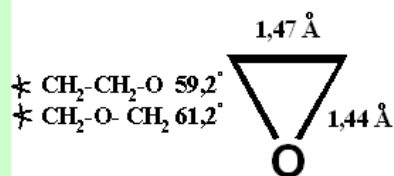
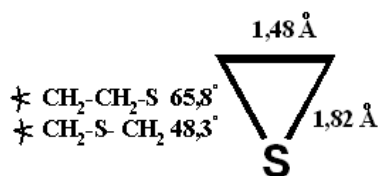


I. Alifatyczne związki Heterocykliczne

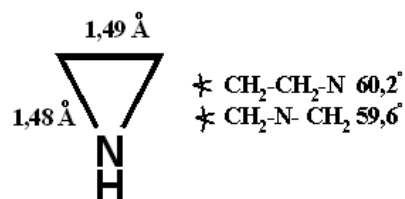
Właściwości fizyczne i charakterystyka spektroskopowa trój- i czteroczłonowych związków heterocyklicznych



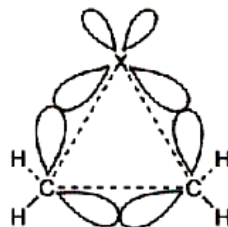
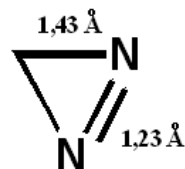
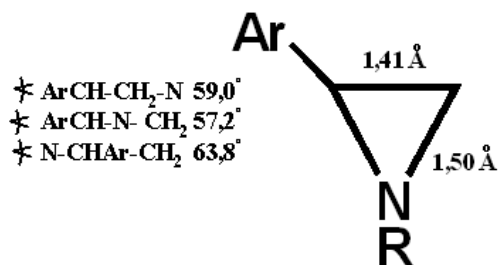
OKSIRAN



TIIRAN



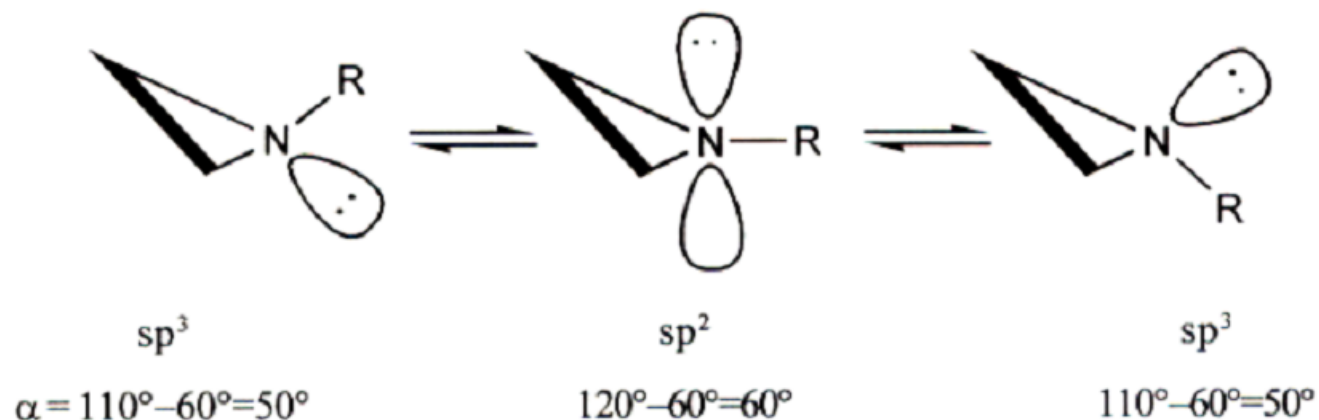
AZIRYDYNA



X-heteroatom

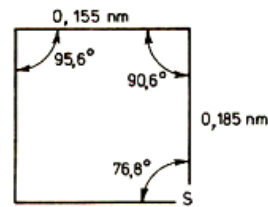
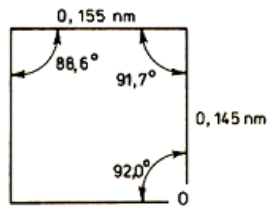
Właściwości fizyczne i charakterystyka spektroskopowa trój- i czteroczłonowych związków heterocyklicznych

2

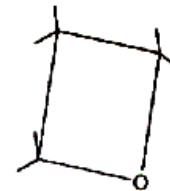
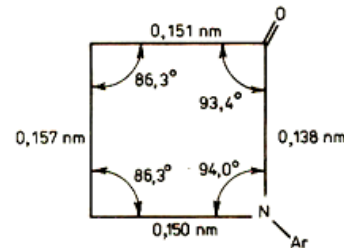
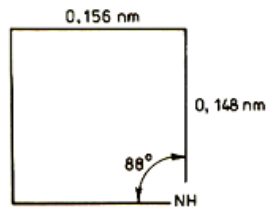


Piramidalna inwersja w azirydynach-związki zawierające atom wodoru lub podstawnik przy atomie azotu ulegają inwersji, (duża bariera inwersji na atomie azotu) trwale izomery.

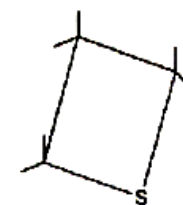
R = C_2H_5	81.0 kJ/mol.
R = $C(CH_3)_3$	71.0 kJ/mol.
R = C_6H_5	49.0 kJ/mol.
R = $CON(CH_3)_2$	41.0 kJ/mol.
R = $COOCH_3$	30.0 kJ/mol.
R = NH_2, Cl, OCH_3	90.0 kJ/mol.



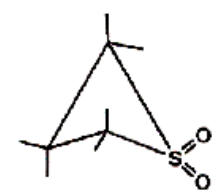
azetydyne



oksetan



tietan



Bariery inwersji pierścieni są niewielkie i wynoszą ;

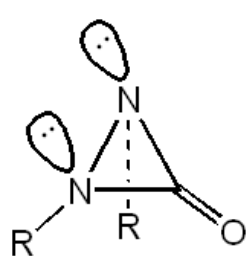
•oksetan 0.0 kJ/mol – płaski;

•tietan 3.14 kJ/mol;

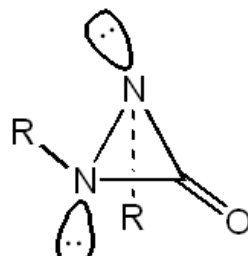
•azetydyne 5.27 kJ/mol ;

•utlenienie tietanu do sulfonu powoduje zmniejszenie oddziaływań torsyjnych i zgięcie cząsteczki;

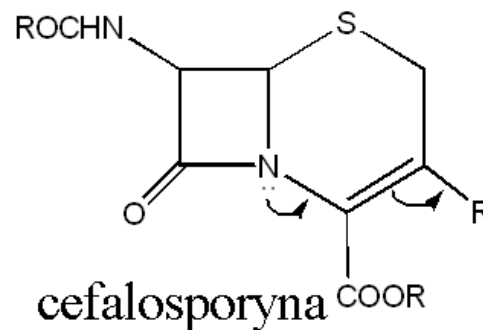
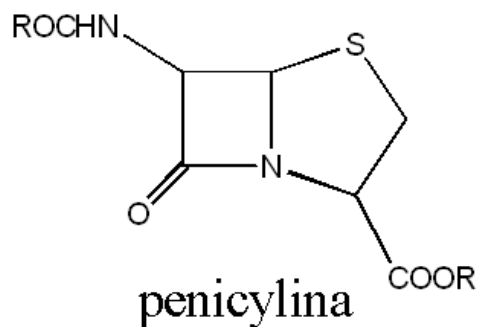
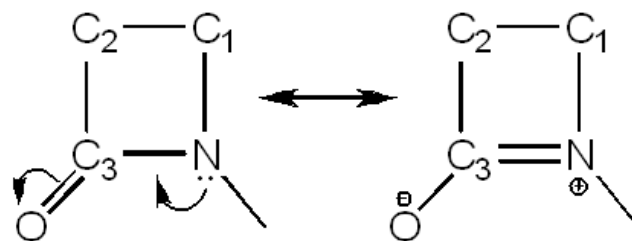
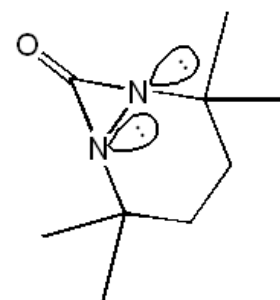
Naprężenia torsyjne występujące w pierścieniach trój- i czteroczlonowych:



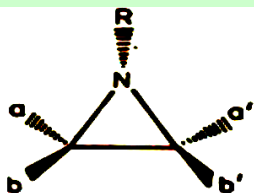
a



b



Isotope	Natural abundance [%]	Spin quantum number, I	Frequency [MHz] at 2.35 Tesla	Relative sensitivity of nucleus	Relative sensitivity at natural abundance	Electric quadrupole moment [$e \times 10^{-24} \text{ cm}^2$]
^1H	99.985	1/2	100.0	1	1	
^2H	0.015	1	15.4	9.6×10^{-3}	1.5×10^{-6}	2.8×10^{-3}
^3H	0.000	1/2	106.7	1.2	0	
^{10}B	19.58	3	10.7	2.0×10^{-2}	3.9×10^{-3}	7.4×10^{-2}
^{11}B	80.42	3/2	32.1	1.6×10^{-1}	1.3×10^{-1}	3.6×10^{-2}
^{13}C	1.108	1/2	25.1	1.6×10^{-2}	1.8×10^{-4}	
^{14}N	99.635	1	7.3	1.0×10^{-3}	1.0×10^{-3}	1.9×10^{-2}
^{15}N	0.365	1/2	10.1	1.0×10^{-3}	3.8×10^{-6}	
^{17}O	0.037	5/2	13.6	2.9×10^{-2}	1.1×10^{-5}	-2.6×10^{-2}
^{19}F	100.000	1/2	94.1	8.3×10^{-1}	8.3×10^{-1}	
^{31}P	100.000	1/2	40.5	6.6×10^{-2}	6.6×10^{-2}	
^{33}S	0.76	3/2	7.6	2.3×10^{-3}	1.7×10^{-5}	-6.4×10^{-2}
^{117}Sn	7.61	1/2	35.6	4.5×10^{-2}	3.4×10^{-3}	
^{119}Sn	8.58	1/2	37.3	5.2×10^{-2}	4.4×10^{-3}	
^{195}Pt	33.8	1/2	21.5	9.9×10^{-3}	3.4×10^{-3}	
^{199}Hg	16.84	1/2	17.8	5.7×10^{-3}	9.5×10^{-4}	
^{207}Pb	22.6	1/2	20.9	9.2×10^{-3}	2.1×10^{-4}	

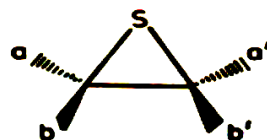


$$\delta = 1,48 \text{ ppm (a, a', b, b')}$$

$$J_{ab} = 0,9-4 \text{ Hz}$$

$$J_{aa'} = 2-7 \text{ Hz}$$

$$J_{ab'} = 5-9 \text{ Hz}$$

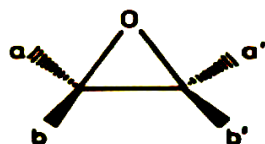


$$\delta = 2,27 \text{ ppm (a, a', b, b')}$$

$$J_{ab} = \text{od } -14 \text{ do } 1 \text{ Hz}$$

$$J_{ad} = 6-7 \text{ Hz}$$

$$J_{ab'} = 5-6 \text{ Hz}$$

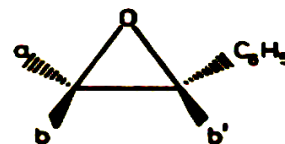


$$\delta = 2,54 \text{ ppm (a, a', b, b')}$$

$$J_{ab} = 5-7 \text{ Hz}$$

$$J_{ad} = 2-5 \text{ Hz}$$

$$J_{ab'} = 1-3 \text{ Hz}$$



$$\delta = 3,41 \text{ ppm (b')}$$

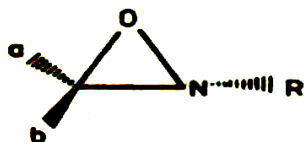
$$\delta = 2,86 \text{ ppm (b)}$$

$$\delta = 2,49 \text{ ppm (a)}$$

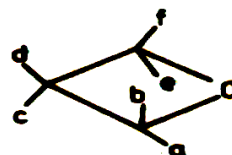
$$J_{ab} = 6 \text{ Hz}$$

$$J_{bb'} = 3,9 \text{ Hz}$$

$$J_{ab'}^F = 2,4 \text{ Hz}$$

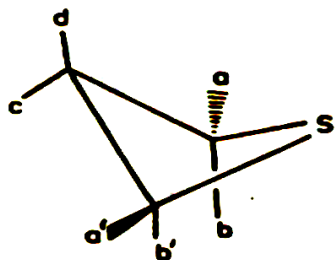


$$\delta = 4,5-5 \text{ ppm (a, b)}$$



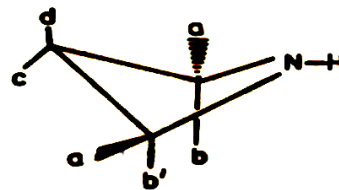
$$\delta = 4,73 \text{ ppm (a, b, e, f)}$$

$$\delta = 2,72 \text{ ppm (c, d)}$$



$$\delta = 3,21 \text{ ppm (a, a', b, b')}$$

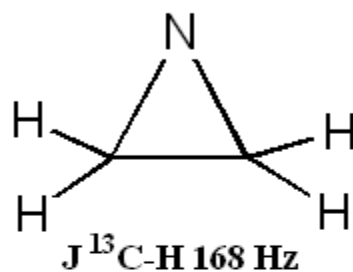
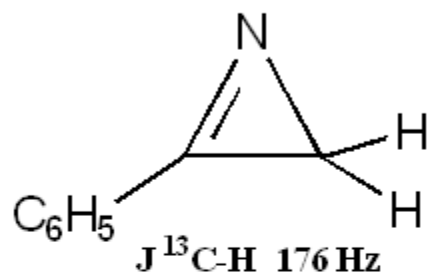
$$\delta = 2,94 \text{ ppm (c, d)}$$



$$\delta = 3,95 \text{ ppm (NH)}$$

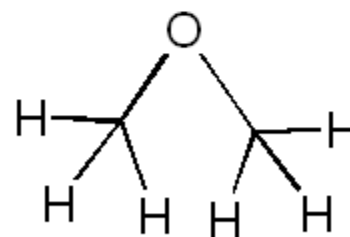
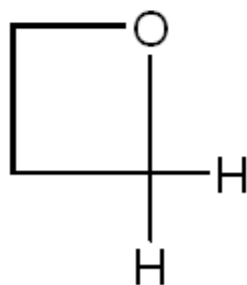
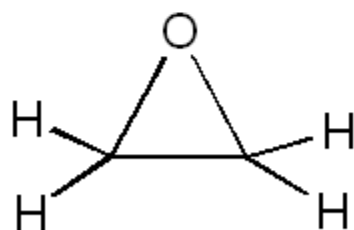
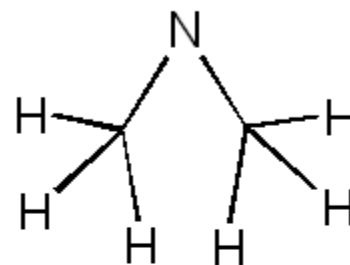
$$\delta = 3,70 \text{ ppm (a, a', b, b')}$$

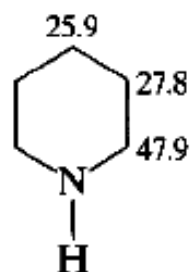
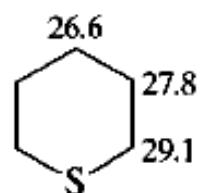
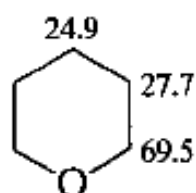
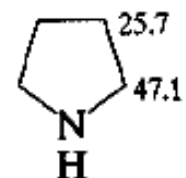
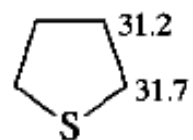
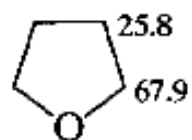
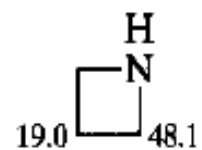
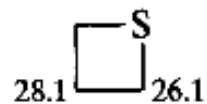
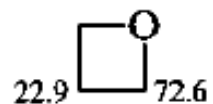
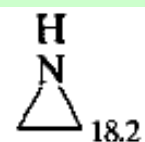
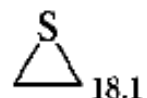
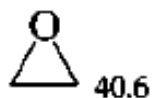
$$\delta = 3,40 \text{ ppm (c, d)}$$



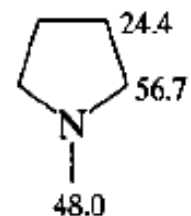
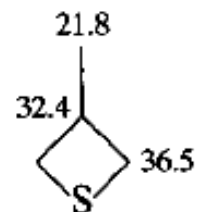
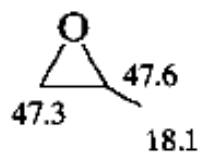
$\delta \text{CH}_2 \text{ } 18.2 \text{ ppm}$


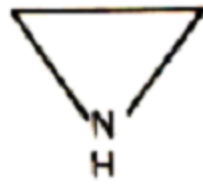

$\delta^{15}\text{N } -393.3 \text{ ppm}$





Substituted

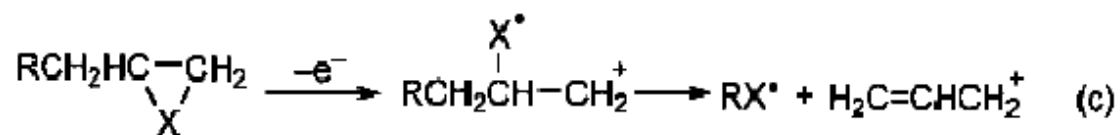
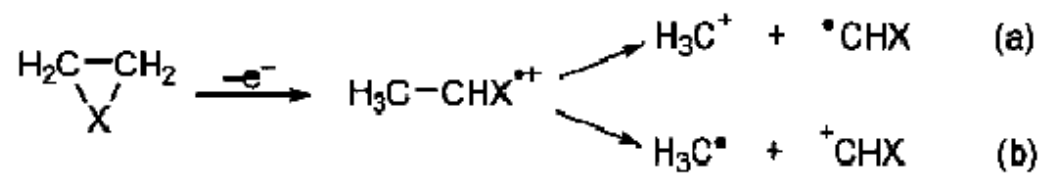


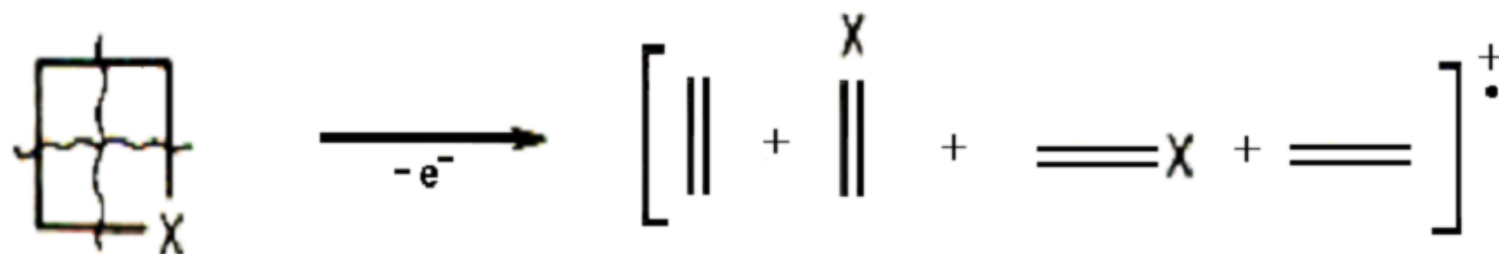
Związek	$\nu_{\text{C-H}}$ [cm ⁻¹]	$\nu_{\text{C-C}}$ (szkieletowe) [cm ⁻¹]	$\delta_{\text{C-H}}$ (nożycowe) [cm ⁻¹]	$\delta_{\text{C-H}}$ (zginające) [cm ⁻¹]
	3079,3063 3016,3005	1266	1490,1470	1153,1120
	3078,3012	1268,1210	1475,1455	1128,1133 1088, 998
	3080,3000	1112	1466,1427	1051

Widma UV – charakterystyczne cechy ułatwiające określanie struktury **trój- i czteroczłonowych związków heterocyklicznych**:

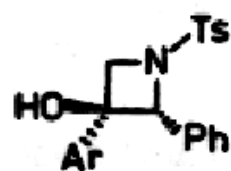
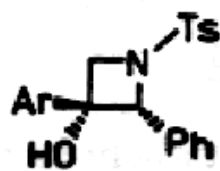
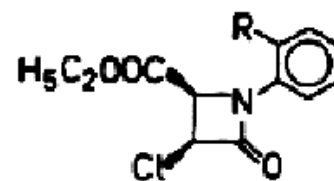
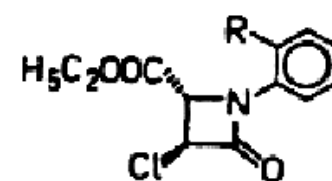
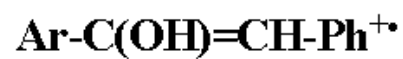
Związek	λ_{\max} [nm]	ϵ	Związek	λ_{\max} [nm]	ϵ
Azirydyna	179	4200	Azetydyna	192	
	145	6100	Oksetan	187	2000
	118	6300		174	2750
Oksiran	171	5600		161	
	158		153		
	143				
Tiiran	260	40	Tietan	275	30
	205	4000		218	600

Widma mas – charakterystyczne cechy ułatwiające określenie struktury trój- i czteroczłonowych związków heterocyklicznych:

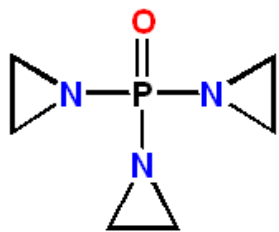




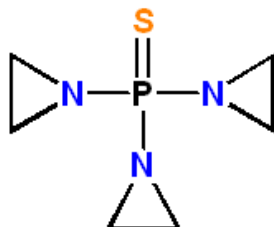
R= OH

*cis**trans**cis**trans*

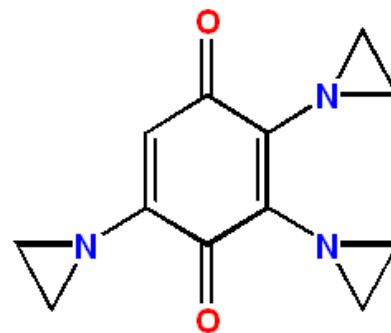
Znaczenie związków heterocyklicznych o małych pierścieniach



TEPA



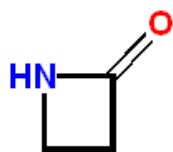
TioTEPA



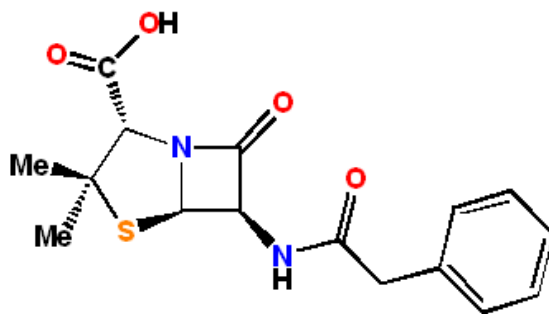
Trenimon

(lek przeciwnowotworowy)

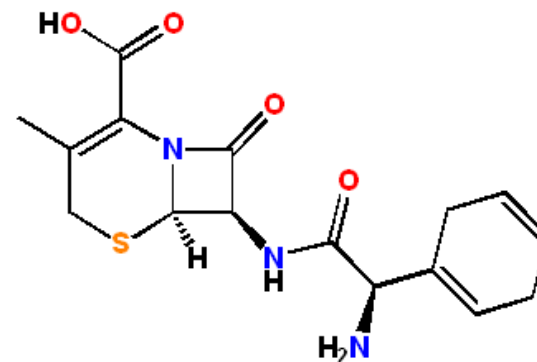
Antybiotyki penicylinowe i cefalosporynowe



Azetydyn-2-on



Penicylina G



Sefril

Właściwości fizyczne i charakterystyka spektroskopowa niearomatycznych pięcio- i sześcioczłonowych związków heterocyklicznych 15



(a)

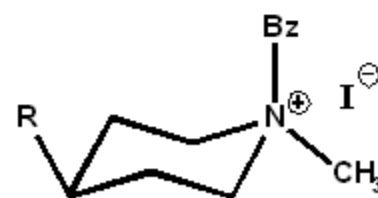
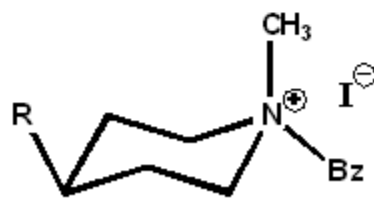
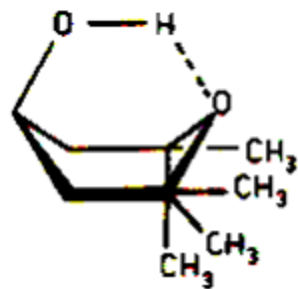
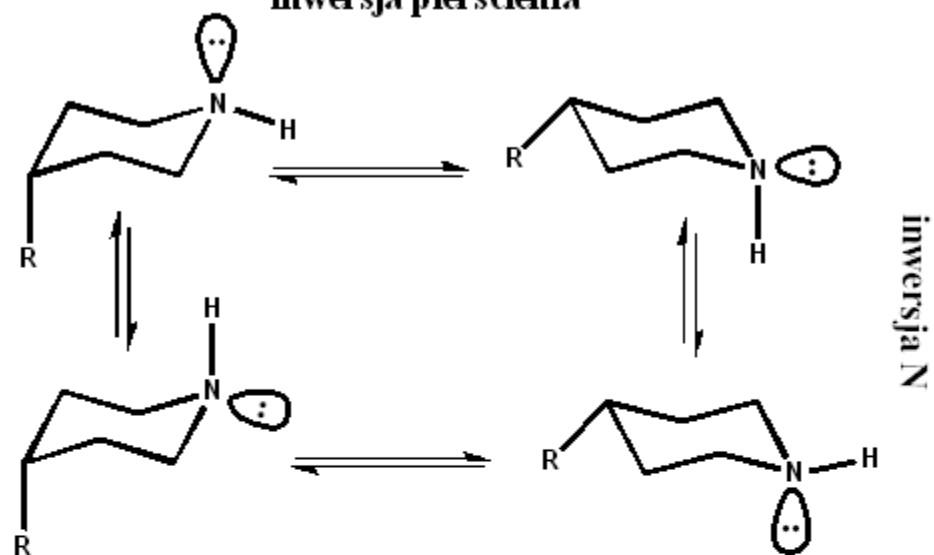


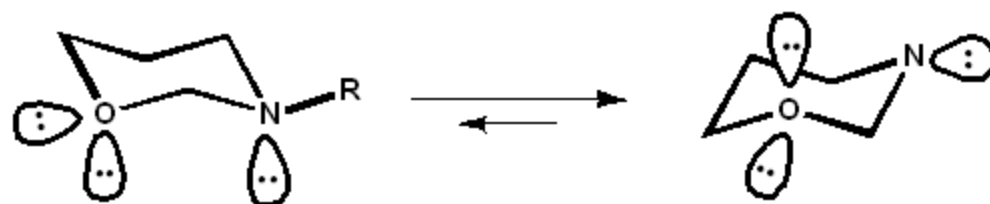
(b)



(c)

inwersja pierścienia





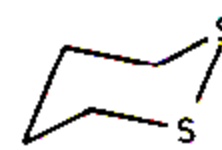
9,2 kJ/mol



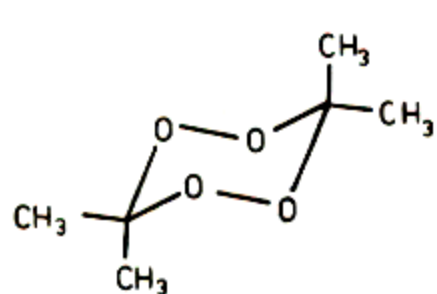
16,0 kJ/mol



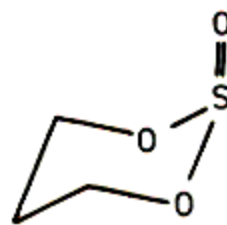
35,2 kJ/mol



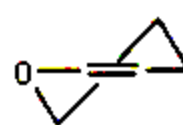
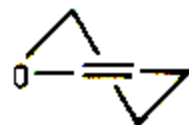
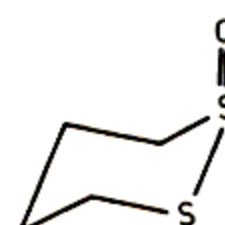
46,1 kJ/mol

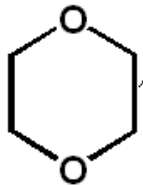
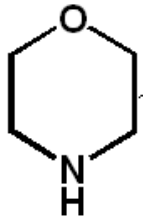
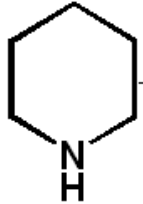


62,8 kJ/mol



Konformacje gdzie S=O zorientowane aksjalnie

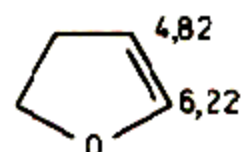
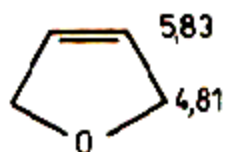
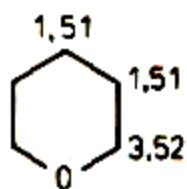
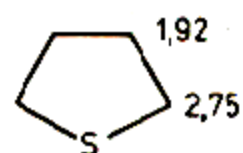
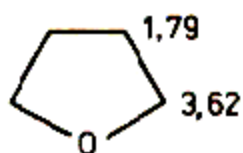
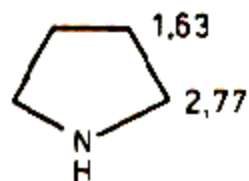


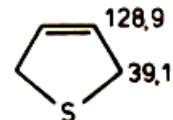
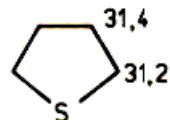
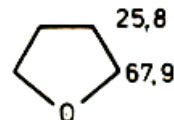
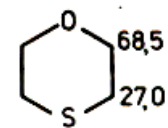
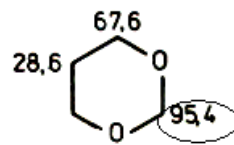
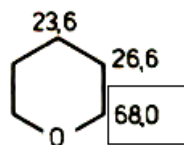
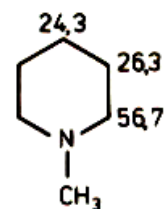
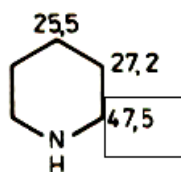
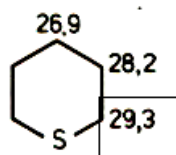
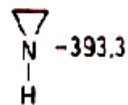
$O < NH < S$


Związek	T. topn. [°C]	T. wrz. [°C/Tor]
Oksolan (tetrahydrofuran)	-108	67
Tiolan (tetrahydrotiofen)	-96,2	121,1
Oksan (tetrahydropiran)		88
Tian (tetrahydropyridan)	19	141,9
Azinan (piperidyna)	-9	106
1,4-Oksazinan (morfolina)	-4,7	128,3
1,4-Dioksan	11,8	100-102
1,4-Ditian	111	199
Oksan-2-on	-12,5	218-220
Oksolan-2,5-dion (bezw. bursztynowy)	119,6	261
2-Azinanon (2-pirolidon)	24,6	250,5/742
Pirolidyn-2,5-dion (imid kwasu bursztynowego)	127	288
1-Metylo-2-azinanon (1-metylo-2-piperidon)		105-106/12

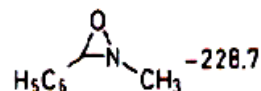
Widma NMR – charakterystyczne cechy ułatwiające określanie struktury
pięcio- i sześcioczłonowych związków heterocyklicznych:

^1H

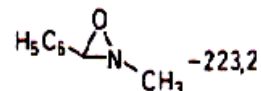


^{13}C  ^{15}N 

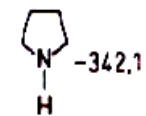
Aziridine



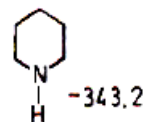
cis-2-Methyl-3-phenyloxaziridine



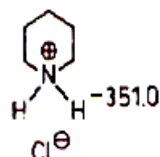
trans-2-Methyl-3-phenyloxaziridine



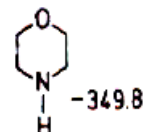
Pyrrolidine



Piperidine



Piperidine hydrochloride



Morpholine

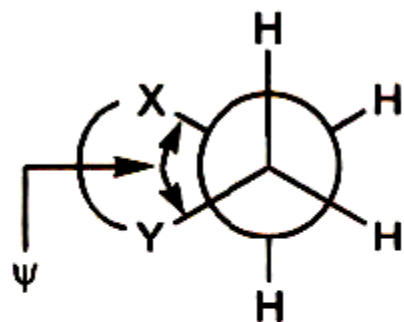


1-Azabicyclo-[2.2.2]octane

$$\frac{J(\text{trans})}{J(\text{cis})} = \frac{A \cos^2 \varphi(\text{trans})}{A \cos^2 \varphi(\text{cis})} = R$$

$$\left[\begin{array}{l} \text{In } \text{CH}_2\text{-CH}_2 \text{ fragment :} \\ J(\text{trans}) = \frac{1}{2} (J_{aa} + J_{ee}) \\ J(\text{cis}) = \frac{1}{2} (J_{ea} + J_{ae}) \end{array} \right]$$

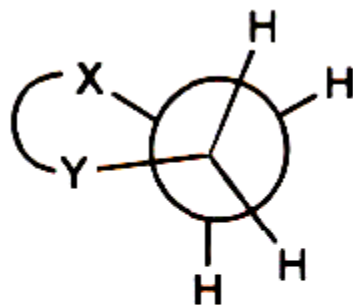
$$\cos \psi = [3/(2 + 4R)]^{1/2}$$



$$R = 1.9\text{--}2.2$$

$$\psi = 56\text{--}58^\circ$$

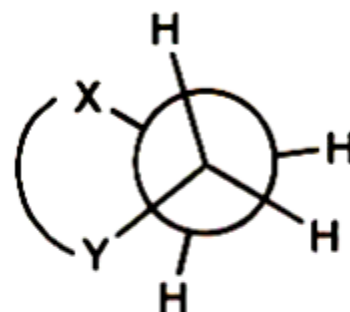
1



$$R < 1.8$$

$$\psi < 55^\circ$$

2



$$R > 2.3$$

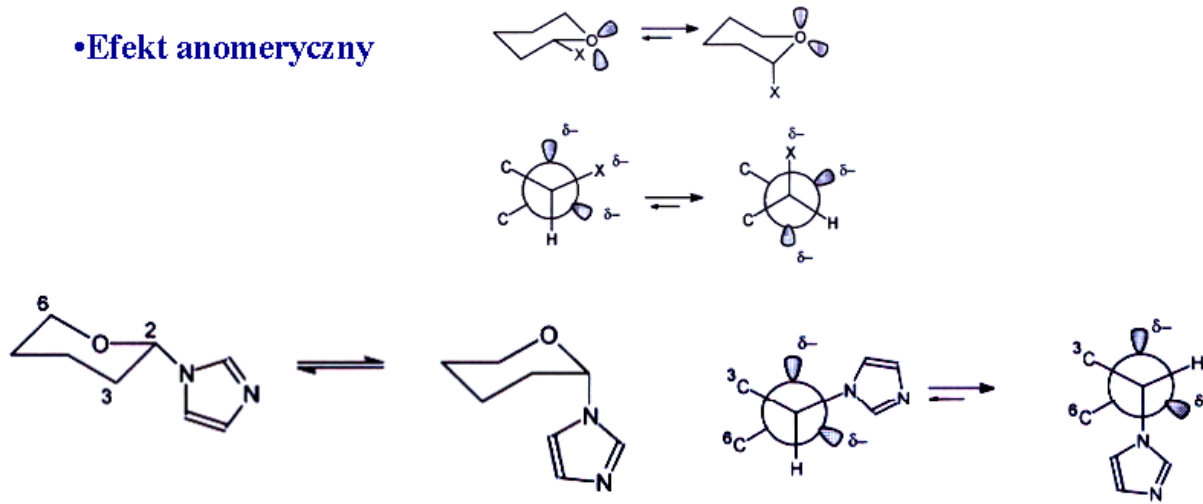
$$\psi > 59^\circ$$

3

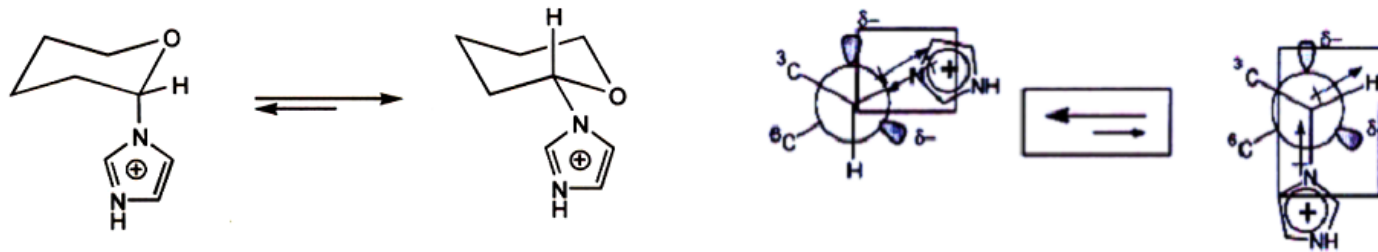
Konformacje pierścienia określane przy pomocy R

Hetero group	Segment	J(trans) (Hz)	J(cis) (Hz)	R	ψ
: NH	α, β	7.88	3.77	2.09	57
: N-CH ₃	α, β	7.52	3.65	2.06	57
O	α, β	7.41	3.87	1.91	56
S	α, β	8.15	2.96	2.65	61
S	β, γ	8.47	3.28	2.58	60
: SH	α, β	8.5	3.9	2.2	58
SCH ₃ I	α, β	8.63	3.24	2.66	61

•Efekt anomeryczny

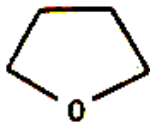


•Odwrotny efekt anomeryczny



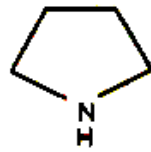
•Efekt Gauche





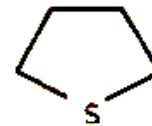
$$\lambda = 190, 172 \text{ nm}$$

$$\epsilon = 600, 2500$$



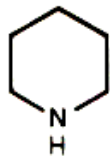
$$\lambda = 196 \text{ nm}$$

$$\epsilon = 3000$$



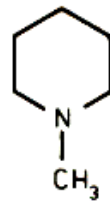
$$\lambda = 240, 219 \text{ nm}$$

$$\epsilon = 50, 810$$



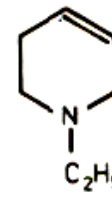
$$\lambda = 198 \text{ nm}$$

$$\epsilon = 2000$$



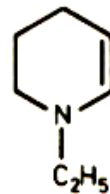
$$\lambda = 213 \text{ nm}$$

$$\epsilon = 1600$$



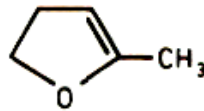
$$\lambda = 218 \text{ nm}$$

$$\epsilon = 1700$$



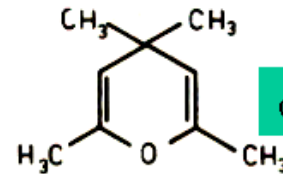
$$\lambda = 230 \text{ nm}$$

$$\epsilon = 6000$$



$$\lambda = 210 \text{ nm}$$

$$\epsilon = 6000$$

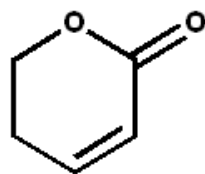


$$\lambda = 248, 218 \text{ nm}$$

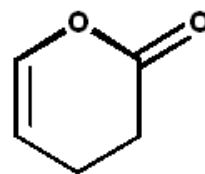
$$\epsilon = 8900, 6200$$

**Widma IR – charakterystyczne cechy ułatwiające określanie struktury
pięcio- i sześcioczłonowych związków heterocyklicznych:**

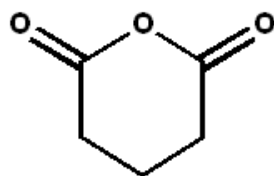
25



$\nu_{\text{C=O}} = 1720 \text{ cm}^{-1}$

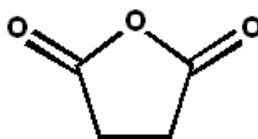


$\nu_{\text{C=O}} = 1760 \text{ cm}^{-1}$



$\nu_{\text{C=O sym}} = 1800-1825 \text{ cm}^{-1}$

$\nu_{\text{C=O asym}} = 1740-1760 \text{ cm}^{-1}$



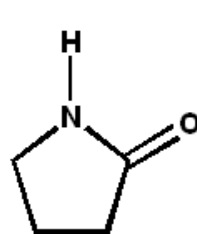
$\nu_{\text{C=O sym}} = 1850-1870 \text{ cm}^{-1}$

$\nu_{\text{C=O asym}} = 1770-1790 \text{ cm}^{-1}$

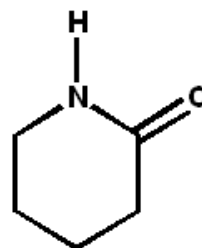


$\nu_{\text{C=O sym}} = 1810-1835 \text{ cm}^{-1}$

$\nu_{\text{C=O asym}} = 1760-1770 \text{ cm}^{-1}$



$\nu_{\text{C=O (pasmo A-I)}} = 1680-1700 \text{ cm}^{-1}$



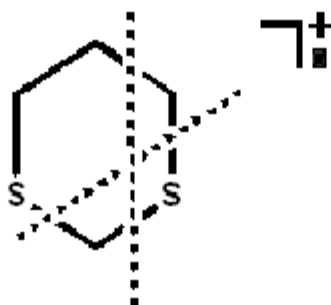
$\nu_{\text{C=O (pasmo A-I)}} = 1658-1690 \text{ cm}^{-1}$

Widma mas – charakterystyczne cechy ułatwiające określanie struktury **pięcio- i sześcioczłonowych związków heterocyklicznych:**

- w widmach mas obserwuje się jony molekularne, z których powstają jony M-1 zazwyczaj poprzez odszczępienie wodoru α (dla piperolidyny, oksolanu, tiolanu);
- odszczępienie atomu wodoru β :



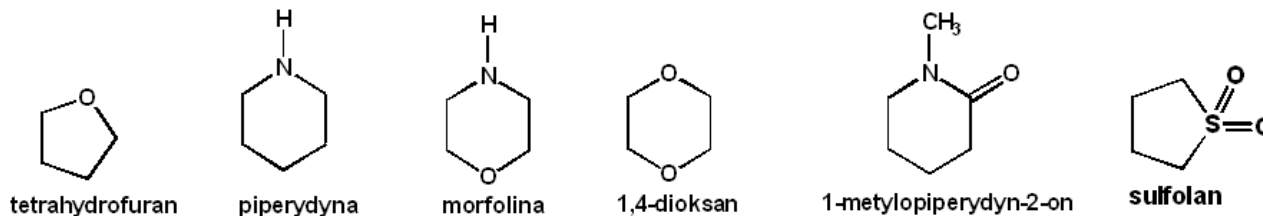
- dalsze fragmentacje z utworzeniem jonu o mniejszej masie cząsteczkowej;
- fragmentacja pierścieni zawierających siarkę przebiega najczęściej poprzez odszczępienie atomu siarki lub fragmentów zawierających ten atom np. 1,3-ditian;



Znaczenie związków heterocyklicznych o średnich pierścieniach

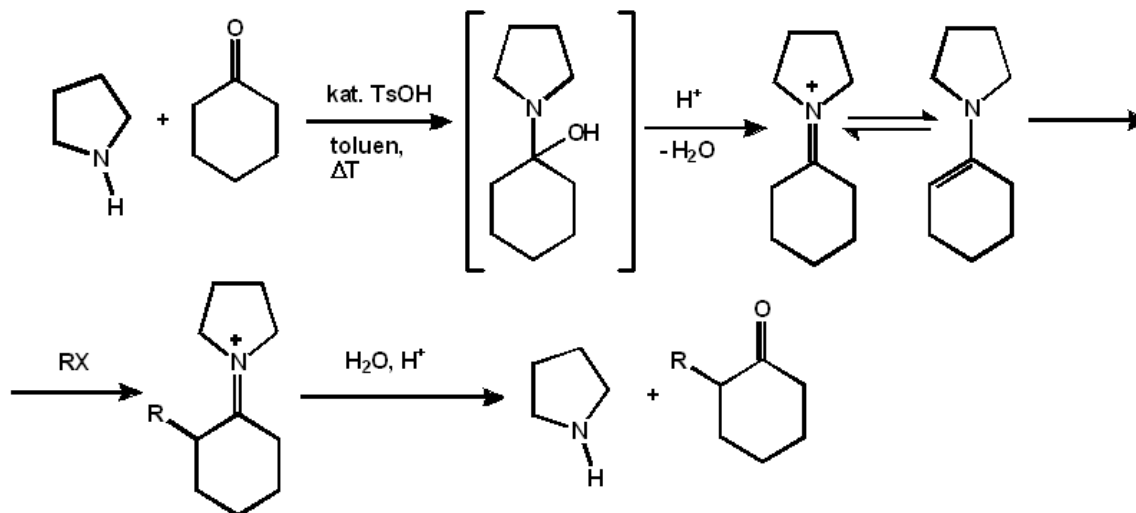
28

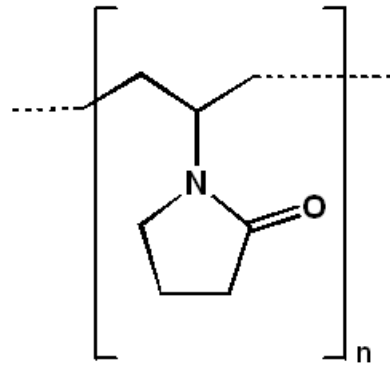
- Zastosowanie jako polarne, aprotonowe rozpuszczalniki:



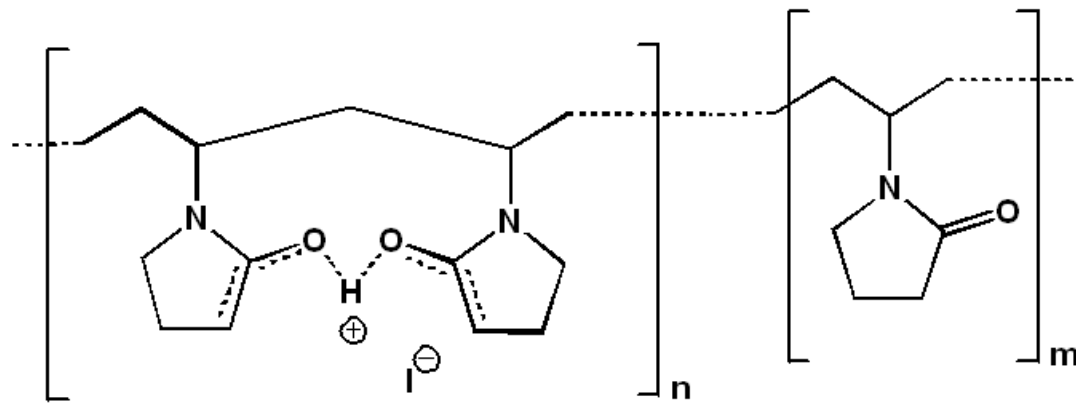
•Pirolidyna zachowuje się jak mocna zasada i często stosowana w reakcjach homogenicznych w środowiskach niewodnych; stosowana także w otrzymywaniu enamin w reakcjach z ketonami;

•Enaminy są cenne w syntezach organicznych, umożliwiają substytucję elektrofilową w pozycji α wyjściowych ketonów, pozwalając na uniknięcie problemów z reakcjami aldolizacji i polimeryzacji.





poliwinylpirolidon



Jodopowidon