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Note Title 3/29/2005

Allotropes of Nitrogen

N_2

controlling factor:	Bond Energies (kJ/mol)	
☆ Propellants	single	160
☆ Explosives	double	418
☆ High Energy Density	triple	954

$N_5^{\oplus}$

$N_3^{\ominus}$

↑

polynitrogen ions

$N_2F_2 + SbF_5 \rightarrow N_2F^{\oplus}\ SbF_6^{\ominus}$

frozen → liq HF

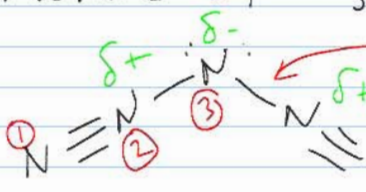
HN_3

$HF + N_5^{\oplus}\ SbF_6^{\ominus}$

1.5 g white powder

Possible new allotrope: N_8

Structure of $N_5^{\oplus}$:



a r = 1.30 Å

b r = 1.11 Å

ref $r N_2$ = 1.098 Å

IR/Raman

9 fundamentals

after 20 ppm correction

ν_7 2205 (s) cm^{-1}

^{15}N NMR:

	calcd*	obsd
①	−235	−237
②	−166	−165
③	−95	−100

CH_3NO_2 neat reference.

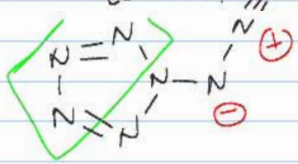
$N_5^{\oplus}$ synthetic strategy:

$$HN_3 + FN_2^{\oplus} \rightarrow N_5^{\oplus}$$

$$N_3^{\ominus} + N_2^{\oplus\oplus} \Longleftarrow$$ given this, what about other nitrogen allotropes??

Possibility of $N_3^{\ominus} + N_5^{\oplus} \rightarrow N_8$

18 kcal barrier to dec.!

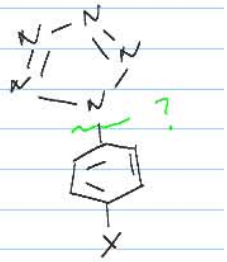


azidopentazole!

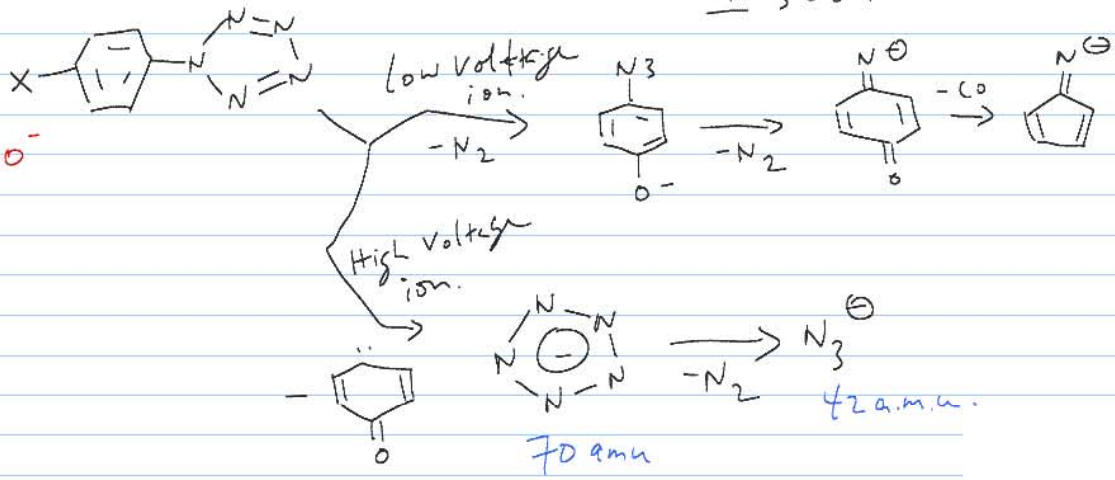
What about $N_5^{\ominus}$? Pentazolate ion

Huisgen + Ugi
40 years ago:

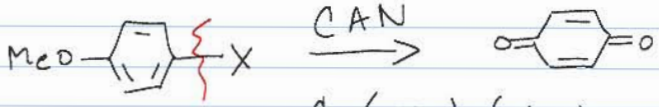
Arylpentazoles



Negative Ion Mass Spec Angew. 2002
41 3051



2003: Chem Commun pg. 1016

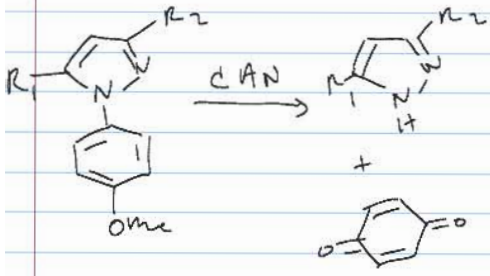


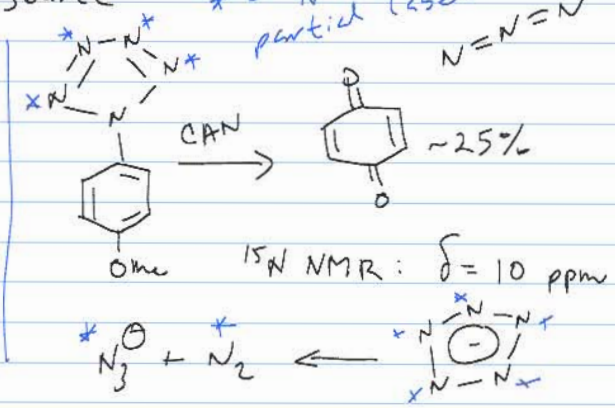
$Ce(NH_4)_2(NO_3)_6$

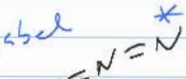
Ce(IV) source

* = ^{15}N partial label

Azoles







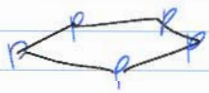
$N_5^+ + N_5^{\ominus} \longrightarrow N_{10}$! ! !

$Me_3Si\,N_3$ substitutes for HN_3 in $N_5^{\oplus}$ synthesis.

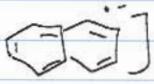
⇒ much safer.

Metals? not yet for $N_5^{\ominus}$, but $P_5^{\ominus}$

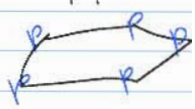
John Ellis, Science 2002, 295, 832.



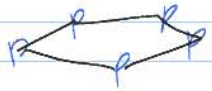
$TiCl_4(THF)_2$ → 18-C-6 → 2.5 P_4 →

6 K^+ 

$[K^+(18\text{-}C\text{-}6)]_2$



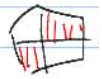
a delta-bonded metallocene



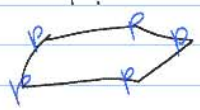
2- Ti is zerovalent

d^4 - diamagnetic.

δ-acceptor



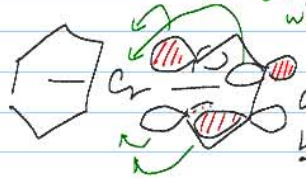
Ti:



ring orbitals: π-sym

donor

oriented for good overlap with d_{xy} or $d_{x^2-y^2}$



also dominated by delta bonding