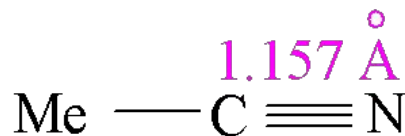
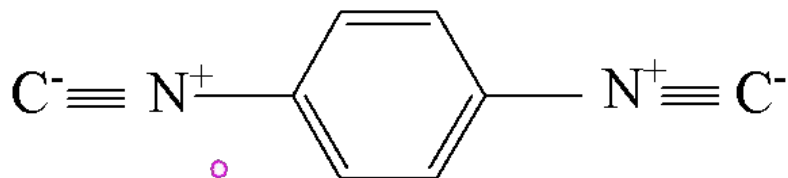
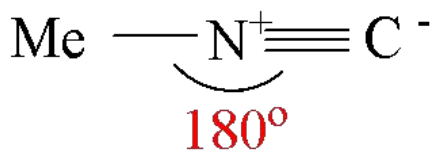
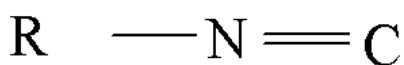
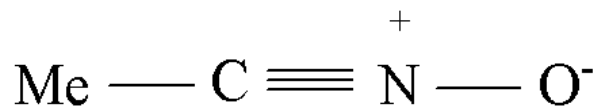
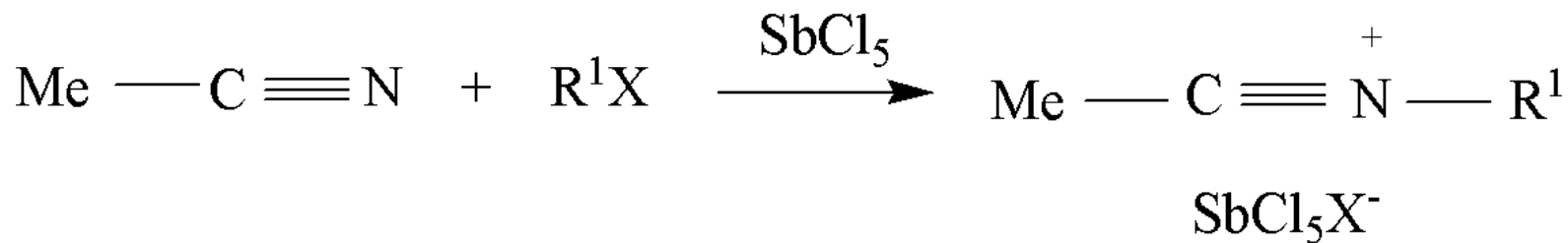


$$\Delta E_{\pi} = 2\beta (1 - a_{ot}) = 2\beta (1 - \sqrt{\frac{1}{2}})$$

Соли нитрилов, окиси нитрилов, изонитрилы



Бент ?



$\mu = 0$