Теоретические основы органической химии

Азотцентрированные соединения. Теория гибридизации.

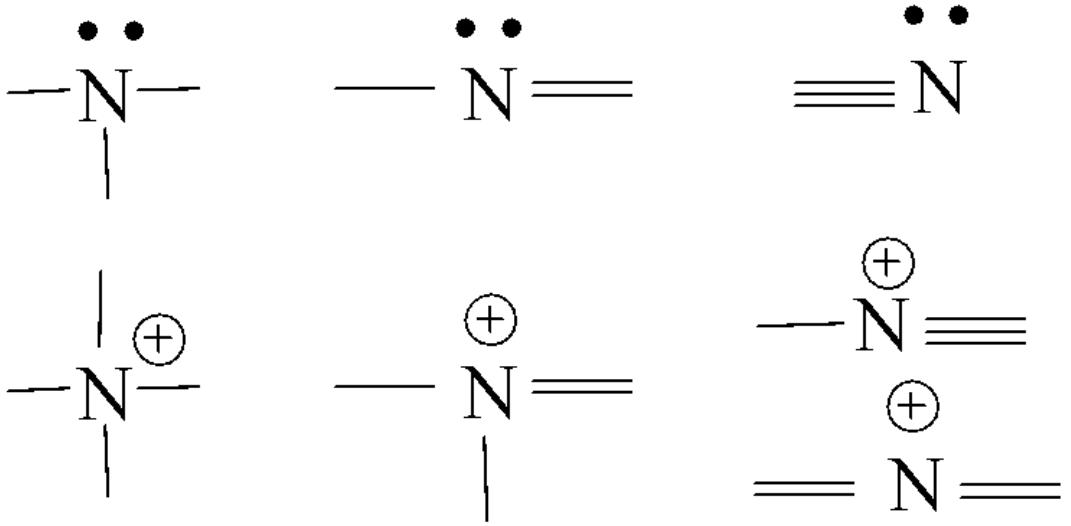
Лекция 5

(электронно-лекционный курс)

Проф. Бородкин Г.И.

Теория гибридизации (N, J, F и др.)

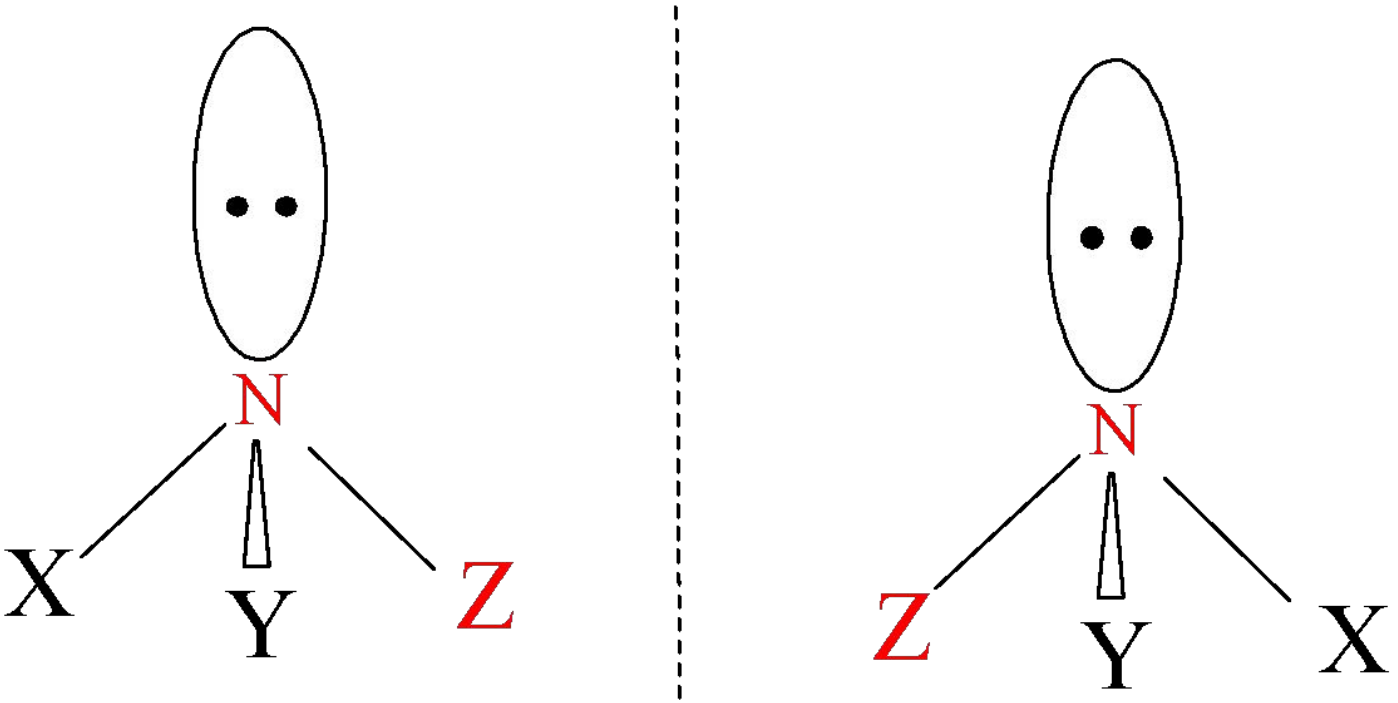
N $1s^2 2s^2 2p^3$



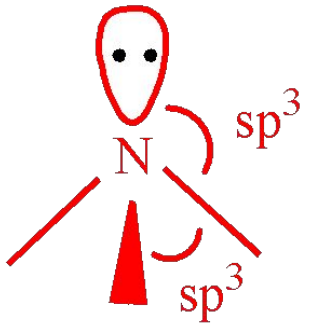
	NMe_3	NH_3	NF_3
$\angle$ XNX	109°	107°	102°
r_w^X	2.0	1.2	1.35 Å

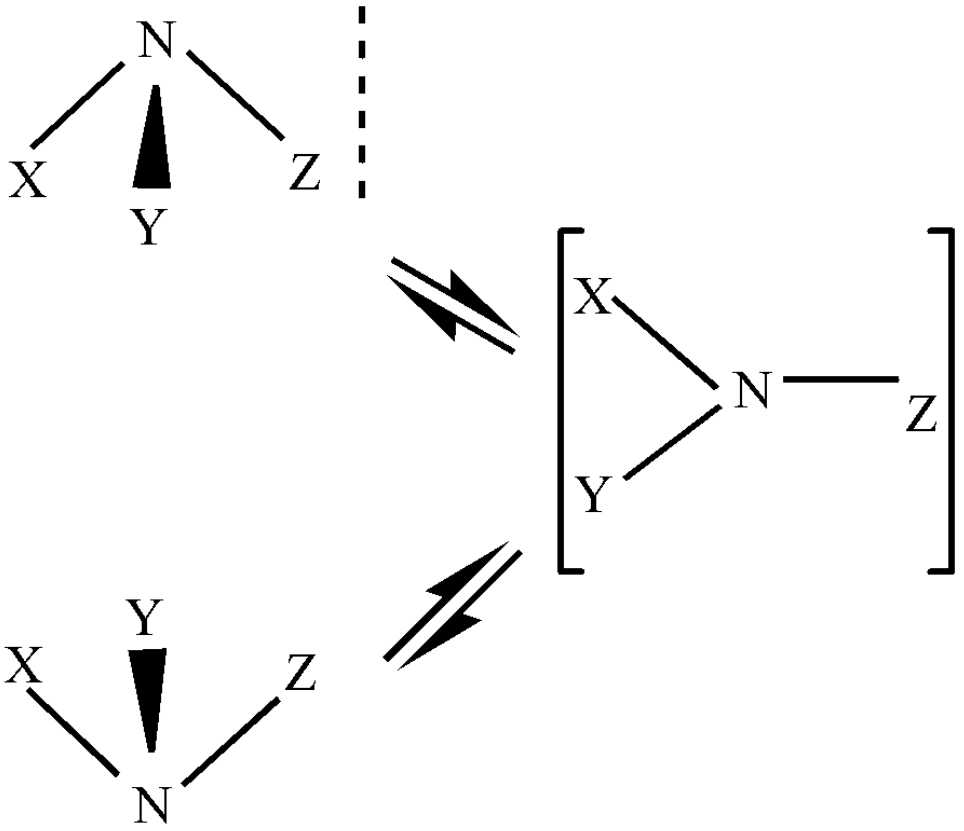
$r_F > r_H$ угол FNF < HNH

правило Бента



Оптическая изомерия ?





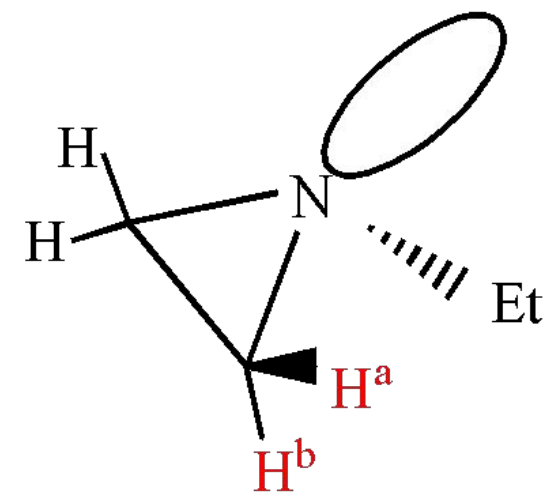
$\Delta G^{\neq}_{\text{инверс.}}$ (ккал/моль)

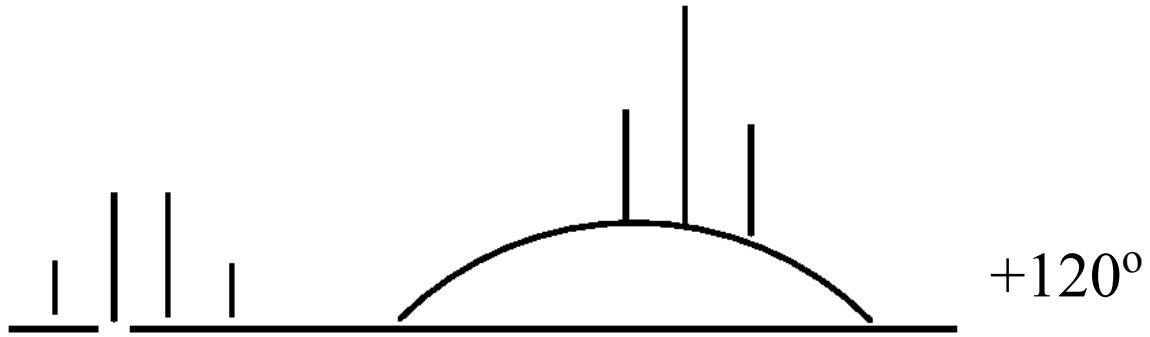
NH_3	5.8 (МВ)
$MeNH_2$	4.8 «-»
Me_2NH	4.4 «-»
Me_3N	7.5 (ИК)

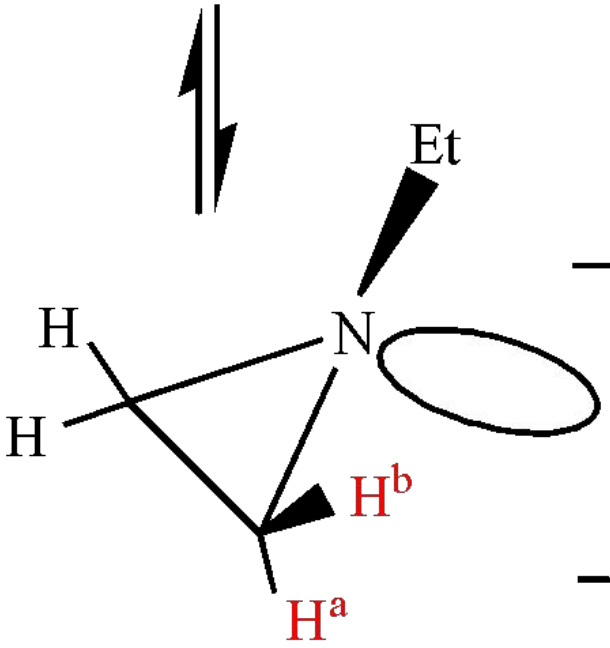
k_{25^o} (NH_3) 10^9 сек$^{-1}$

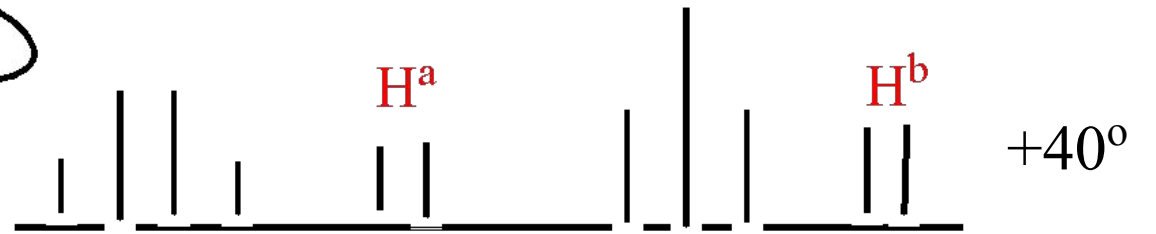
Динамический ЯМР

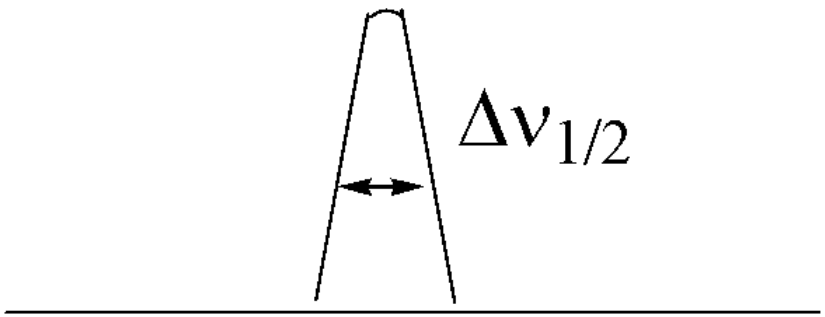
Гейзенберг $\Delta E \, \Delta t \sim \hbar$





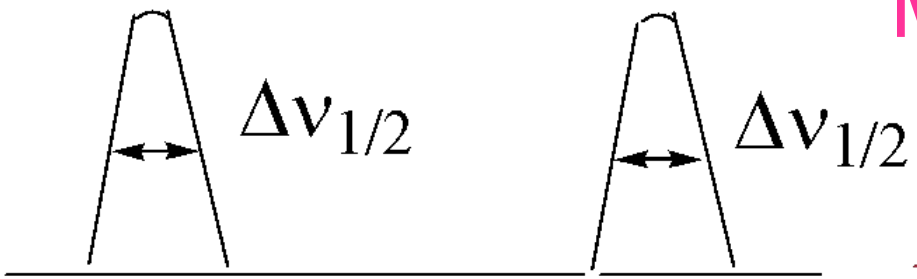






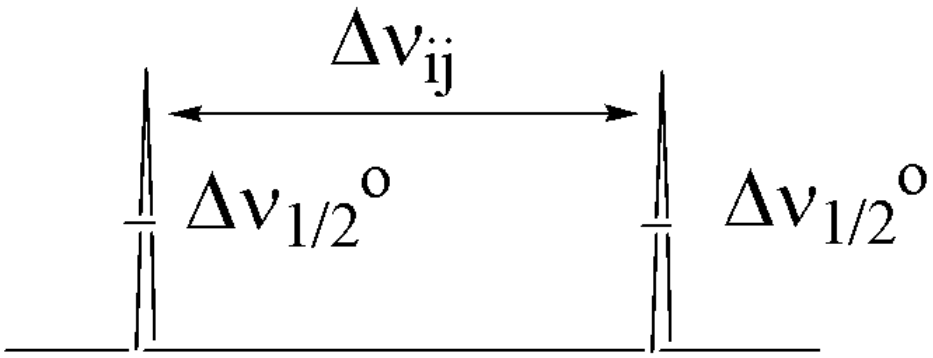
Быстрый обмен

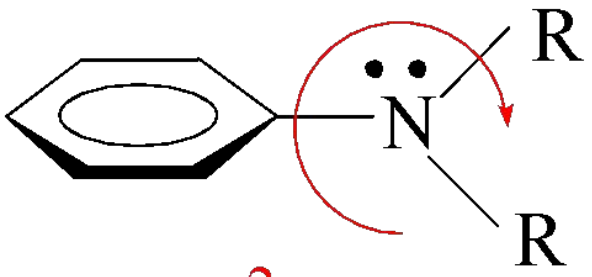
$$k = \frac{\pi \ \Delta\nu_{ij}^{2}}{2\ (\Delta\nu_{1/2} - \Delta\nu_{1/2}^{o})}$$



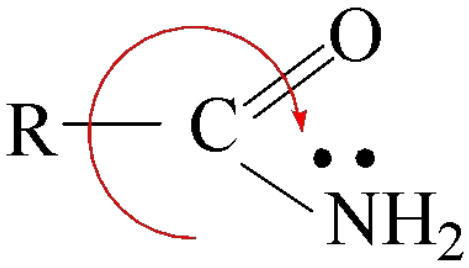
Медленный обмен

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

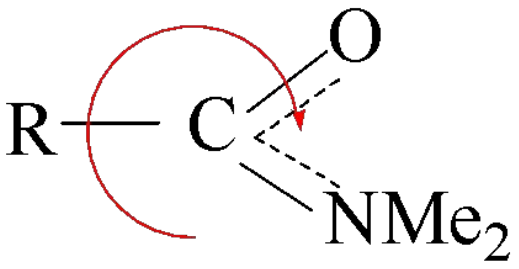




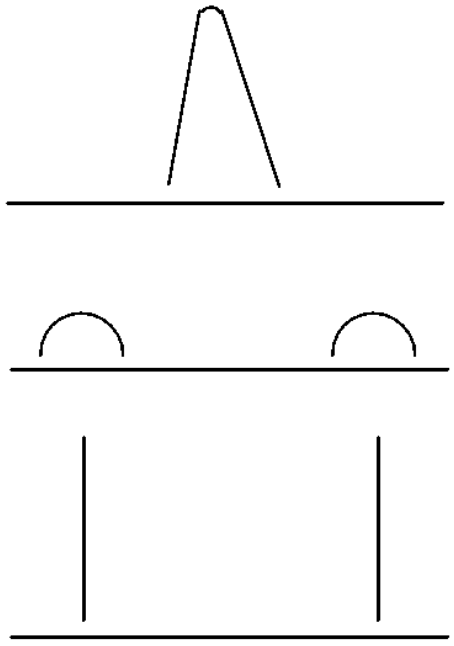
sp^2



sp^2



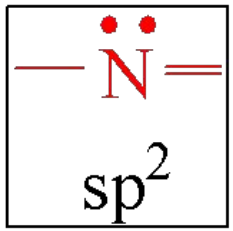
ПМР

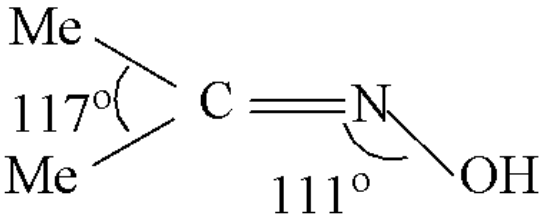


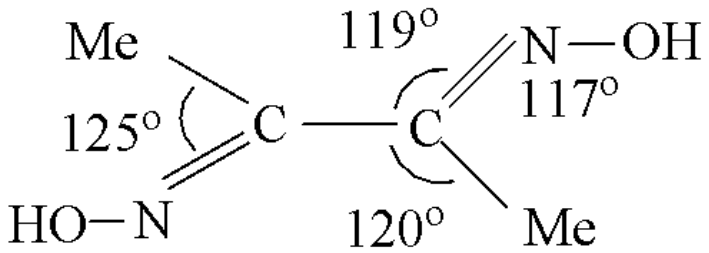
$\Delta G^{\neq}$, ккал/моль

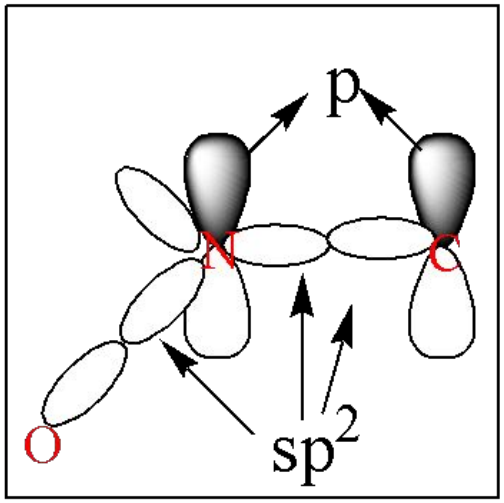
R	
H	21
Me	17
Ph	15

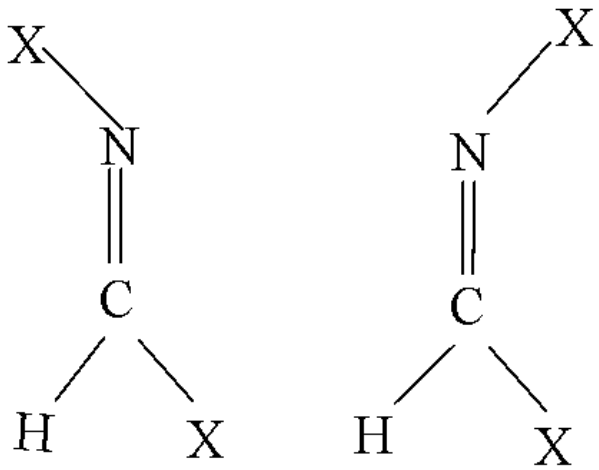
Физический или химический процесс ?

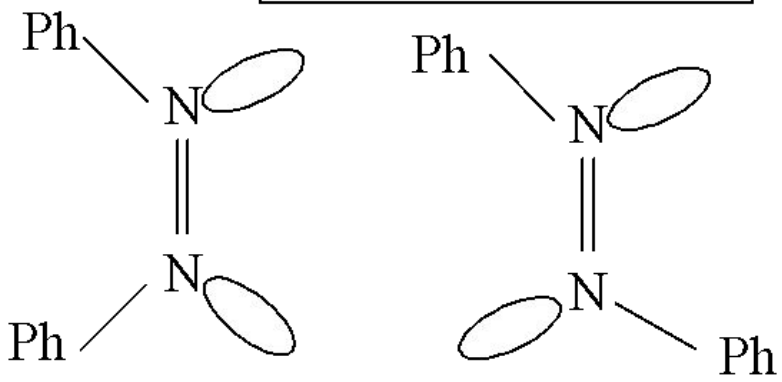








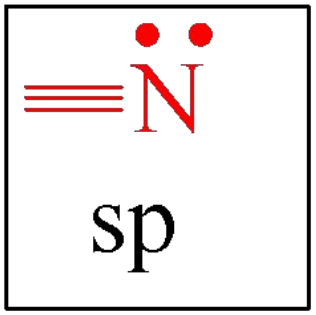


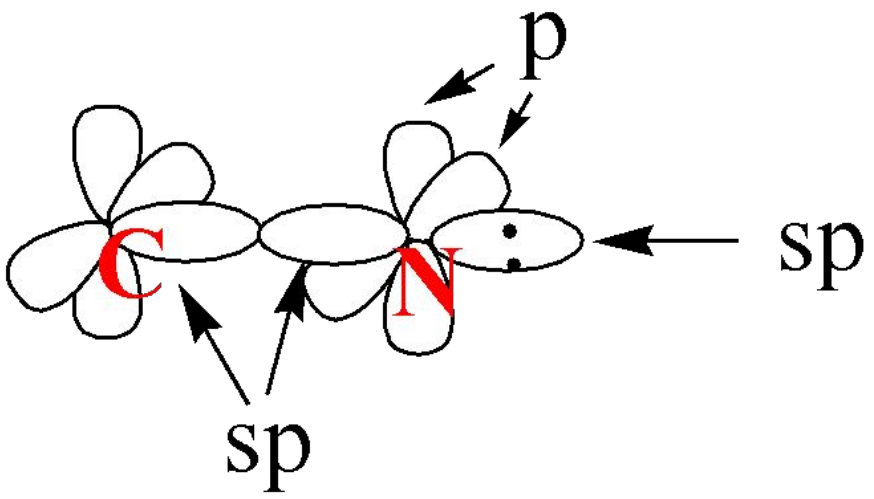


μ = 3 D μ = 0

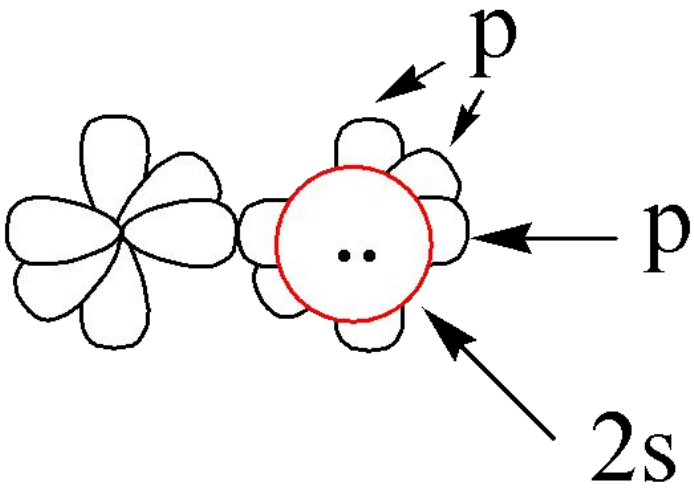
азобензол

геометрические изомеры оксимов





MeCN



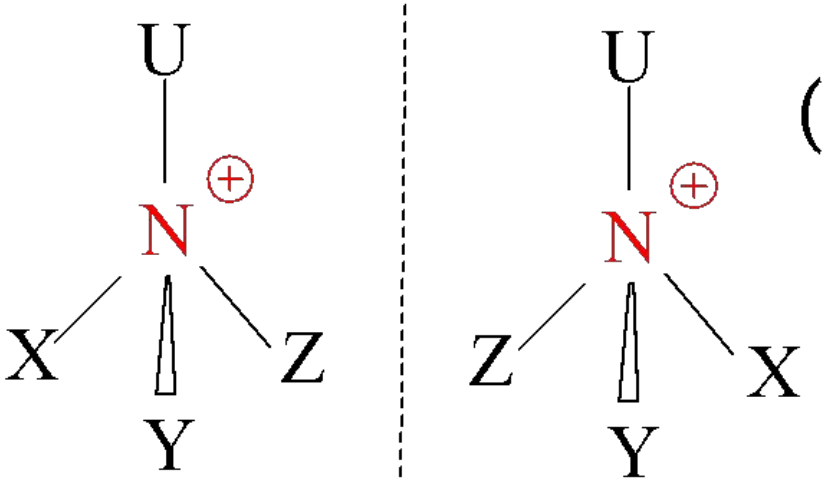
менее выгодна

$N \quad 1s^2 2s^2 2p^3$

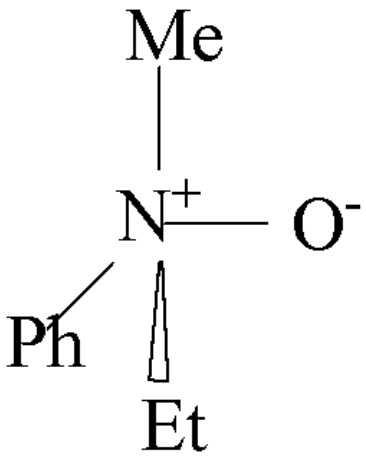
$N^+ \quad 1s^2 2s^2 2p^2$

изоэлектронен С

Принцип изоэлектронности-изоструктурности

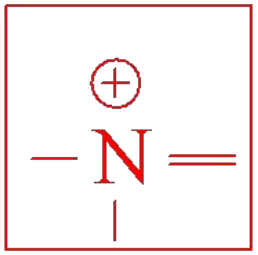


(1899 г., Me, All, Bz, Ph)

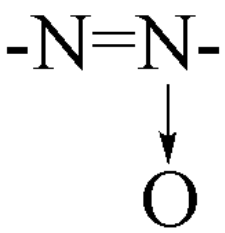


$N^+—O^-$ $\quad N \longrightarrow O$

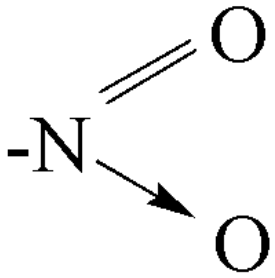
$Me_3N^+—O^-$ $\quad \mu = 5.0$ D



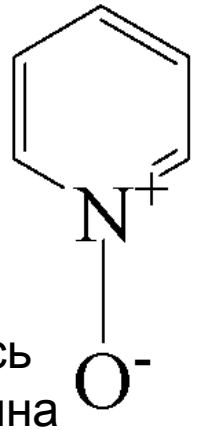
sp^2



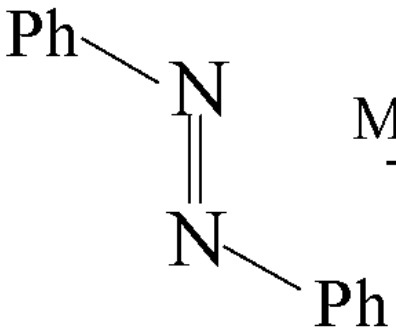
N-оксидная группа



нитро

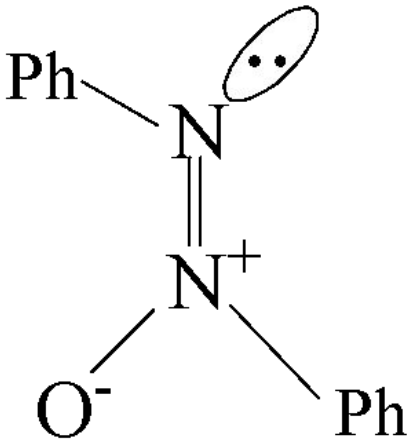


N-окись пиридина



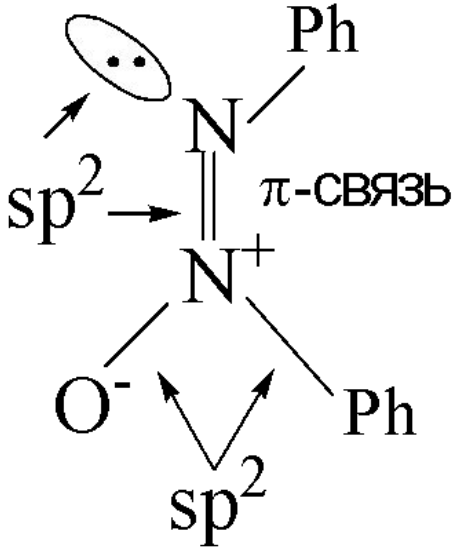
азобензол

MeCOOOH



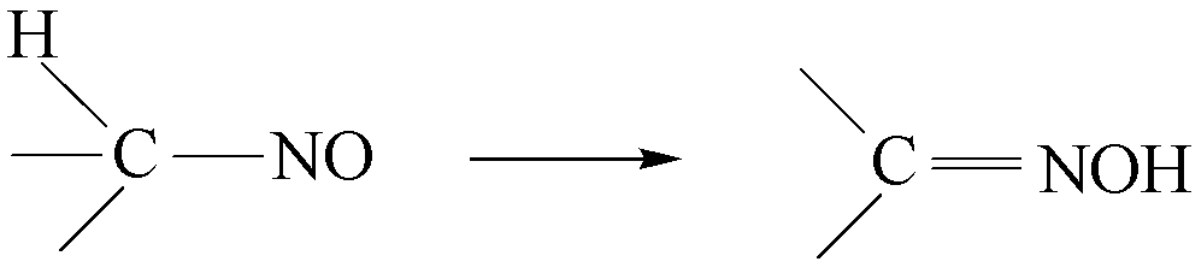
азоксибензол

$\mu = 1.7$ D

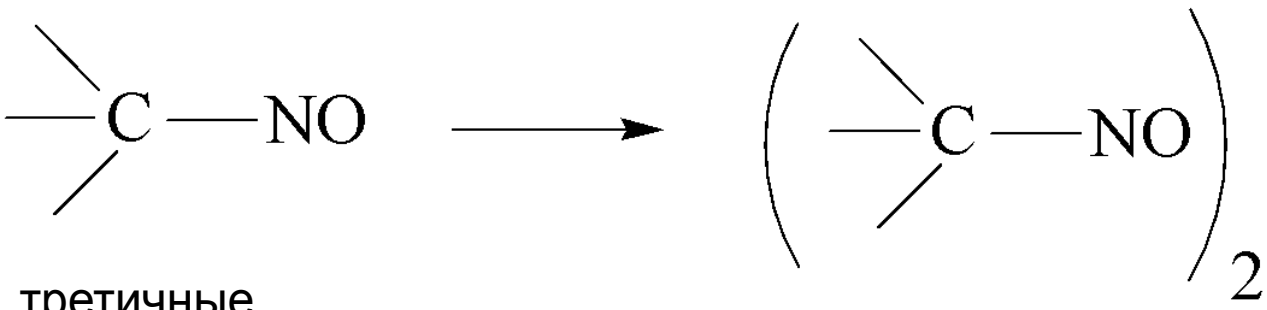


$\mu = 4.7$ D

Нитрозосоединения

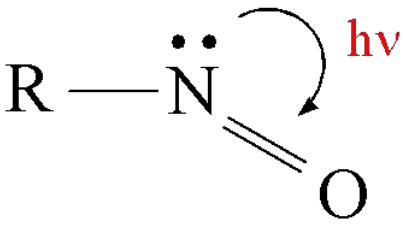


Первичные, вторичные



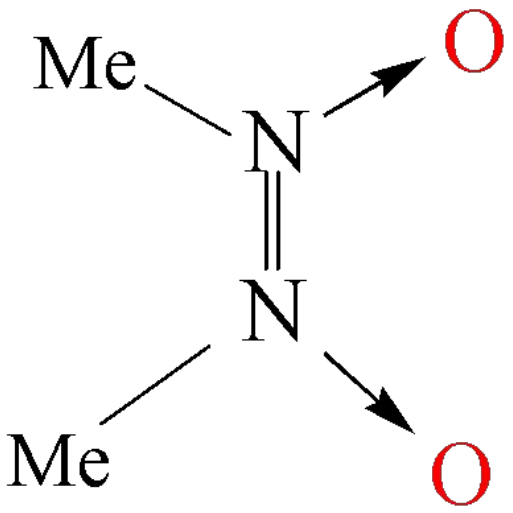
третичные

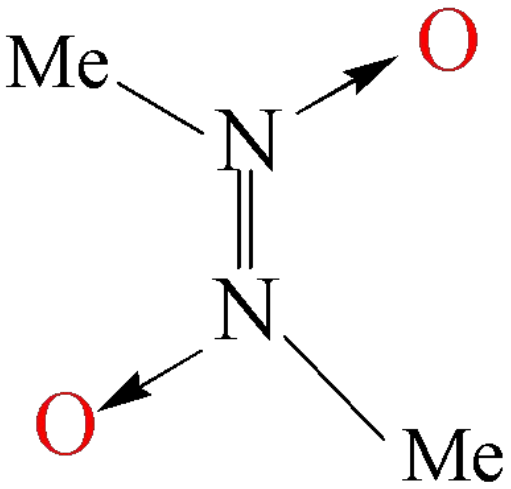
безцветны



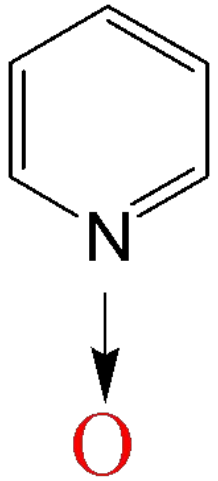
легкость n-π^* перехода
голубая окраска, ArH - зеленая

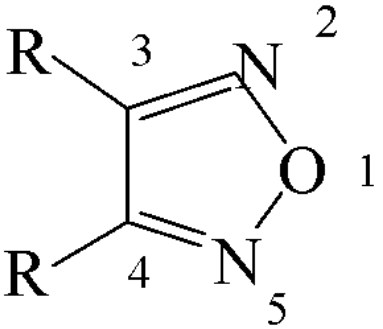
Геометрическая изомерия диокисей



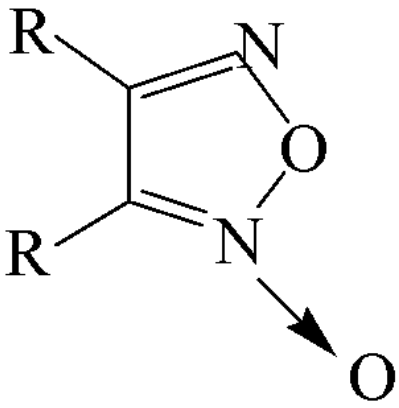


Гетероциклы



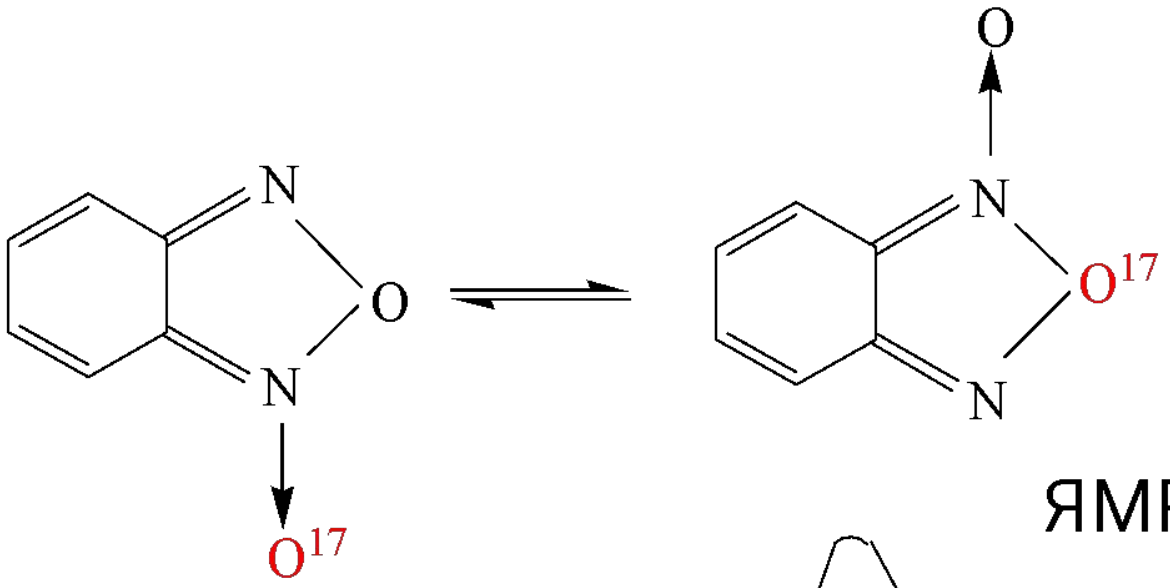


1,2,5-оксодиазол
(фуразаны)

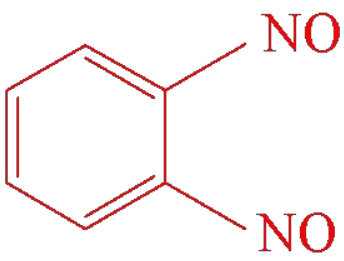


фуразаксаны

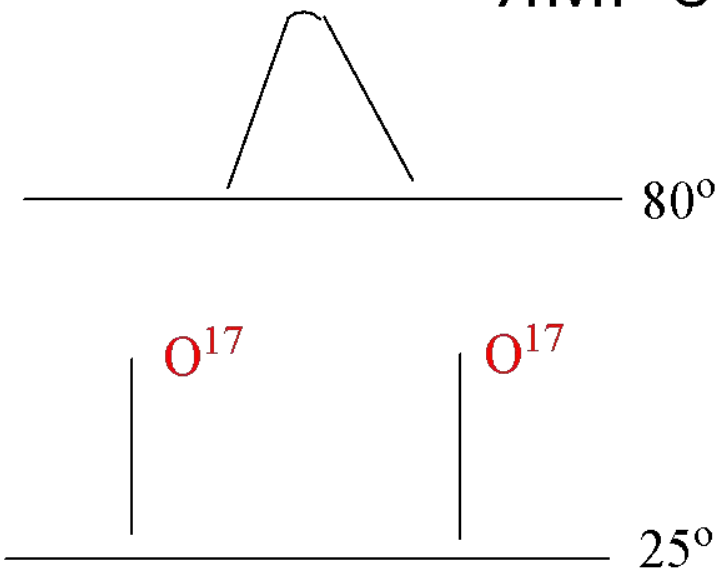
Вырожденная перегруппировка



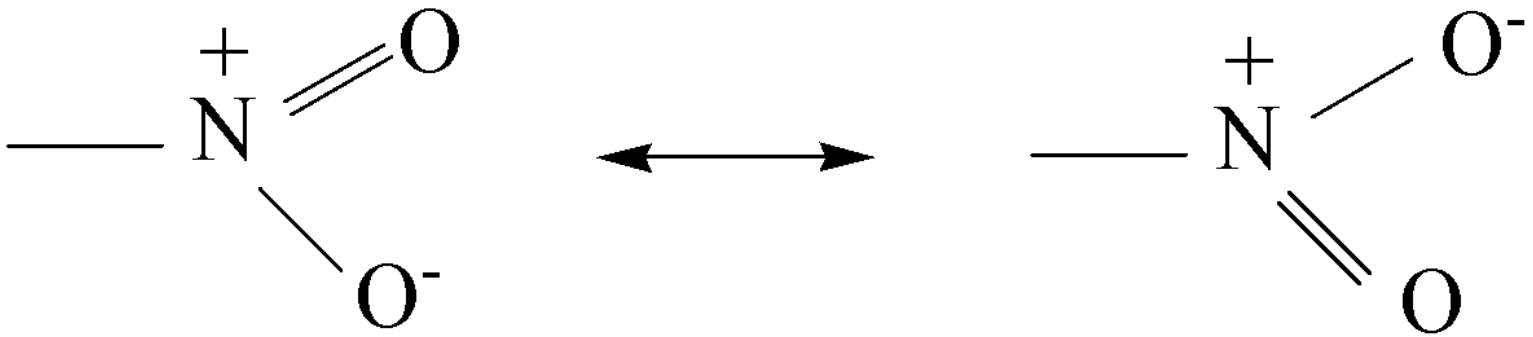
бензофураксан

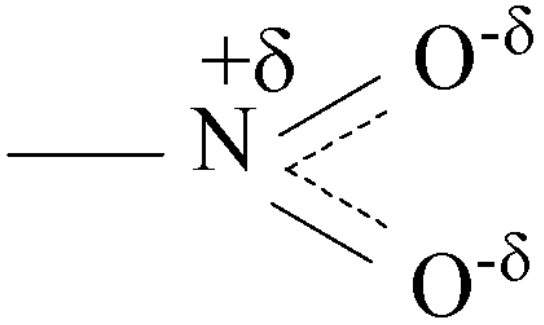


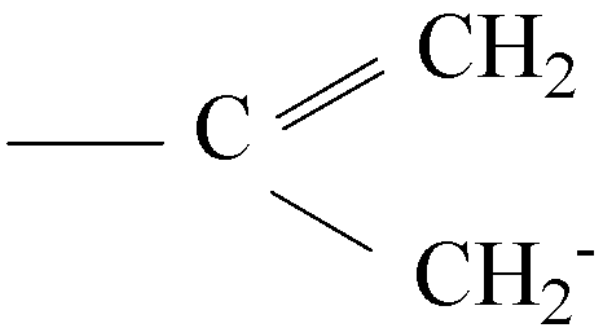
ЯМР O^{17}



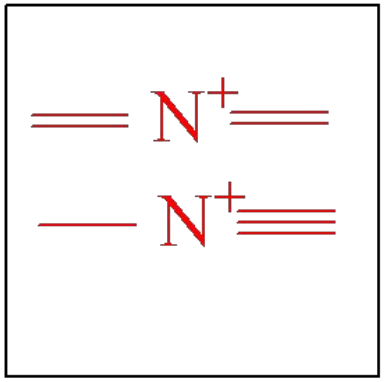
Нитросоединения



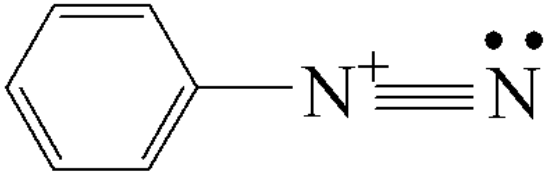




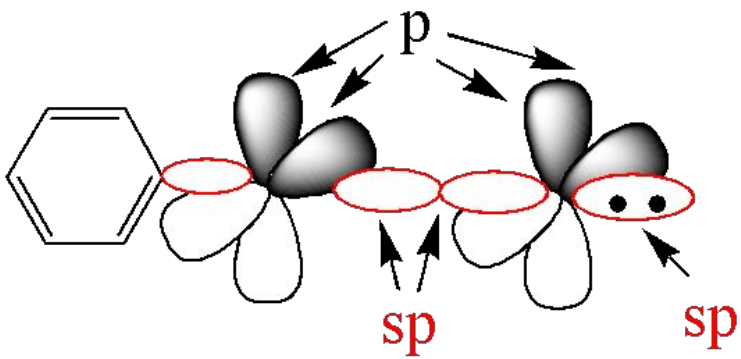
$$\Delta E_{\pi} = 2\beta\,(1 - a_{ot}) = 2\beta\,(1 - \sqrt{\tfrac{1}{2}})$$



sp



sp sp



A B

1.32Å 1.12Å

$H_2C—N—N$

1.10Å

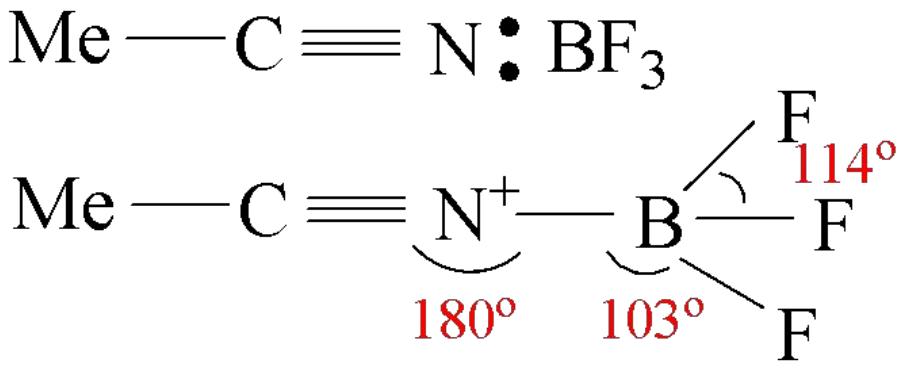
—N≡N

—N=N—

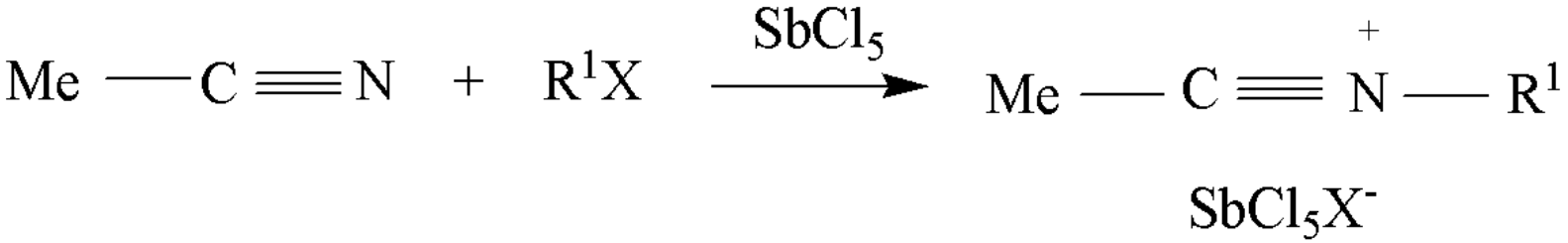
1.26Å

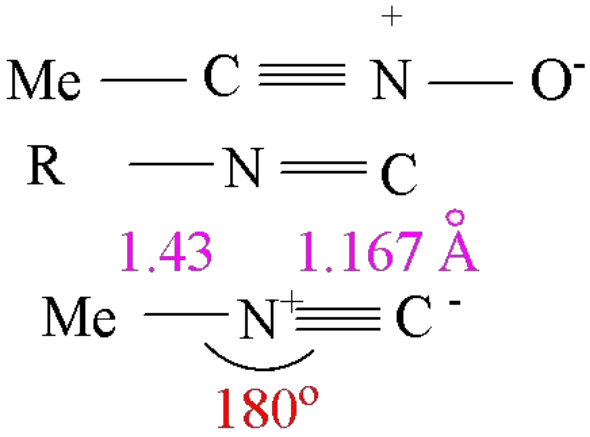
Микроволновая спектроскопия

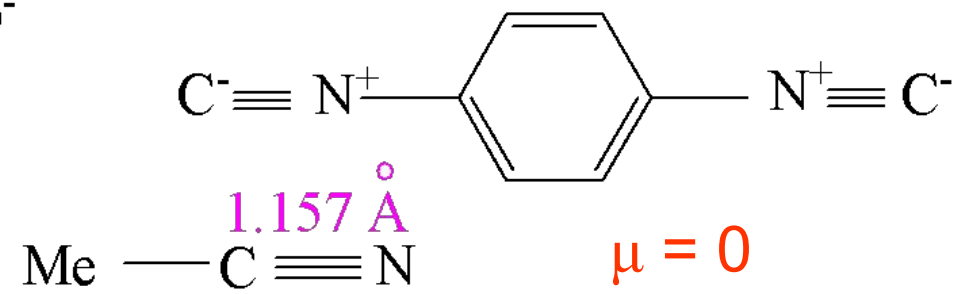
Соли нитрилов, окиси нитрилов, изонитрилы



Бент ?







μ = 0