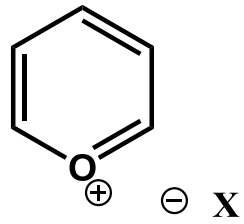
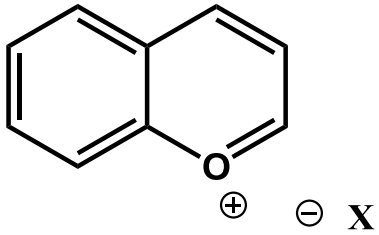
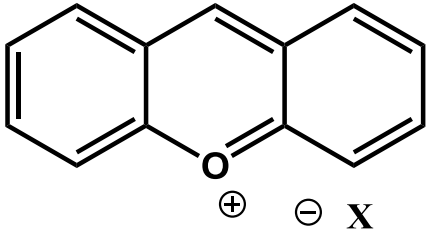
SOLE PIRYLIOWE, PIRANY, PIRONY I ICH BENZOLOGI



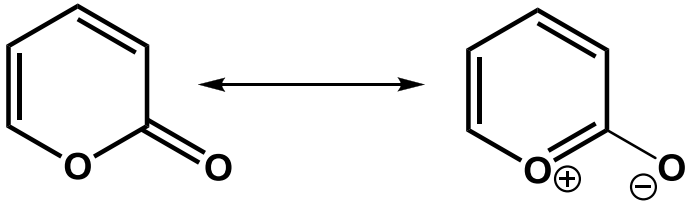
jon piryliowy



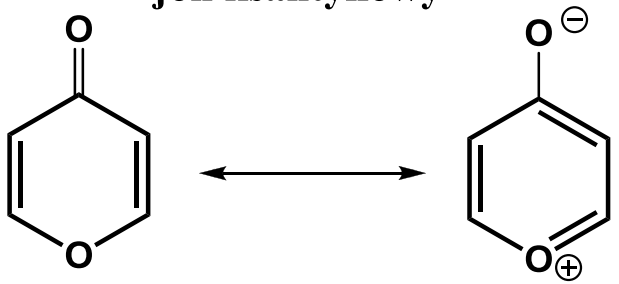
jon chromyliowy



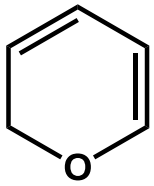
jon ksantyliowy



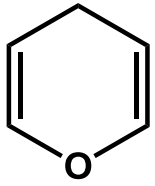
piran-2-on



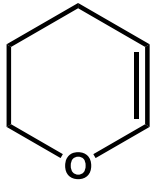
piran-4-on



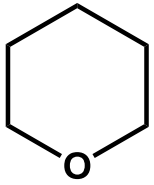
2H- piran



4H- piran

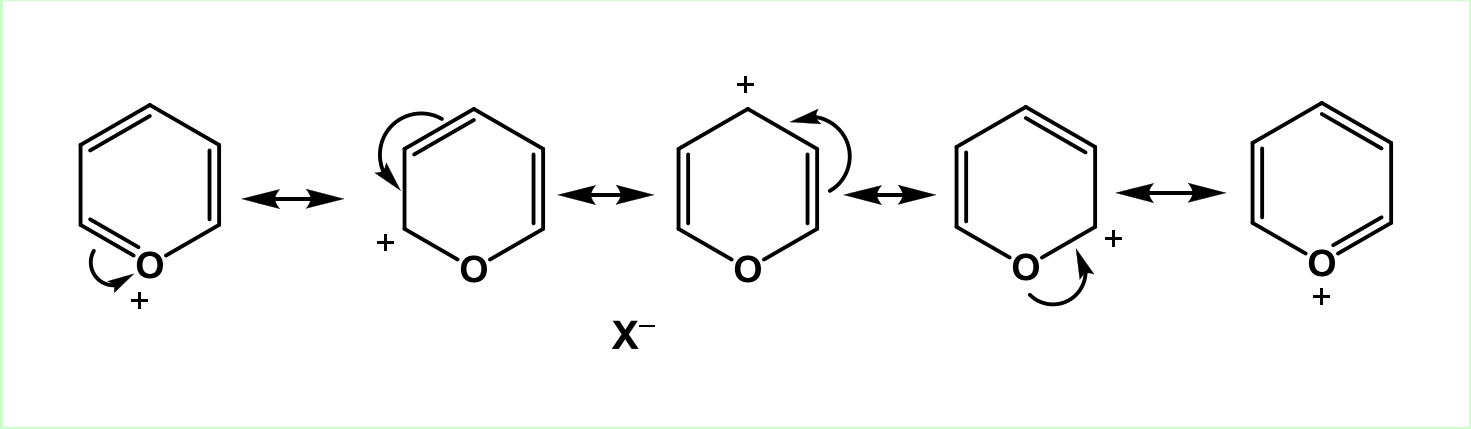


3,4-dihydro-2H- piran

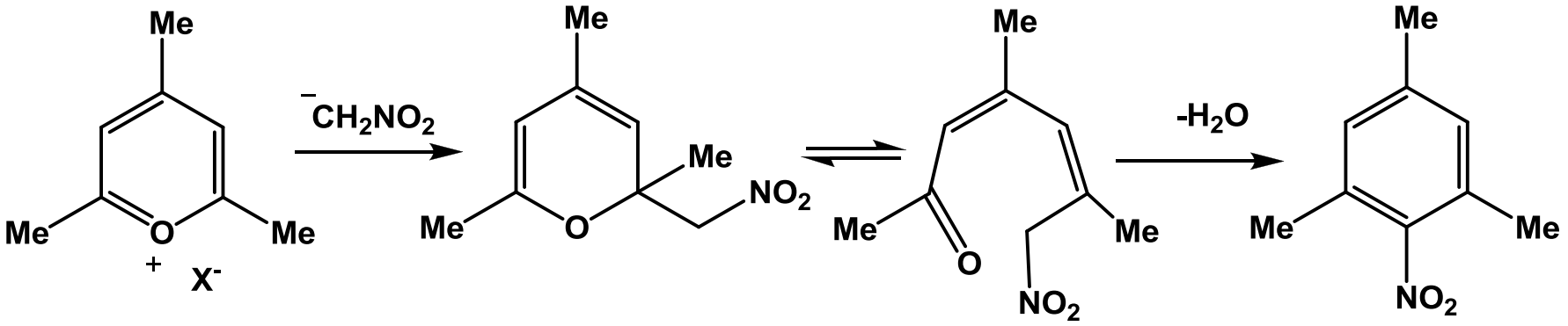


3,4,5,6-2H-tetrahydropiran

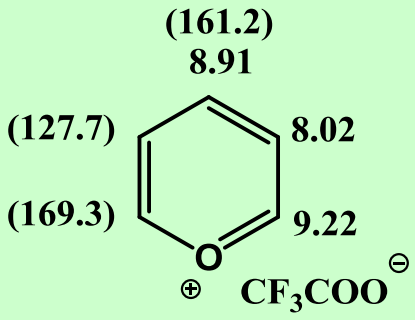
(THP)

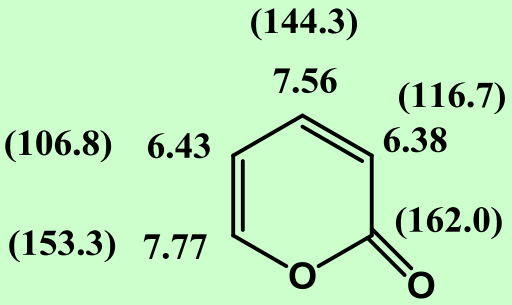


•Kationy piryliowe w połaczeniu z anionami mocnych kwasów są trwałe i dzięki obecności ładunku na tlenie są podatne na reakcję z nukleofilami;



Widma IR, UV i NMR – charakterystyczne cechy ułatwiające określanie struktury układów piryliowych

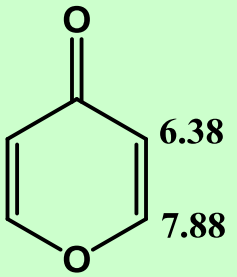




$J_{3,4}$=9.4 Hz

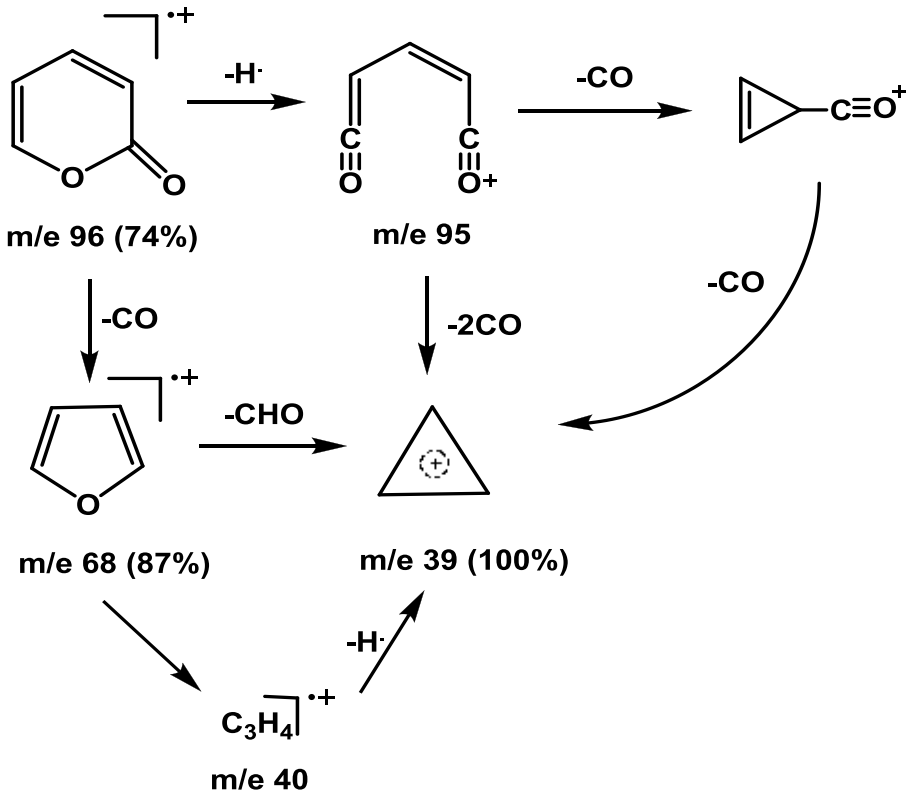
$J_{4,5}$=6.3 Hz

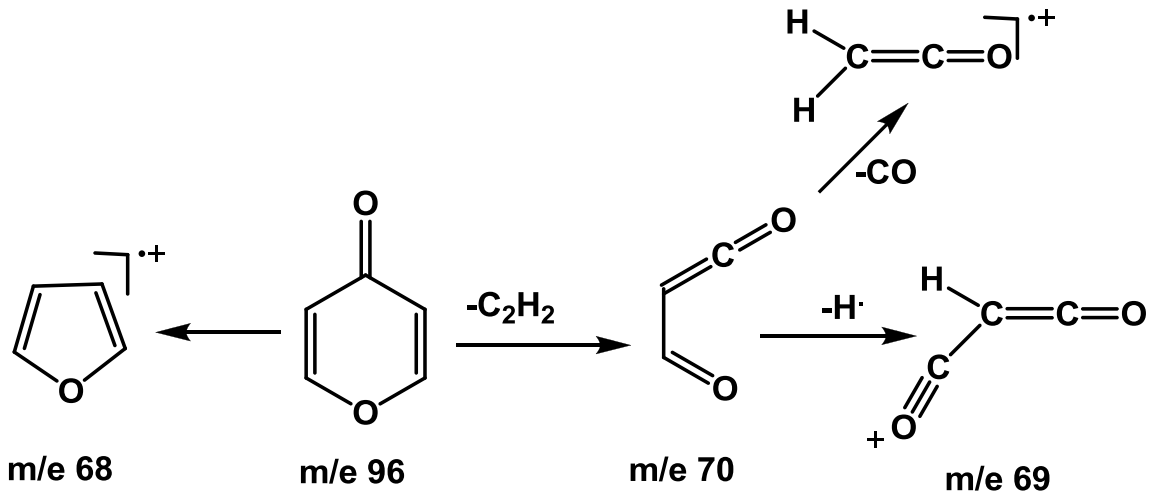
$J_{5,6}$=5.0 Hz



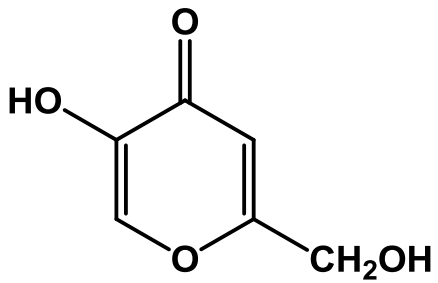
$J_{2,3}$=5.96 Hz

$J_{3,5}$=2.68 Hz

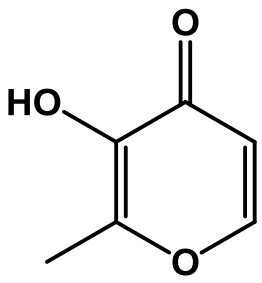

-H·
-CO
m/e 96 (74%)
m/e 95
-CO
-CO
-2CO
-CHO
m/e 68 (87%)
m/e 39 (100%)
-H·
C3H4
m/e 40


-CO
-C2H2
-H·
m/e 68
m/e 96
m/e 70
m/e 69

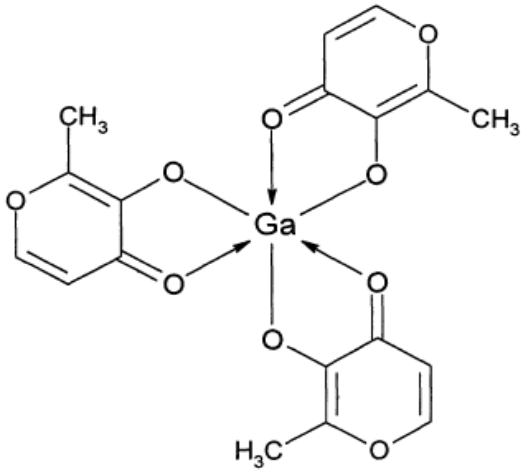
Znaczenie układów piryliowych

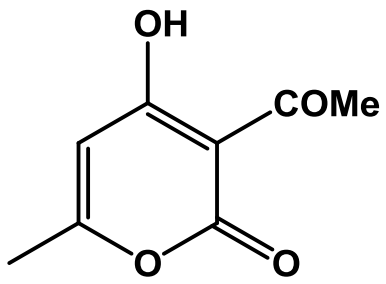


kwas kojowy



maltol

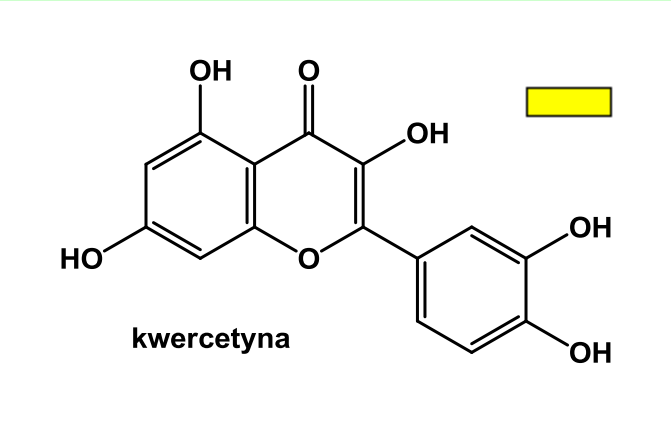


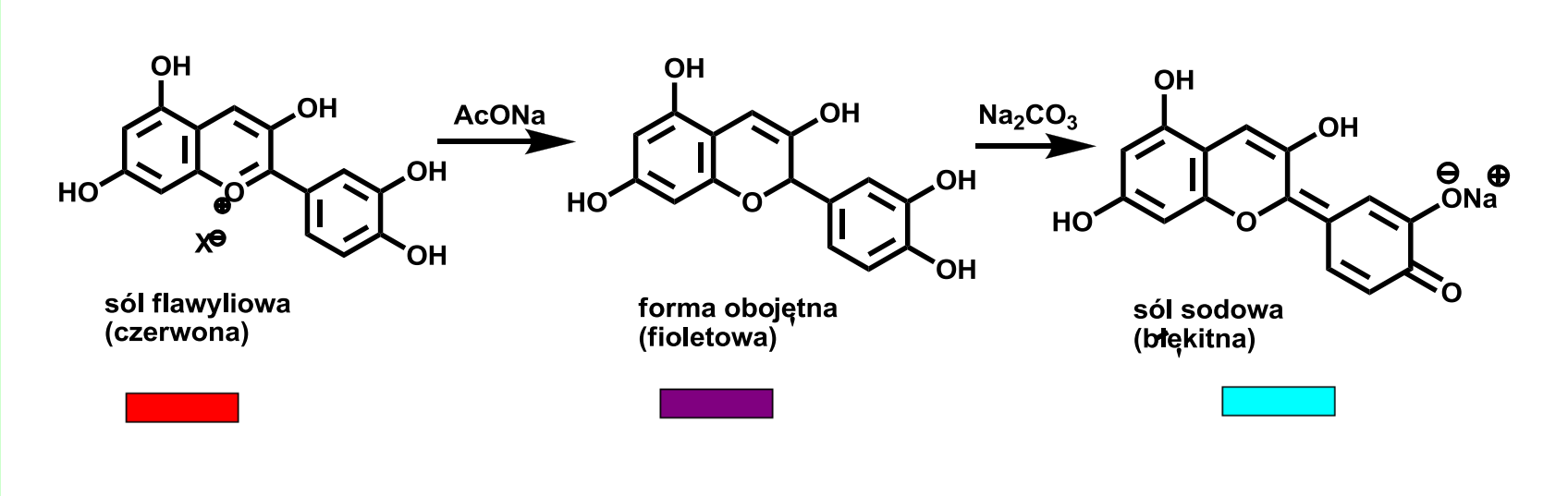


kwas dehydrooctowy

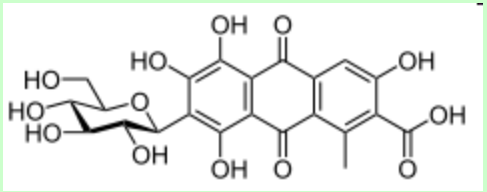
•**Pochodna piran-2-onu kwas dehydrooctowy (DHA)— jest środkiem przeciwgrzybiczym dodawanym do past do zębów i stosowany szeroko w kosmetyce.**

Znaczenie układów piryliowych

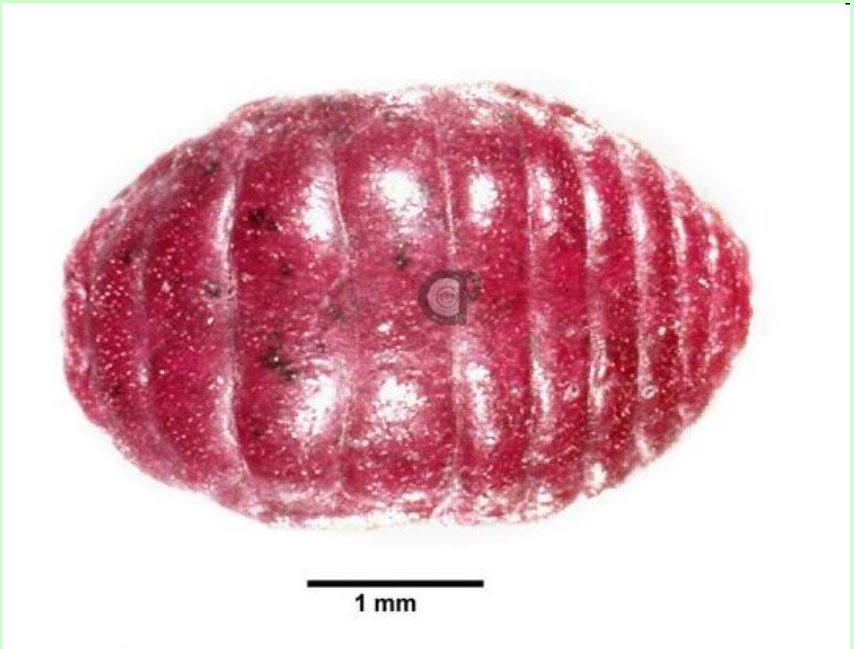




Często w składzie czerwonego jogurtu

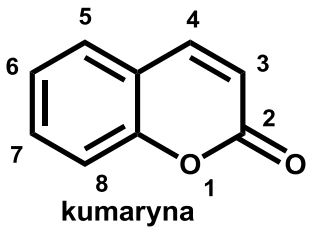


Kwas karminowy, koszenila, karmina (*E120*)

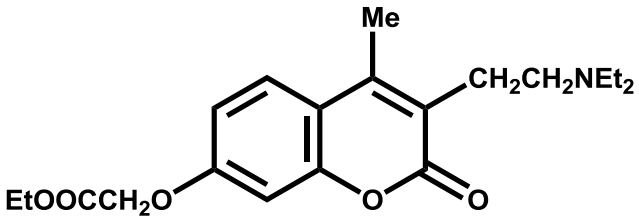


Ze 155 tys. owadów otrzymuje się 1 kg koszenili

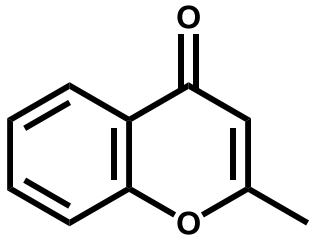
Znaczenie układów piryliowych



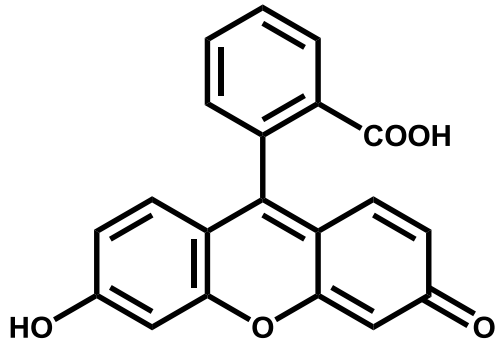
kumaryna



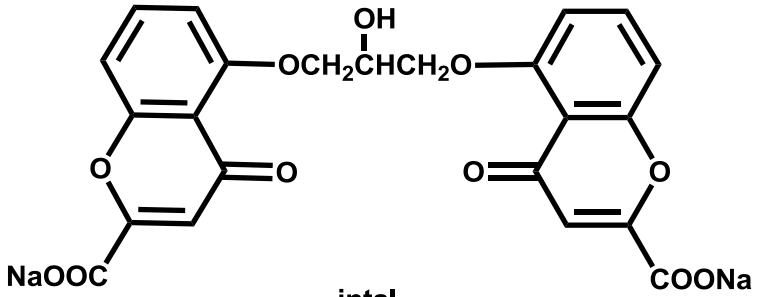
chromonar



tricromyl



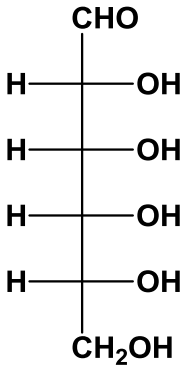
fluoresceina



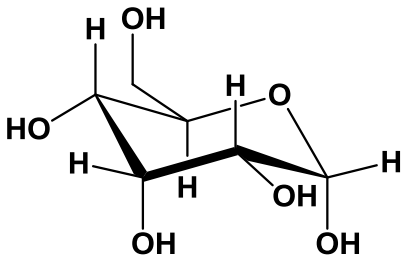
intal

Znaczenie układów piryliowych

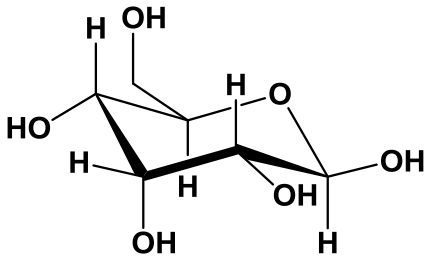
D-Alloza



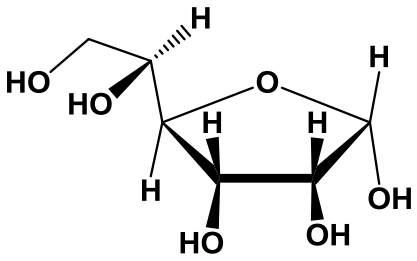
forma otwarta w rzucie Fishera



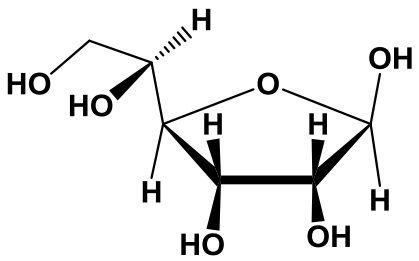
α–piranoza



β–piranoza



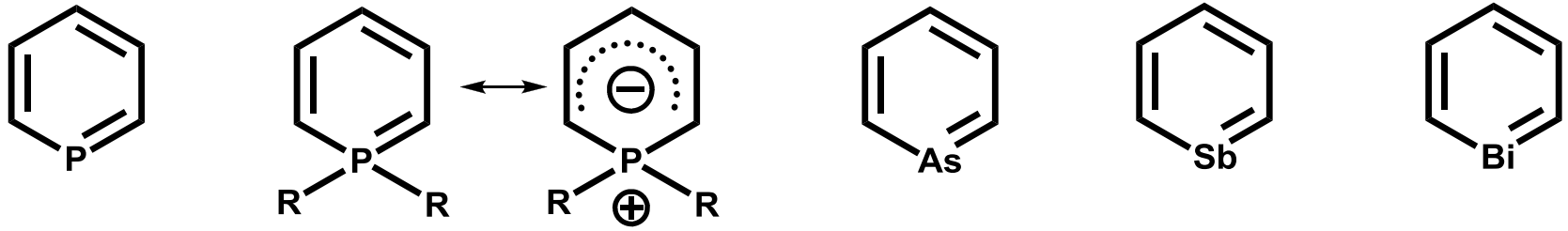
α–furanoza

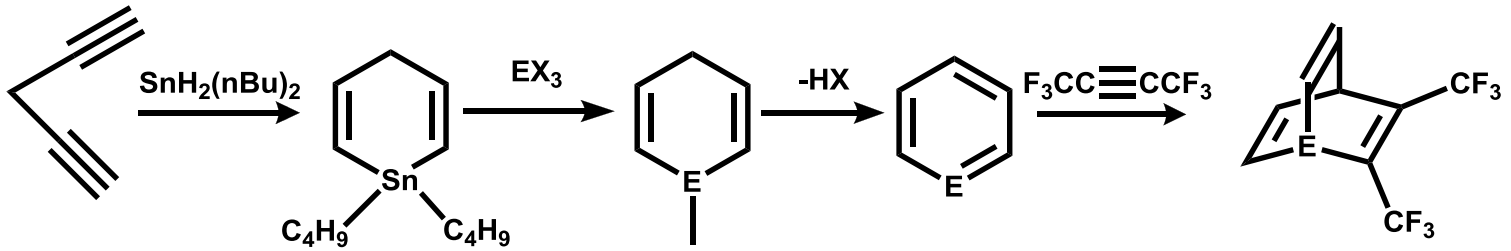


β–furanoza

SZEŚCIOCZŁONOWE PIERŚCIENIE HETEROAROMATYCZNE Z ATOMAMI FOSFORU, ARSENU, ANTYMONU I BIZMUTU

•Analogi pirydyny zawierającymi zamiast atomu azotu atom innego pierwiastka z grupy azotowców są: λ^3-fosforin , λ^5-fosforin , arsenin, antymonin i bizmin:

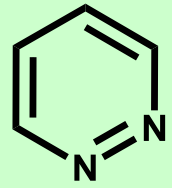




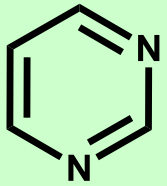
E= P; As; Sb; Bi

SZEŚCIOCZŁONOWE PIERŚCIENIE HETEROAROMATYCZNE Z DWOMA I TRZEMA ATOMAMI AZOTU

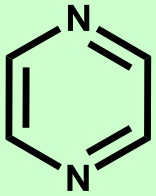
1. Diazyny, Triazyny i ich Benzologi



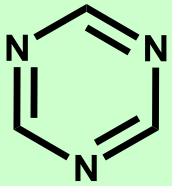
pirydazyna



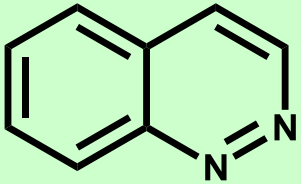
pirymidyna



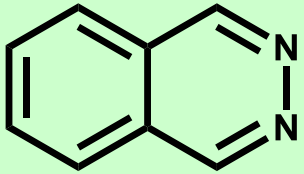
pirazyna



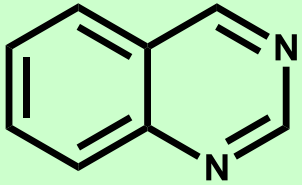
1,3,5-triazyna



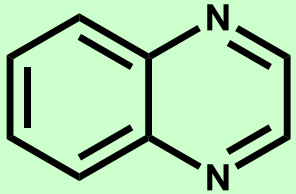
cynnolina



ftalazyna



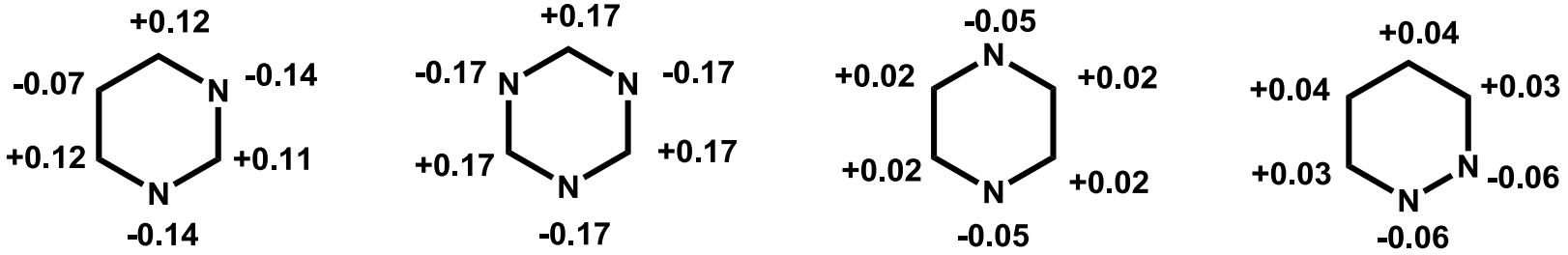
chinazolina



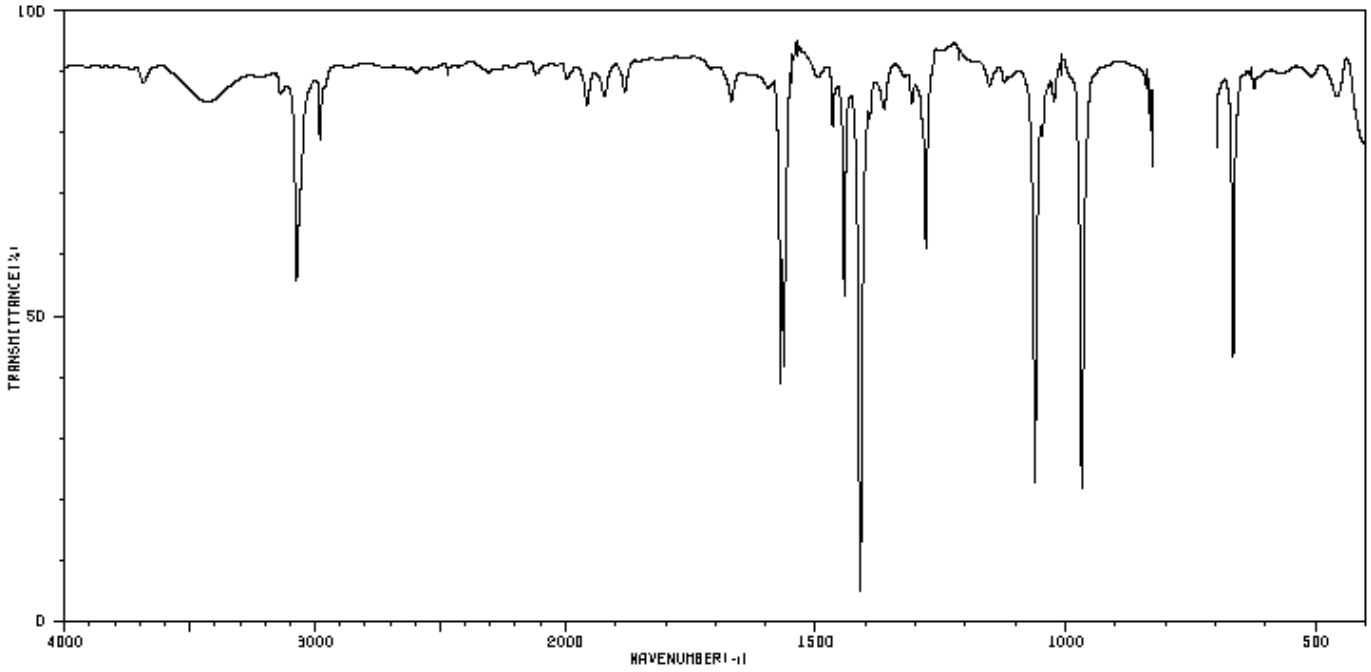
chinoksalina

Związek	T. topn. [°C]	T. wrz. [°C/Tr]	Rozpuszczalność[a]	pK_a
Pirydazyna	−8	208	w, a, e, ac, b	2,33
Pirymidyna	22	123–124	w, a	1,31
Pirazyna	54	115–116/768	w, a, e, ac	0,65
1,3,5-Triazyna	86	114	a, e,	
Cynnolina	40–41	114/0,35	a, e, ac, b	2,29
Ftalazyna	90–91	175/17	w, a, b	3,47
Chinazolina	48	241,5	w, a, e, ac, b	3,43
Chinoksalina	28	229,5	w, a, e, ac, b	0,80

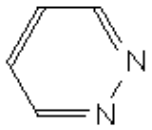
w-woda
a- etanol
e-eter
ac-aceton
b-benzen



Rozkład ładunku π w cząsteczce



3685	84	1922	81	1648	84	1280	68	967	21
3431	81	1881	84	1466	79	1153	84	839	84
3139	84	1668	81	1443	52	1122	84	832	79
3073	63	1596	84	1411	4	1061	21	827	74
2980	77	1584	84	1392	79	1047	77	685	42
2966	84	1571	37	1363	81	1023	81	623	64
1956	81	1563	41	1308	81	1007	86	468	81

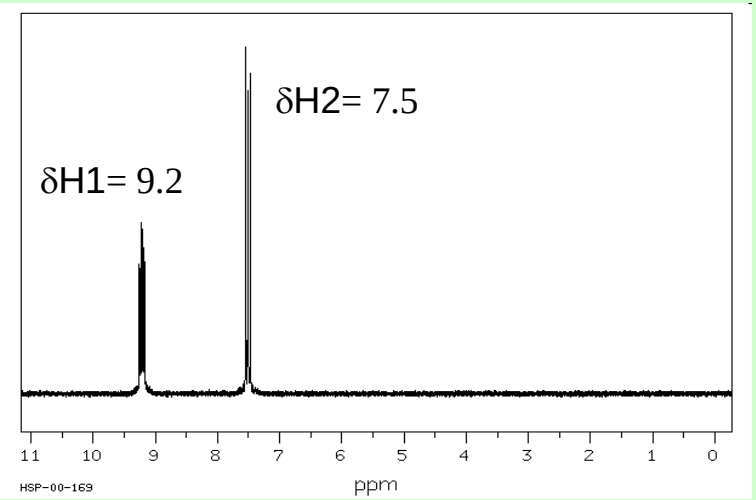


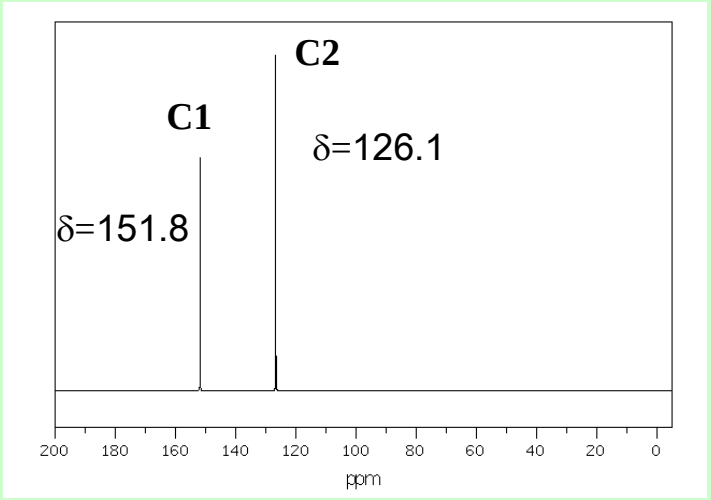
- **Widma IR diazyn są podobne do widm benzenu i pirydyny;**

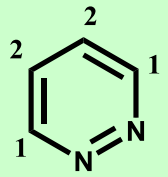
  - drgania walencyjne wiązań C—H są w zakresie 3095-3042 cm^{-1} i wiązań C=C, C=N pierścienia w zakresie 1617-1283 cm^{-1};

Widma NMR – charakterystyczne cechy ułatwiające określanie struktury

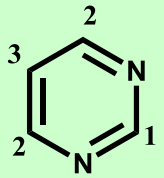
diazyn, triazyn i ich benzologów





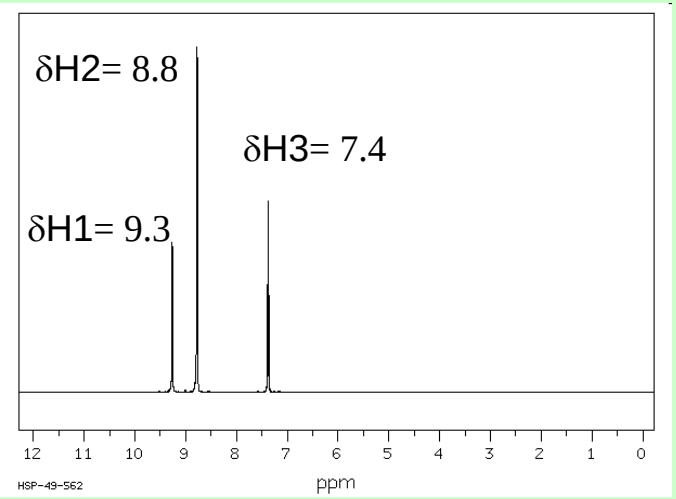


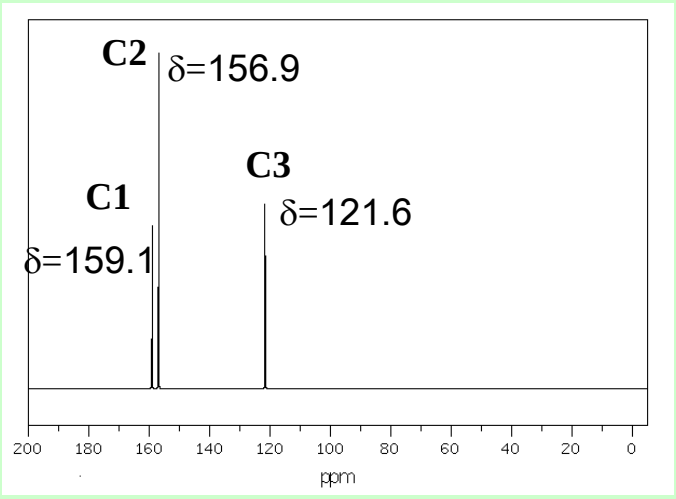
δ ^{15}N= 20.3 ppm

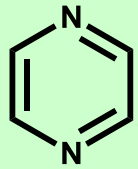


δ ^{15}N= –84.5 ppm

Widmo ^{1}H i ^{13}C NMR pirydazyny w $CDCl_3$



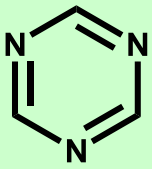




δ ^{1}H= 8.6 ppm

δ ^{13}C= 145.2 ppm

δ ^{15}N= –46.1 ppm

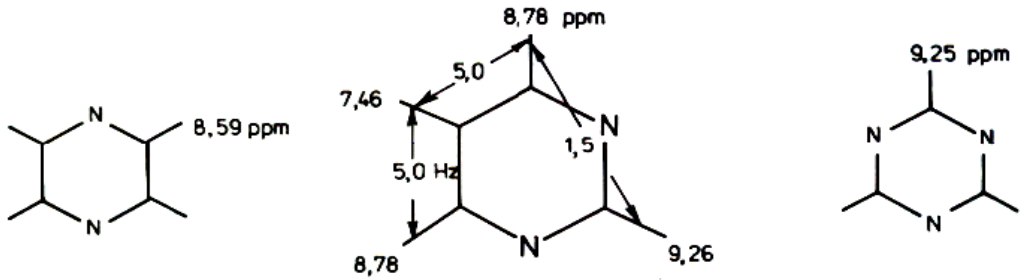


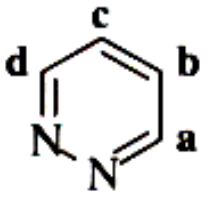
δ ^{1}H= 9.2 ppm

δ ^{13}C= 166.1 ppm

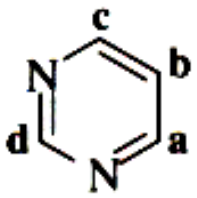
δ ^{15}N= –98.5 ppm

Widmo ^{1}H i ^{13}C NMR pirymidyny w $CDCl_3$

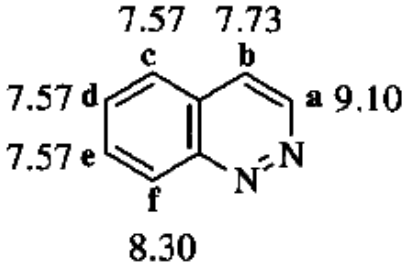




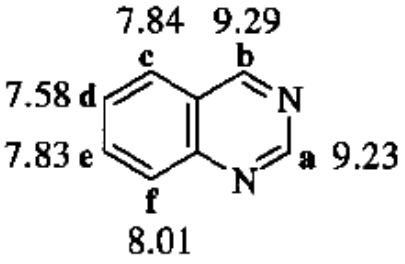
$^3J_{ab}$ 4.9
$^4J_{ac}$ 2.0
$^5J_{ad}$ 3.5
$^3J_{bc}$ 8.4



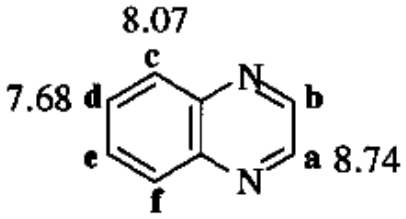
$^3J_{ab}$ 5.0
$^4J_{ac}$ 2.5
$^4J_{ad}$ 0
$^5J_{bd}$ 1.5



$^3J_{ab}$ 5.7 $^3J_{de}$ 6.9
$^5J_{bf}$ 0.8 $^4J_{df}$ 1.3
$^3J_{cd}$ 7.8 $^3J_{ef}$ 8.6
$^4J_{ce}$ 1.5
$^5J_{cf}$ 0.8



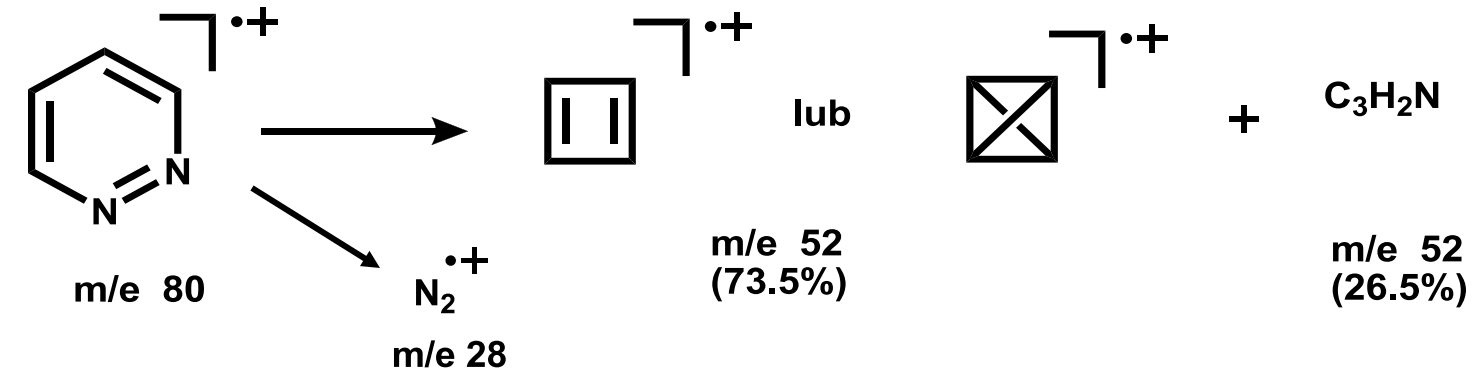
$^4J_{ab}$ 0 $^3J_{de}$ 6.9
$^5J_{bf}$ 0.5 $^4J_{df}$ 1.2
$^3J_{cd}$ 7.9 $^3J_{ef}$ 8.5
$^4J_{ce}$ 1.2
$^5J_{cf}$ 0.8

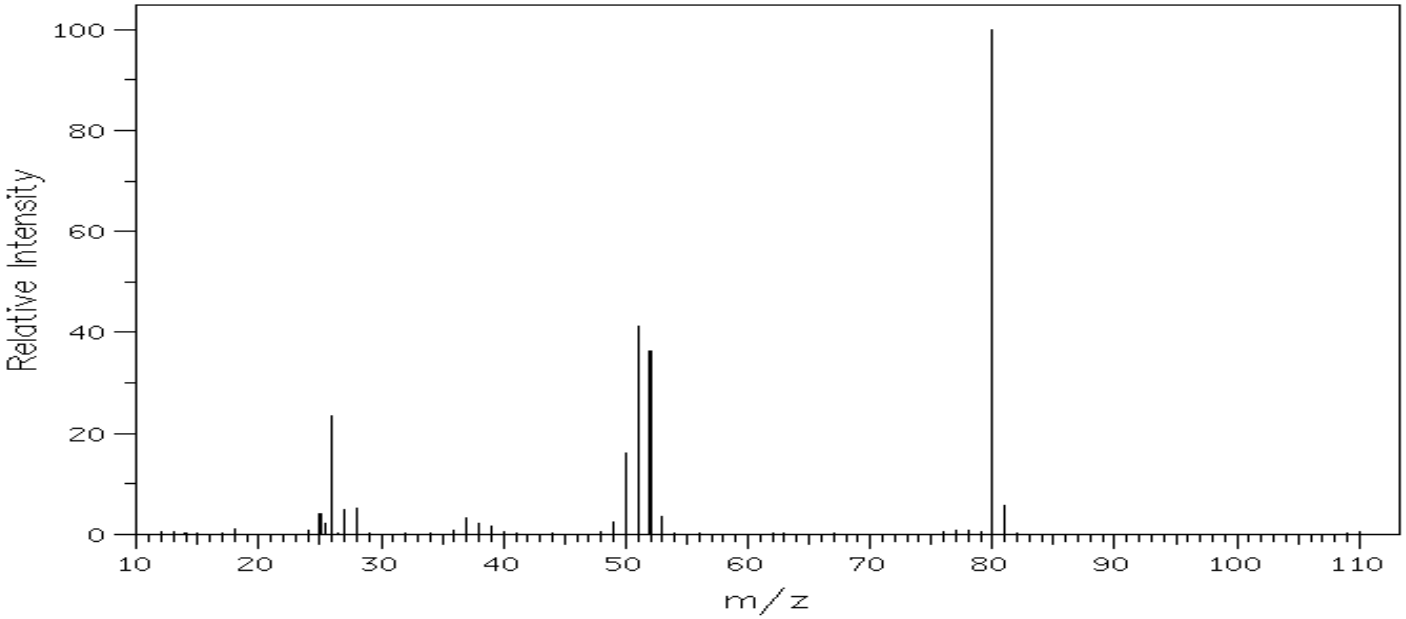


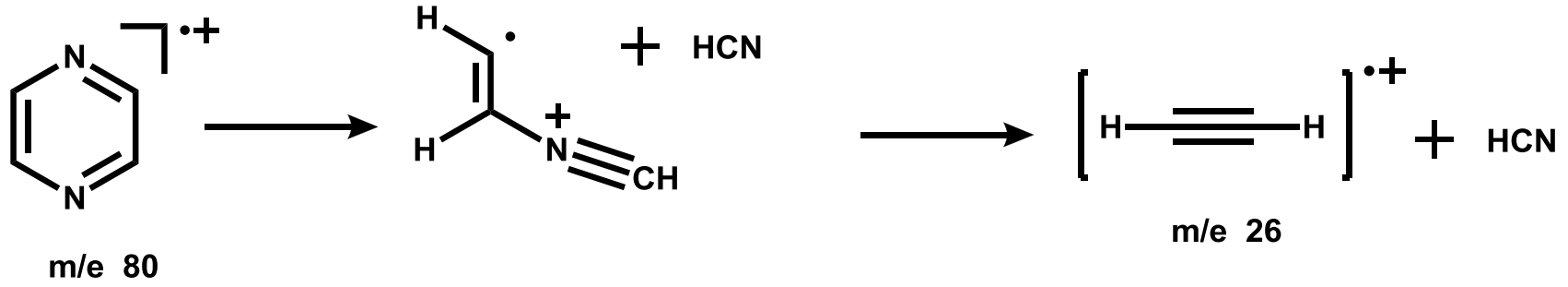
$^3J_{ab}$ 1.8
$^3J_{cd}$ 8.4
$^4J_{ce}$ 1.6
$^5J_{cf}$ 0.6
$^3J_{de}$ 6.9

Widma mas – charakterystyczne cechy ułatwiające określanie struktury

diazyn, triazyn i ich benzologów

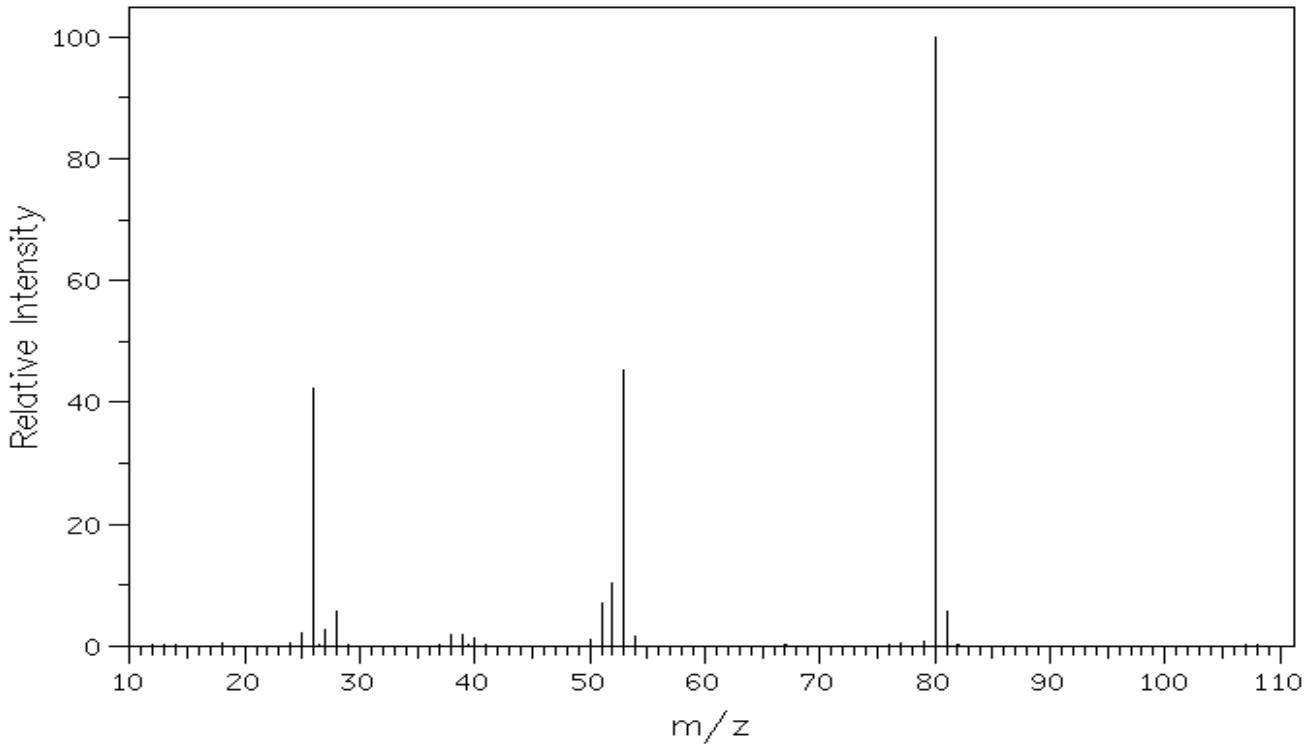




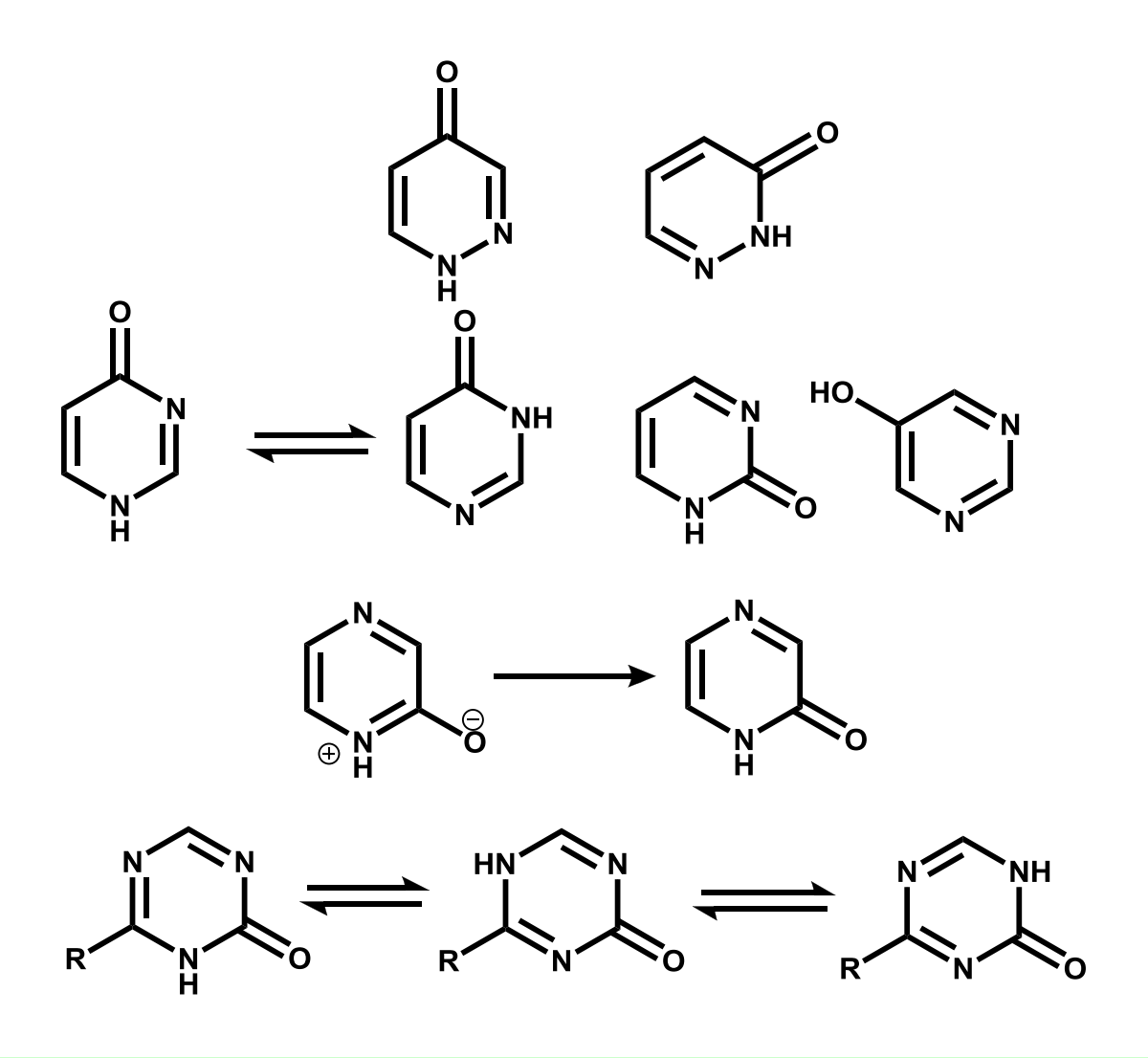

N
N
H
H
N
CH
HCN
H
H
HCN

m/e 80

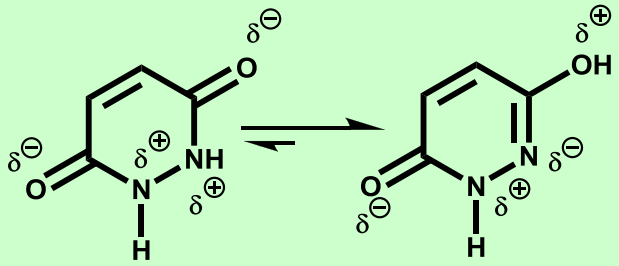
m/e 26


Relative Intensity
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
110
m/z

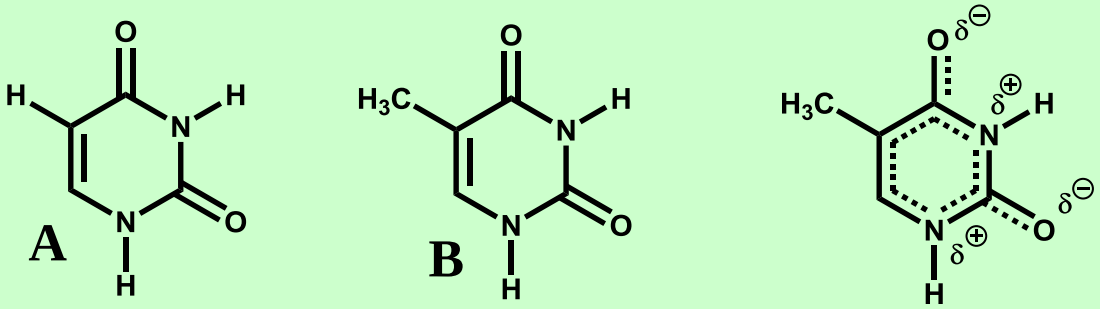
Tautomeria

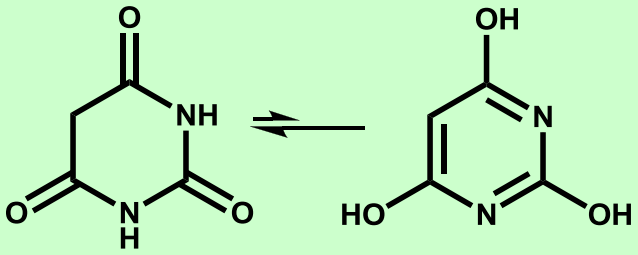


• **Gdy w cząsteczce występują dwie funkcje tlenowe zdarza się często, że jeden z atomów tlenu istnieje w formie karbonylowej, a drugi w wodorotlenowej, jak w 3-hydroksy-6(1H)-pirydazynonie;**

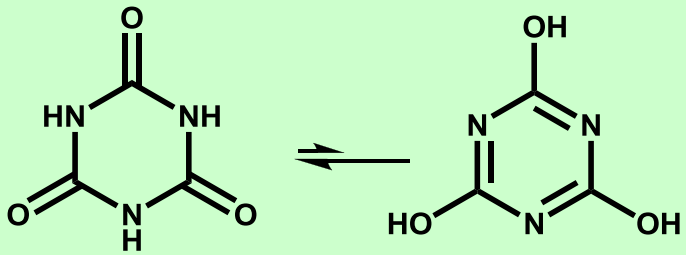


• **Jednak w uracylu (A*)* i tyminie (B*)* występuje forma dikarbonylowa z dużym udziałem struktury spolaryzowanej ;**



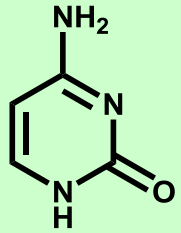


C



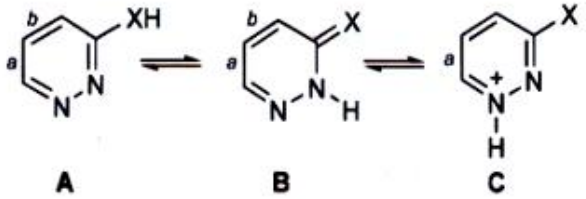
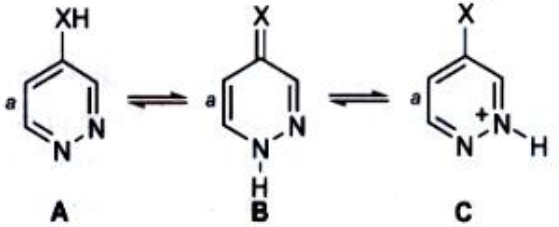
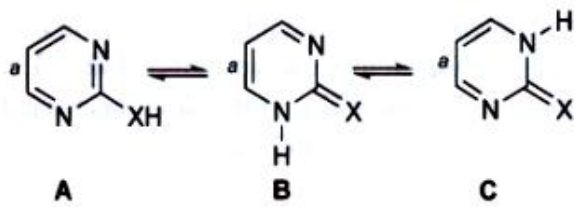
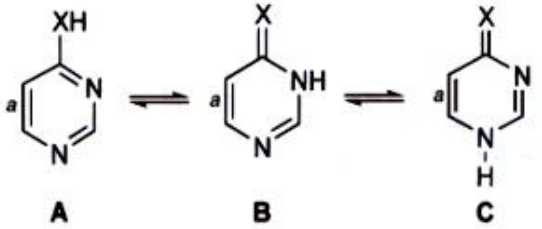
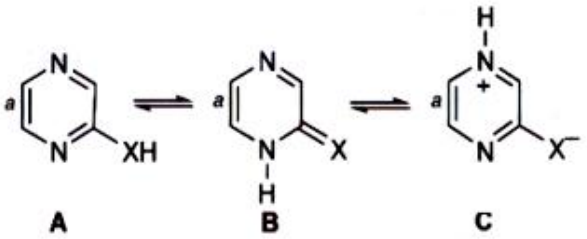
D

•Związki zawierające grupę aminową, w których może występować tautomeria aminowo-iminowa, występują głównie w formie aminowej, tak jak np. cytozyna czy melamina ;

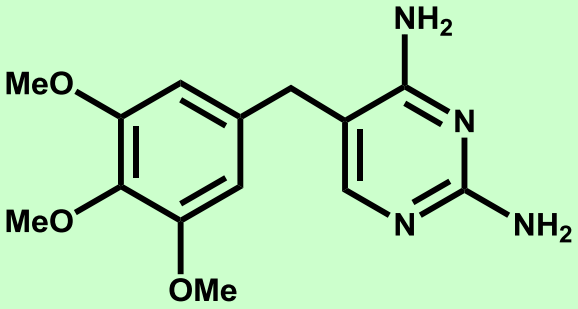


cytozyna

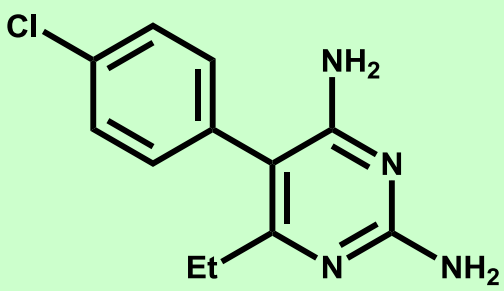
melamina

	X =	O	S	NH
	Parent	B(4.3)	B	A
	Benzo[*a*]	B(2.6)	–	A(8.3 vs. B)
	Benzo[*b*]	B	B	A
	Parent	B(2.6)	B	A
	Benzo[*a*]	B(3.6)	B	A(4.1 vs. B)
	Parent	B≡C	B≡C	A(~6 vs. B)
	Benzo[*a*]	B	–	–
	Parent	B(0.4 vs. C)	B	A(~6 vs. B/C
	Benzo[*a*]	B(0.85 vs. C)	B	A
	Parent	B	B	A
	Benzo[*a*]	B(>1.6 vs. A)	B	A

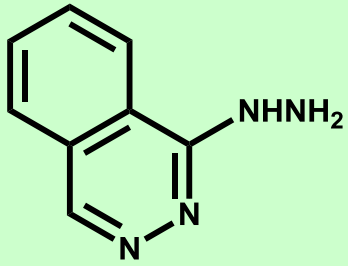
Zastosowanie znaczenie biologiczne diazyn, triazyn i ich benzologów



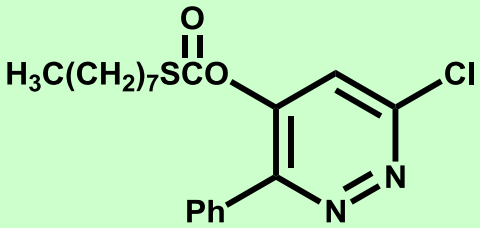
Trimetoprym



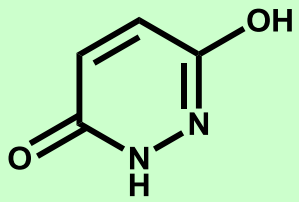
Pirymetamina



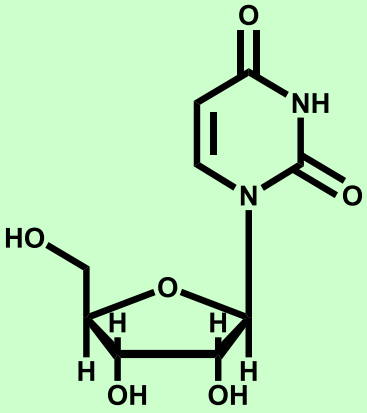
Hydralazyna



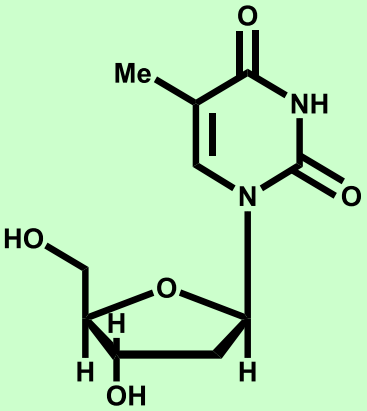
pirydat



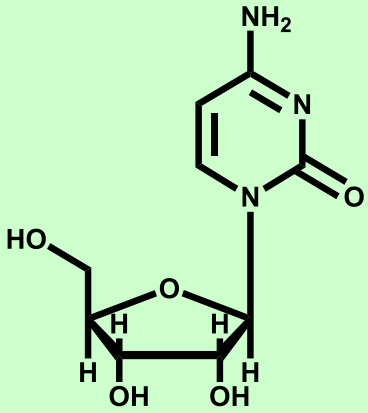
3-hydroxy-6-(1H)-pirydazinon



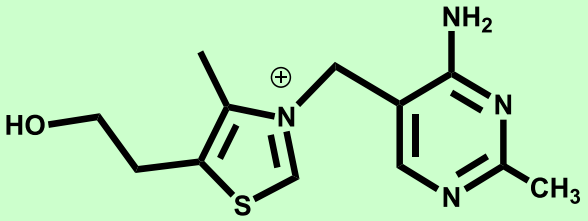
urydyna



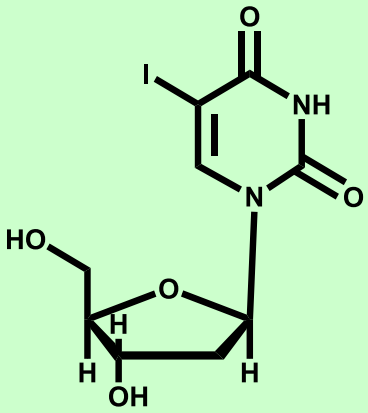
tymidyna



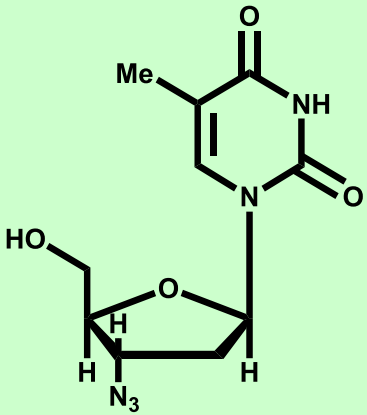
cytydyna



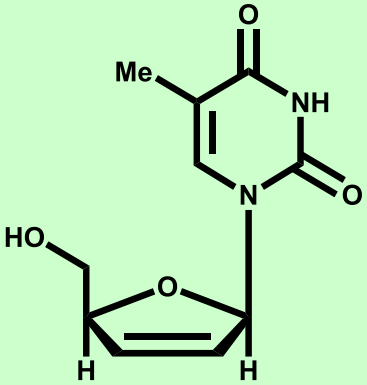
tiamina



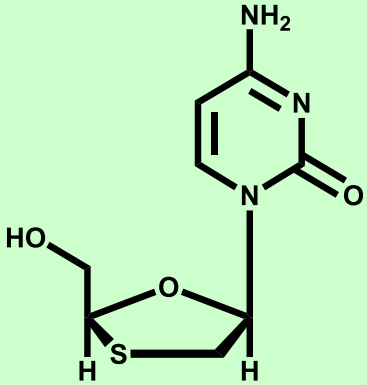
idoksyurydyna



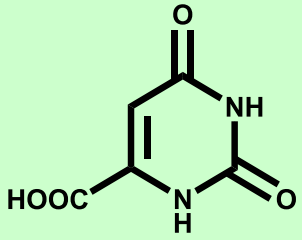
AZT



d4T (Stavudine)



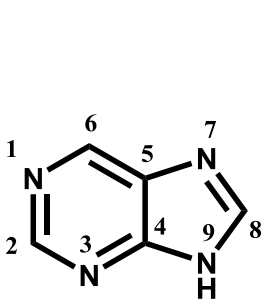
3-TC (Lamivudine)



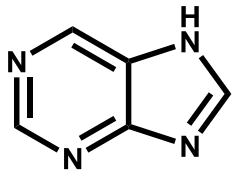
kwas orotowy

SZEŚCIOCZŁONOWE PIERŚCIENIE HETEROAROMATYCZNE Z DWOMA I TRZEMA ATOMAMI AZOTU

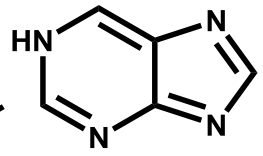
2. Puryny i Pterydyny



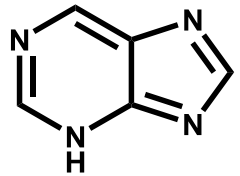
9*H*-puryna



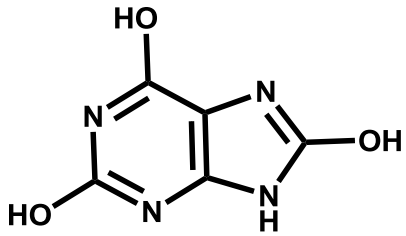
7*H*-puryna

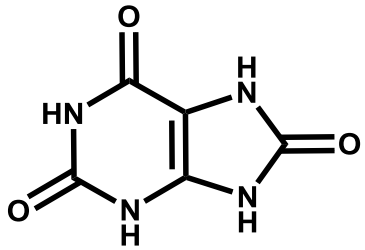


1*H*-puryna

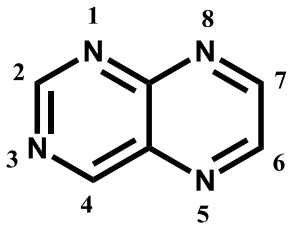


3*H*-puryna

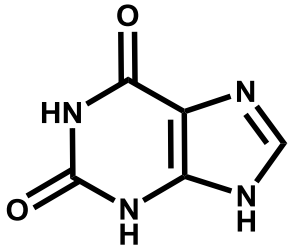




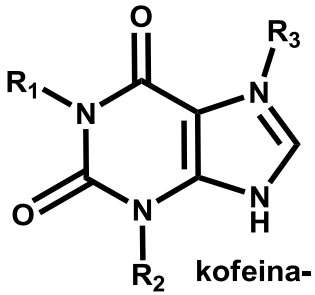
kwas moczowy



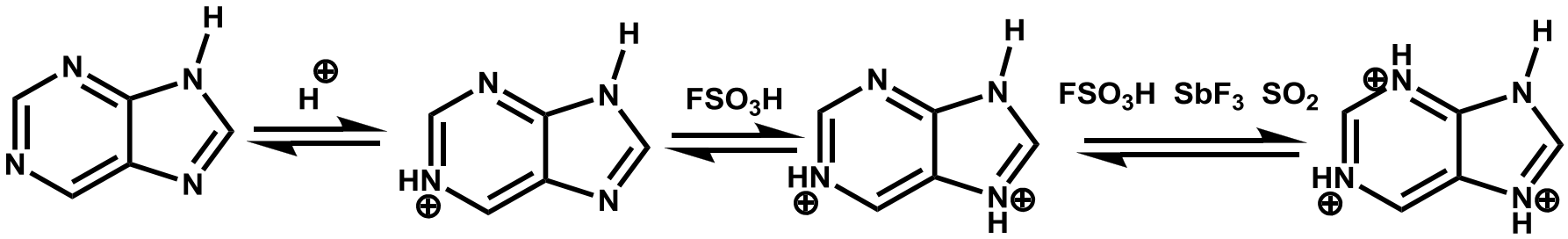
pterydyna



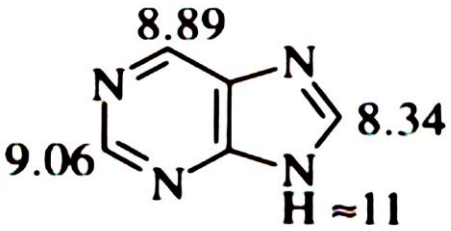
ksantyna



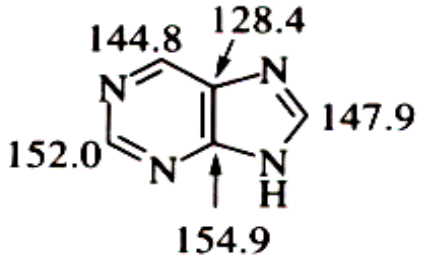
kofeina- R1, R2, R3=CH_3
teobromina- R1=H, R2,R3=CH_3
teofilina- R1,R2 =CH_3, R3=H


H
N
N
N
H⊕
HN⊕
FSO3H
FSO3H SbF3 SO2
H
H
N⊕H

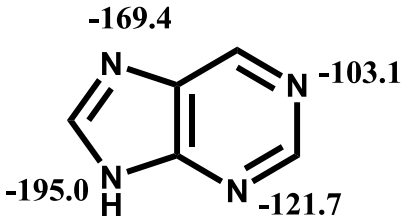
δ ^{1}H NMR puryny

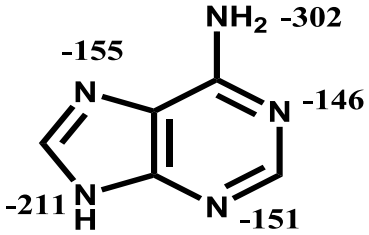


δ ^{13}C NMR puryny

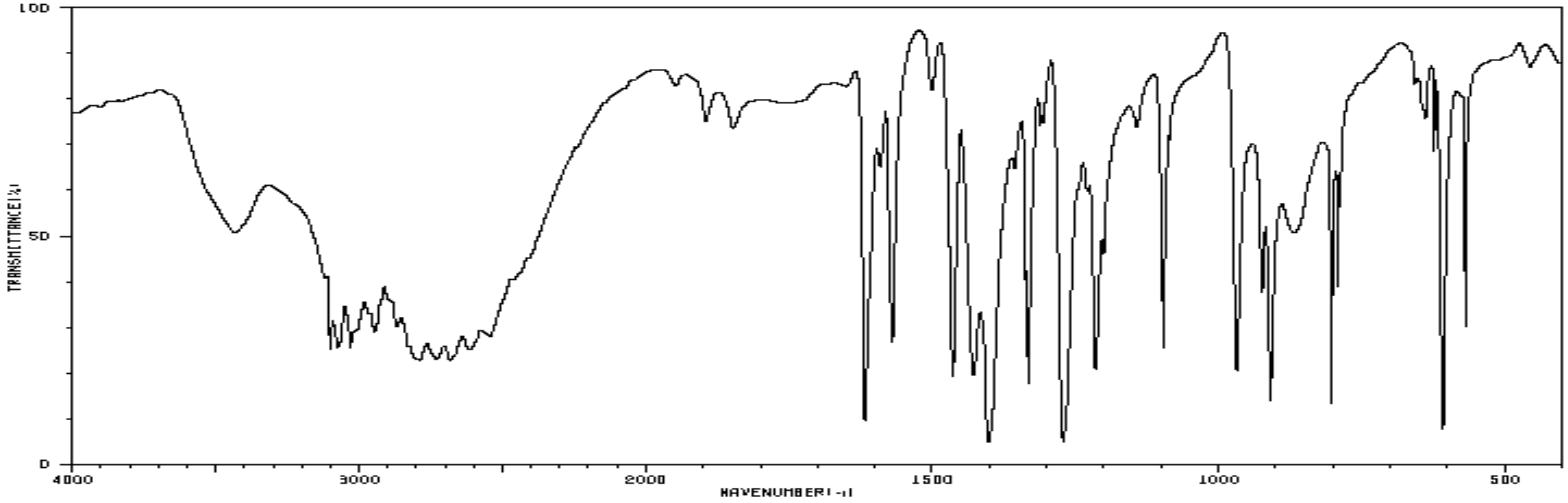


δ ^{15}N NMR puryny

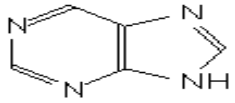




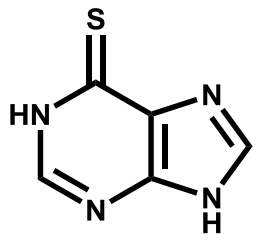
Widmo IR puryny



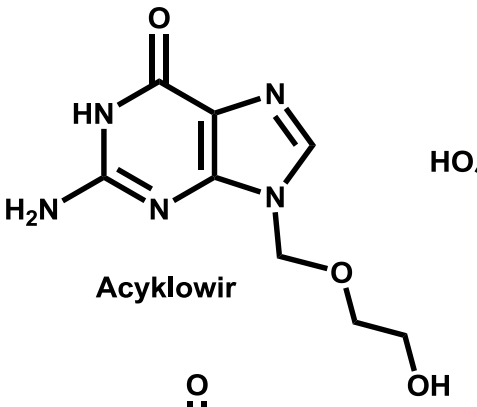
3432	49	2789	21	1691	62	1271	4	909	13
3101	24	2729	22	1570	26	1230	58	869	49
3073	24	2682	21	1464	16	1215	20	803	13
3030	24	2671	22	1428	18	1201	44	792	37
3012	28	2612	24	1402	4	1096	24	624	66
2947	27	2541	26	1356	82	968	20	609	7
2867	29	1618	9	1333	17	924	36	669	29



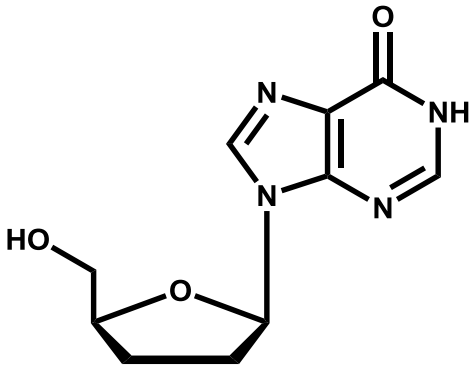
Puryny



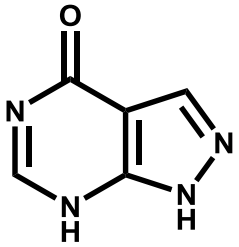
6- merkaptopuryna



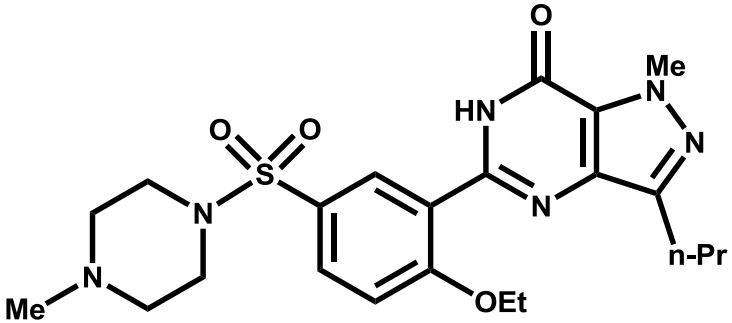
Acyklowir



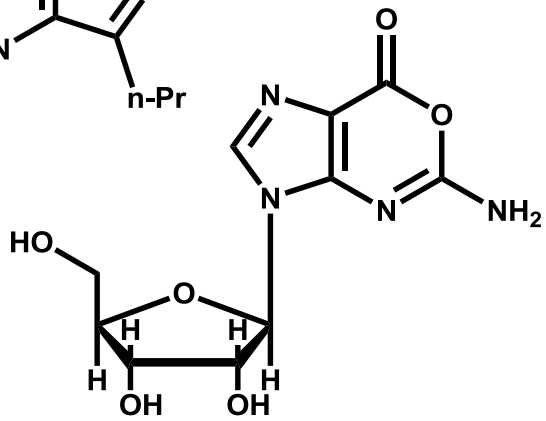
Dideoksyinozyna (DDI)



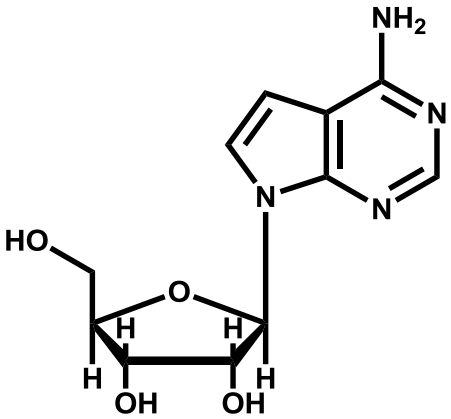
allopurinol



Sildenafil
(Viagra)

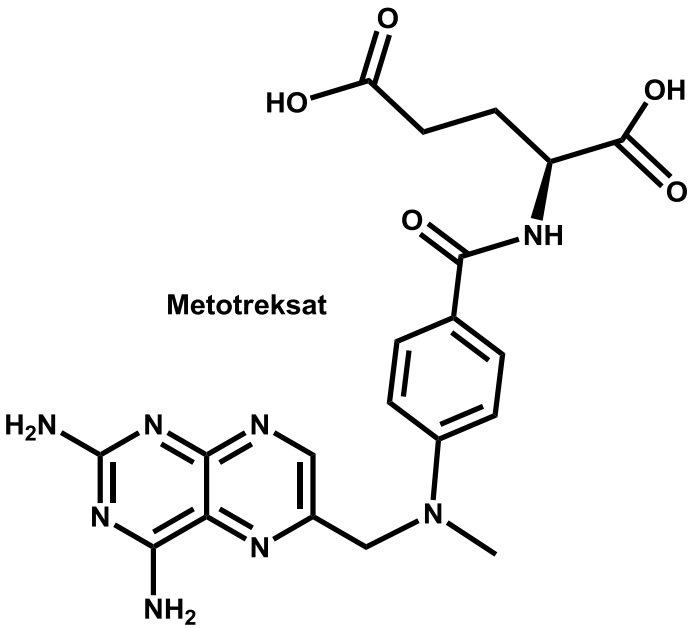


oxanosine

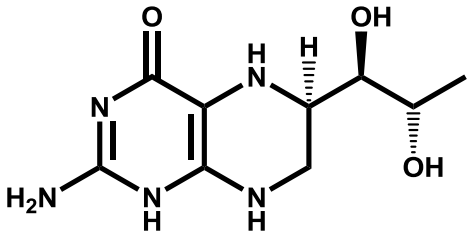


tubercydyna

Pterydyny

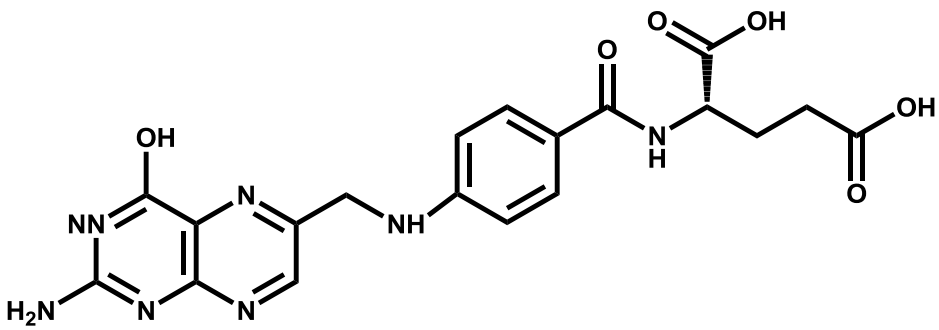


Metotreksat



tetrahydrobiopteryna -BH_4

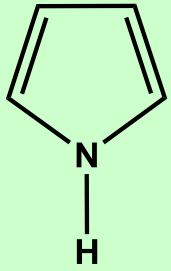
Sapropteryna



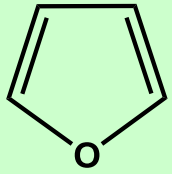
Kwas foliowy (folacyna, witamina B_9, witamina M, witamina B_{11})

PIĘCIOCZŁONOWE PIERŚCIENIE HETEROAROMATYCZNE Z JEDNYM HETEROATOMEM

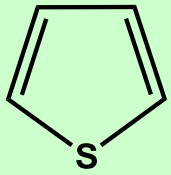
1. Pirol, Furan i Tiofen



pirol



furan



tiofen

•Pirol, furan i tiofen bezbarwne cieczami słabo rozpuszczalnymi w wodzie i dobrze w rozpunikach organicznych.

•Temperatury topnienia i wrzenia wynoszą :

• pirolu -24°C, 131°C;

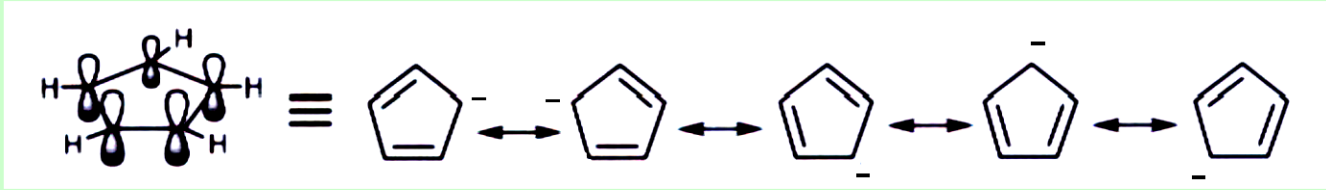
furanu -85,65°C, 31,36 °C;

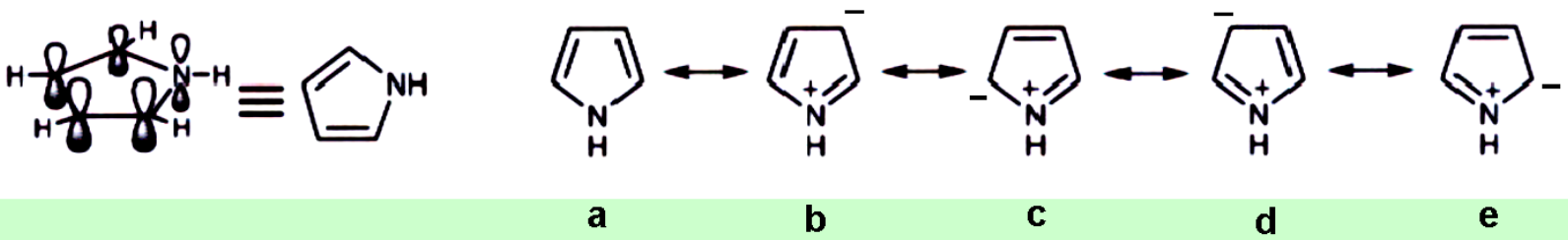
tiofenu -38,25°C, 84,16°C

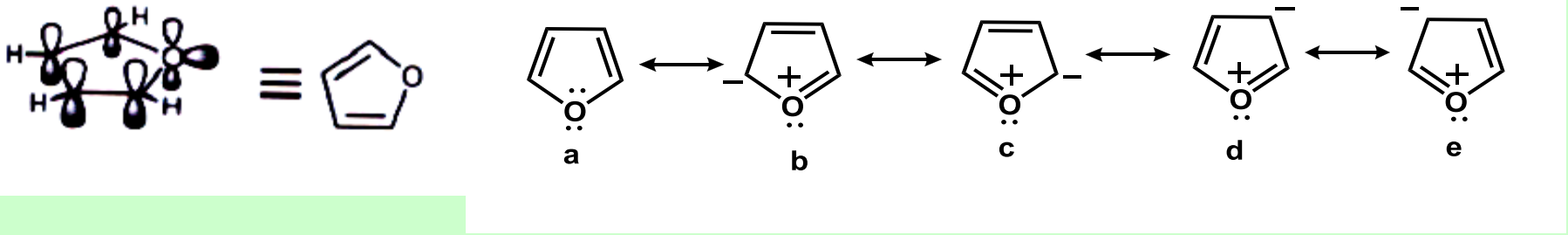
•Wyznaczone doświadczalnie energie rezonansu wskazują na znacznie słabszą aromatyczność pięcioczłonowych związków heterocyklicznych w porównaniu z benzenem (150,0 kJ/mol) malejącą w szeregu :

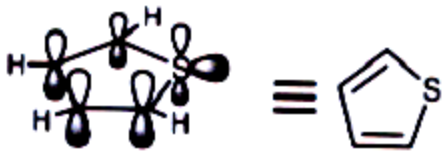
tiofen (121,8 kJ/mol) > pirol (90,4 kJ /mol) > furan (68,7 kJ / mol)

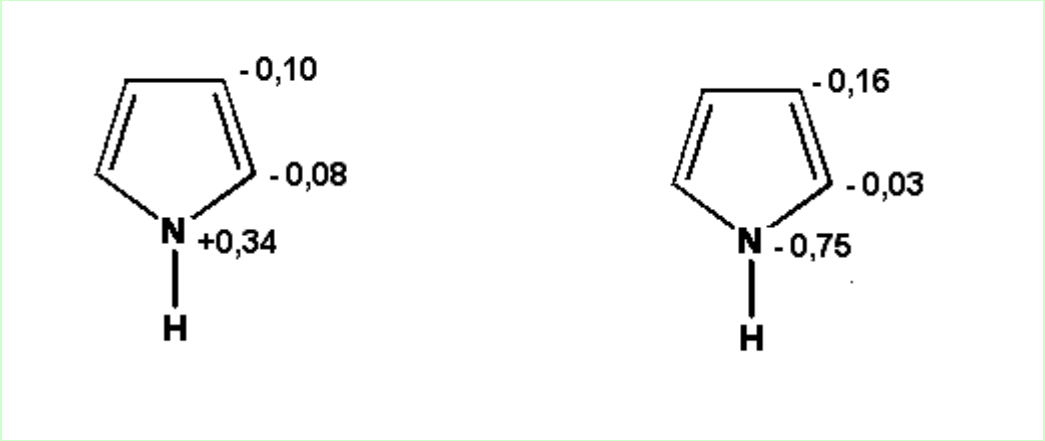
•Ze zwiększeniem rozmiaru heteroatomu wzrastają długości wiązań pomiędzy nim a sąsiednimi atomami węgla, maleje natomiast kąt pomiędzy tymi wiązaniami (pirol 109,8 °, furan 106,5 °, tiofen 92,2 °).



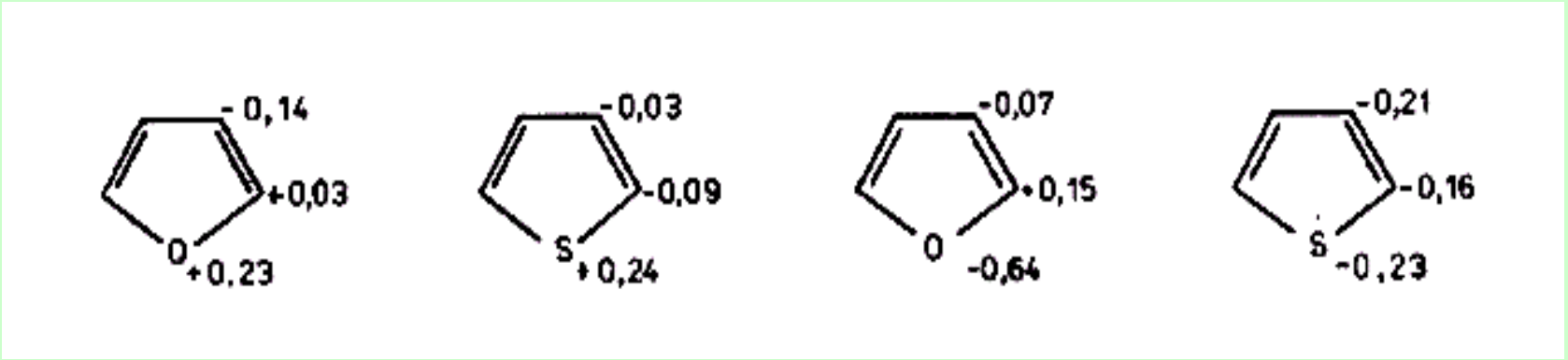

a
b
c
d
e


a
b
c
d
e

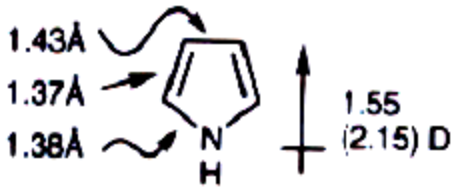




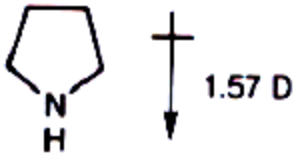
Ładunki π **Ładunki σ**



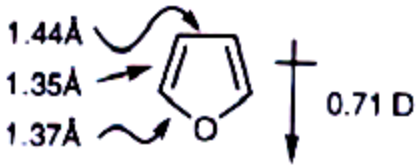
Ładunki π **Ładunki σ**



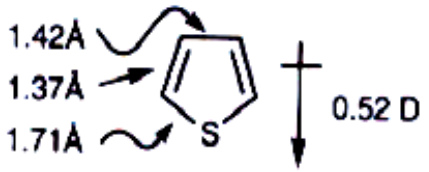
pirol



pirolidyna



furan



tiofen

Tetrahydrofuran – 1.68 D

Tetrahydrotiofen – 1.87 D

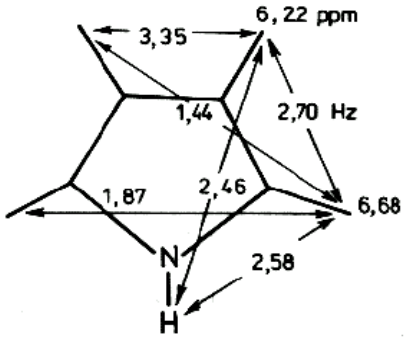
Widma IR, UV i NMR – charakterystyczne cechy ułatwiające określanie struktury pirolu, furanu i tiofenu

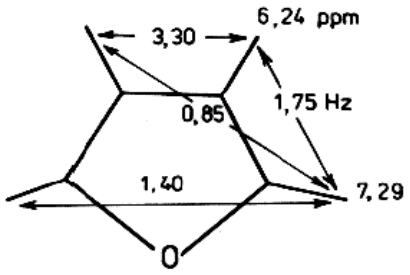
Analiza widm w podczerwieni- Pasma absorpcji w podczerwieni pirolu, furanu i tiofenu

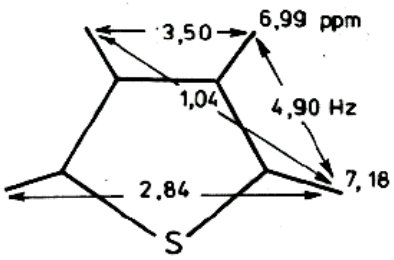
Rodzaj drgania	Pirol [cm^{-1}]	Furan [cm^{-1}]	Tiofen [cm^{-1}]
ν_{CH}	3133–3111	3163–3124	3093–2996
ν_{NH}	3400		
$\nu_{pierścienia}$	1530–1384	1586–1030	1590–1358
β_{CH}	1386–1015	1268–1067	1290–909
β_{NH}	1074		
deformacja pierścienia	1144	995	832
γ_{CH}	838–711	838–660	748–686
γ_{NH}	565		
$\beta_{pierścienia}$	867–711	742–702	872–604
$\gamma_{pierścienia}$	649–618	601–550	565–453

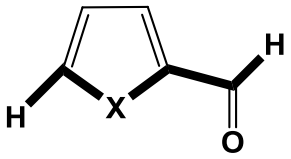
Analiza widm NMR- pirolu, furanu i tiofenu i pochodnych

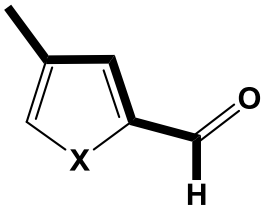
^{1}H





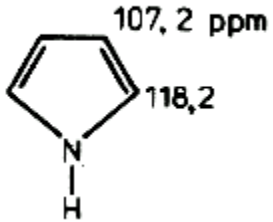


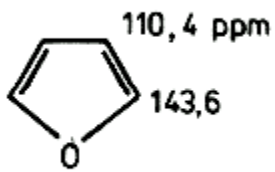


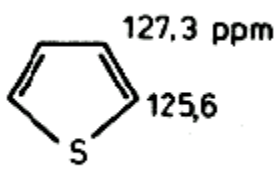


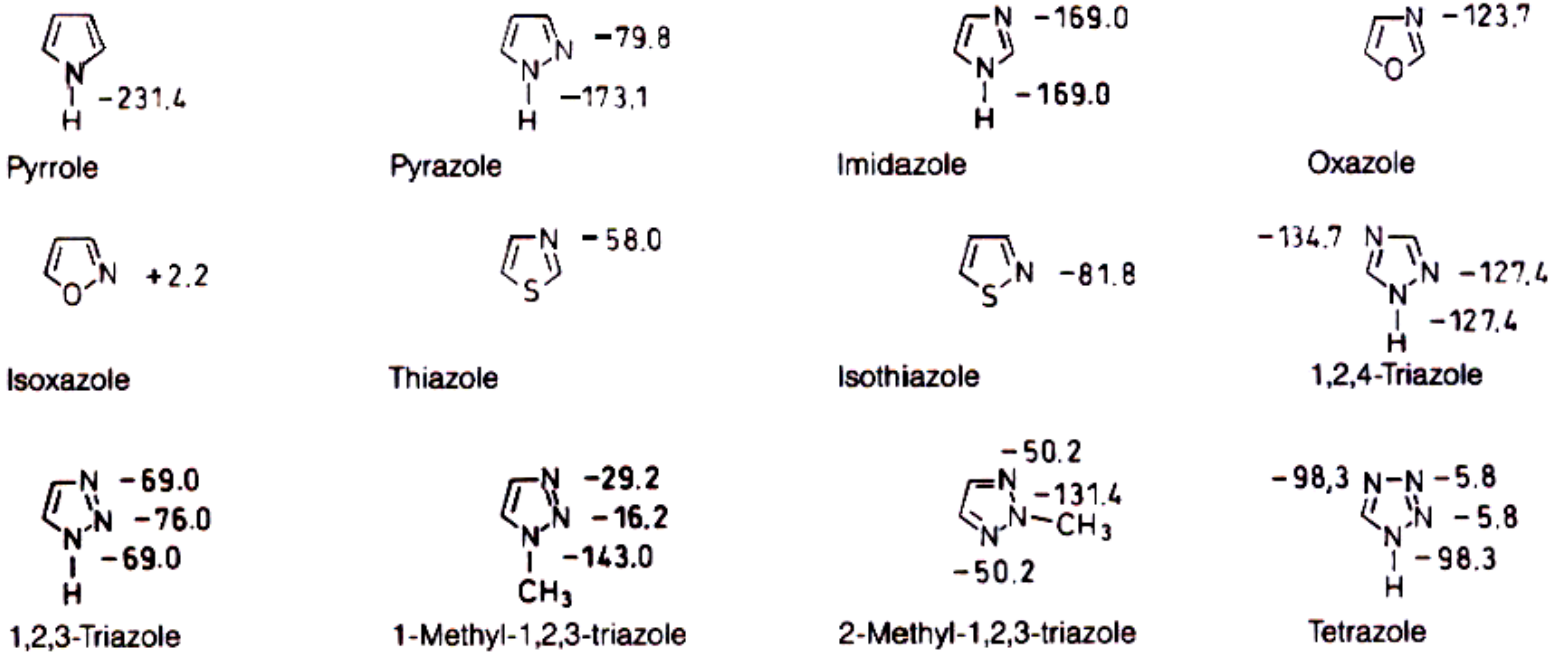
^{5}J= 1Hz

^{13}C









^{15}N

^{17}O **^{17}O przesunie w dół pola o 222 ppm obserwuje w przypadku przejścia od tetrahydrofuranu do furanu.**

^{33}S **^{33}S przesunięcie w dół pola o 309 ppm tetrahydrotiofen ⟶ tiofen.**

Analiza widm mas pirolu, furanu i tiofenu i pochodnych