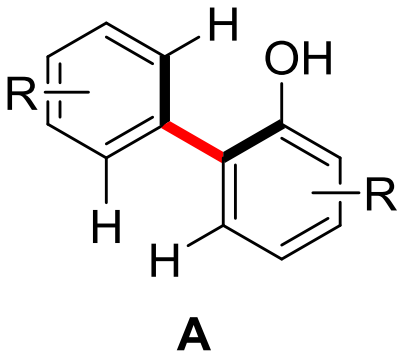
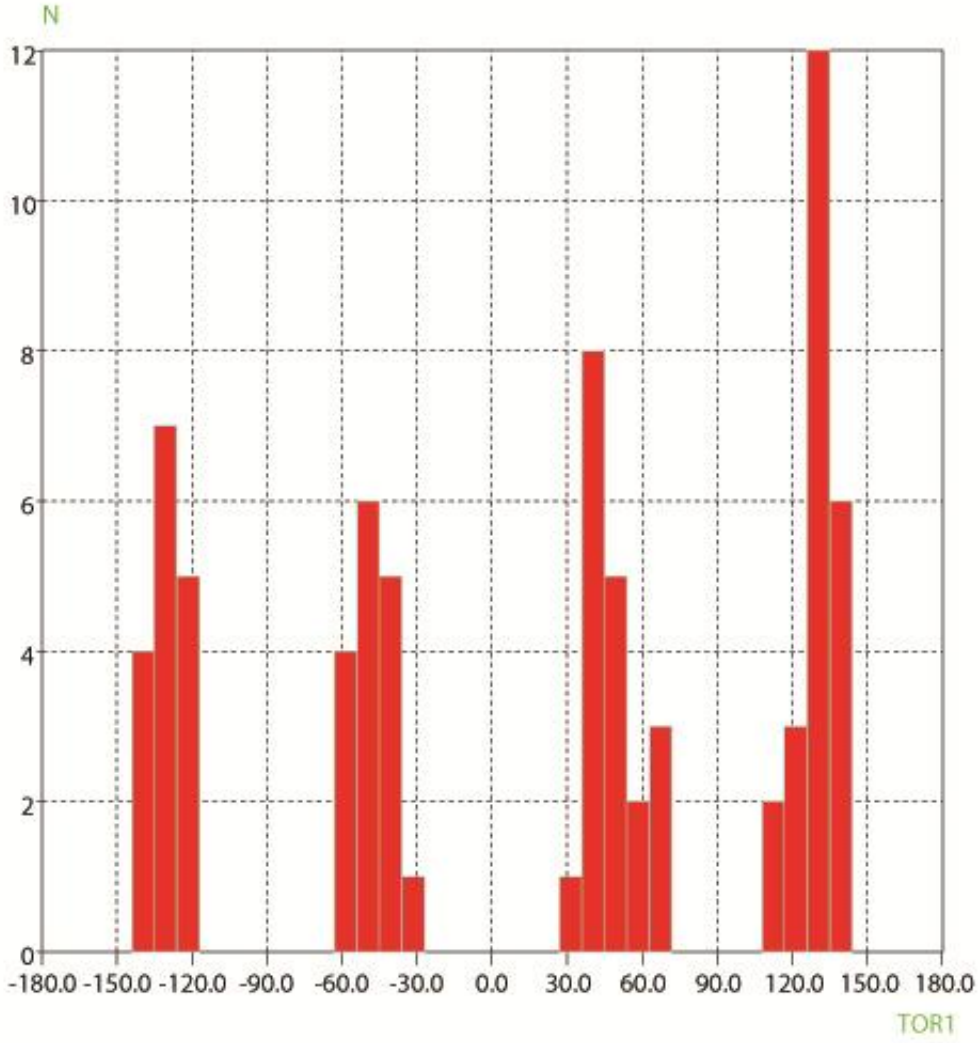
Problem Set - Answers

21.01.2014

Question 1A

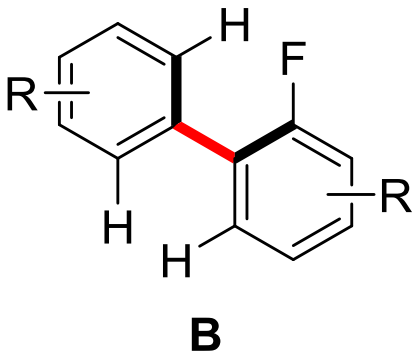


A

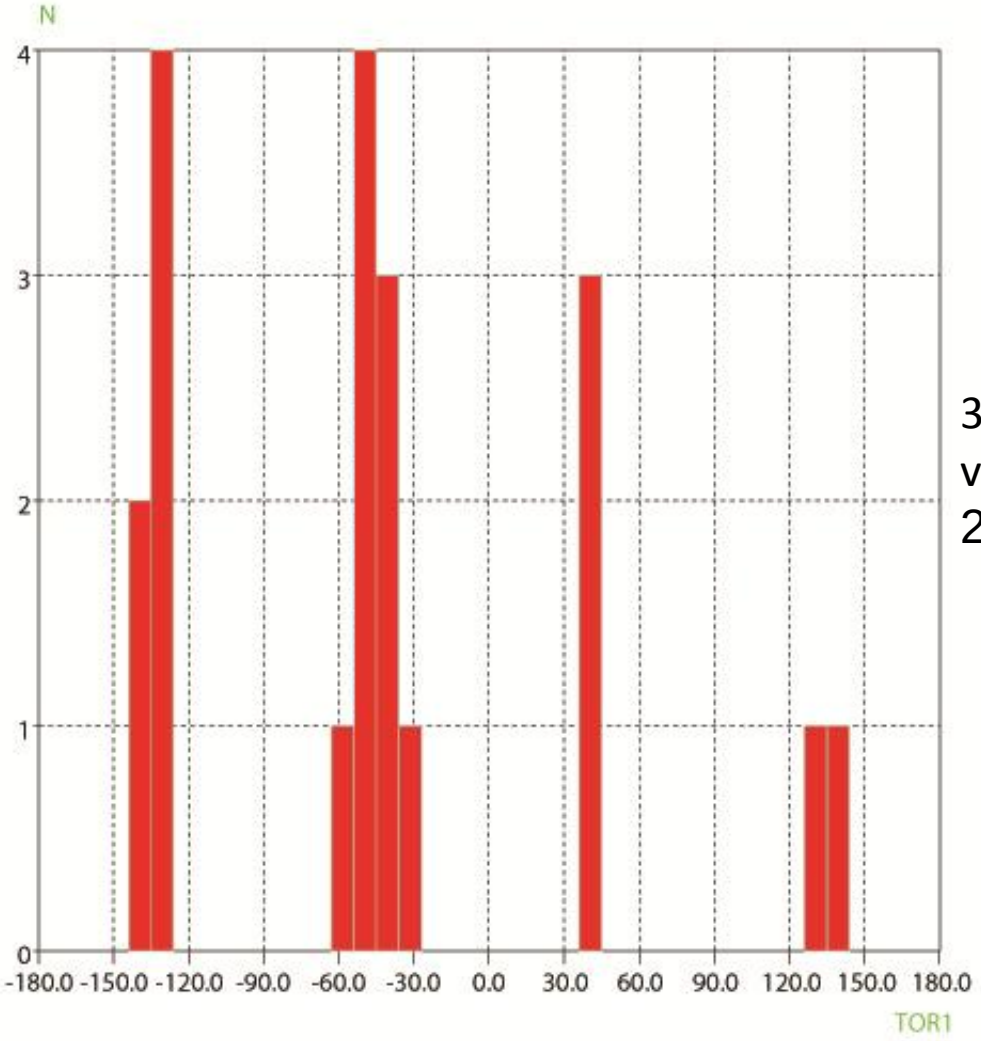


30 – 60°
vdW radius O: 1.52 Å
75 occurrences

Question 1B

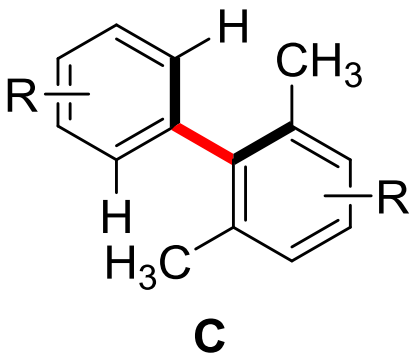


B

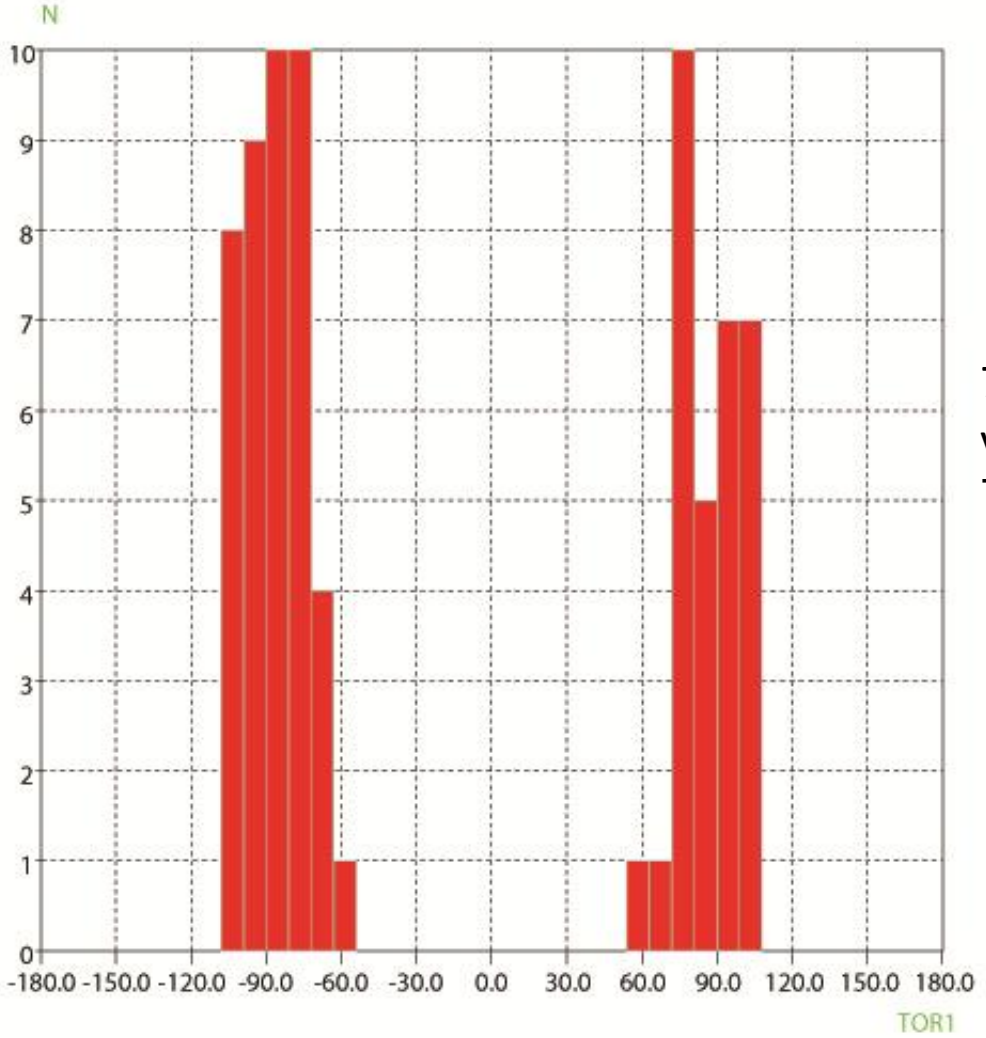


30 – 60°
vdW radius F: 1.47 Å
20 occurrences

Question 1C

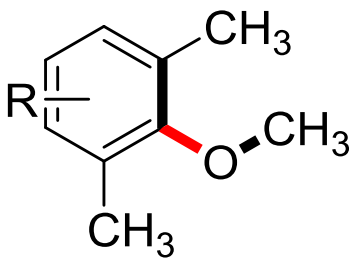


c

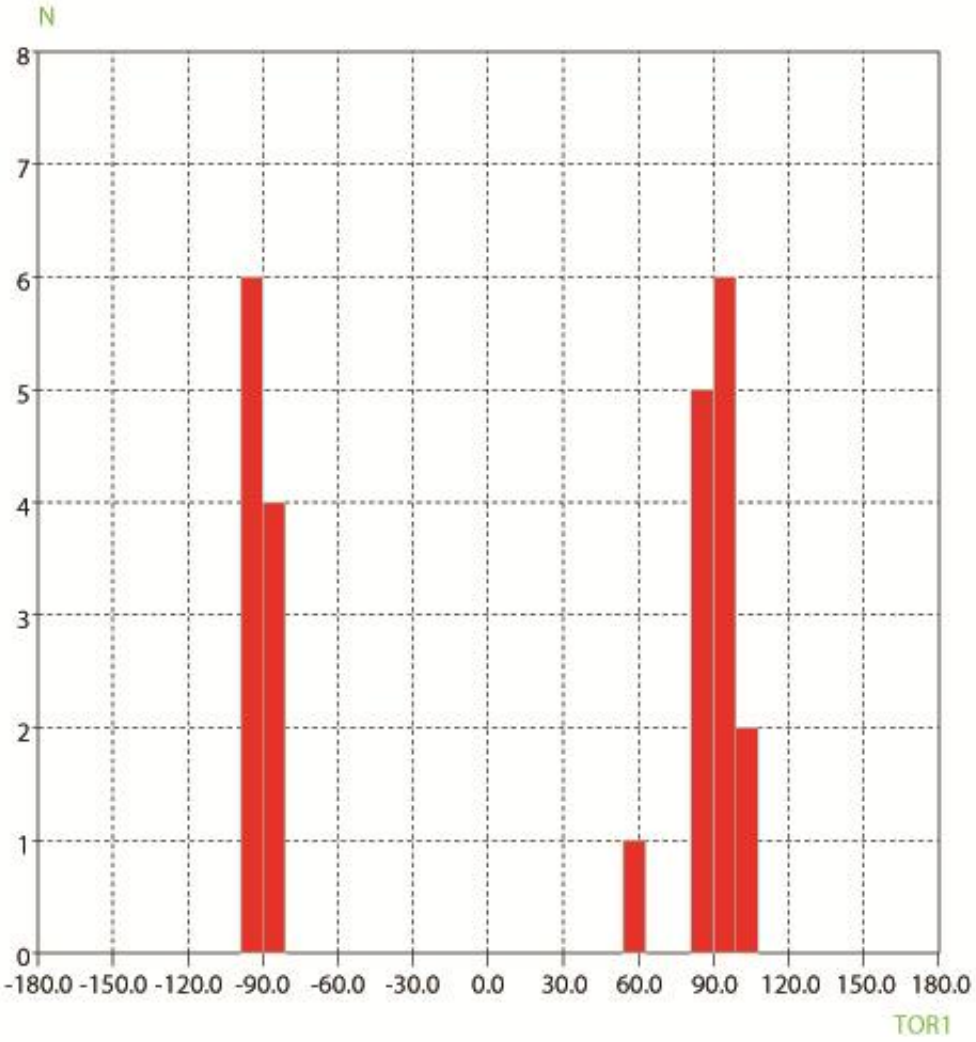


70 – 90°
vdW radius Me: 1.85 Å
77 occurrences

Question 1D



D

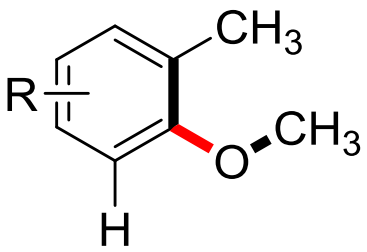


90°

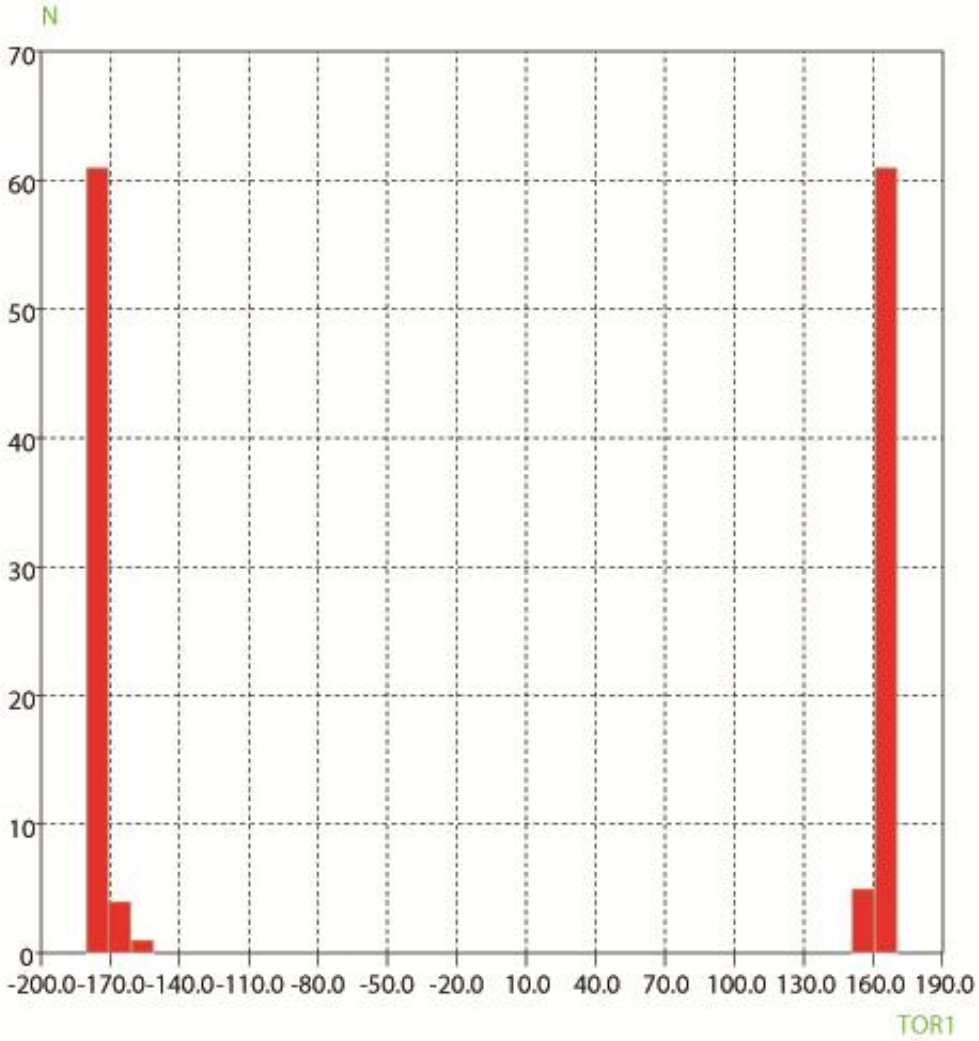
vdW radius Me: 1.85 Å

24 occurrences

Question 1E

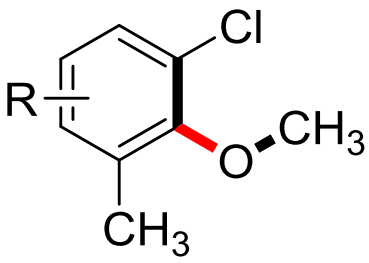


E

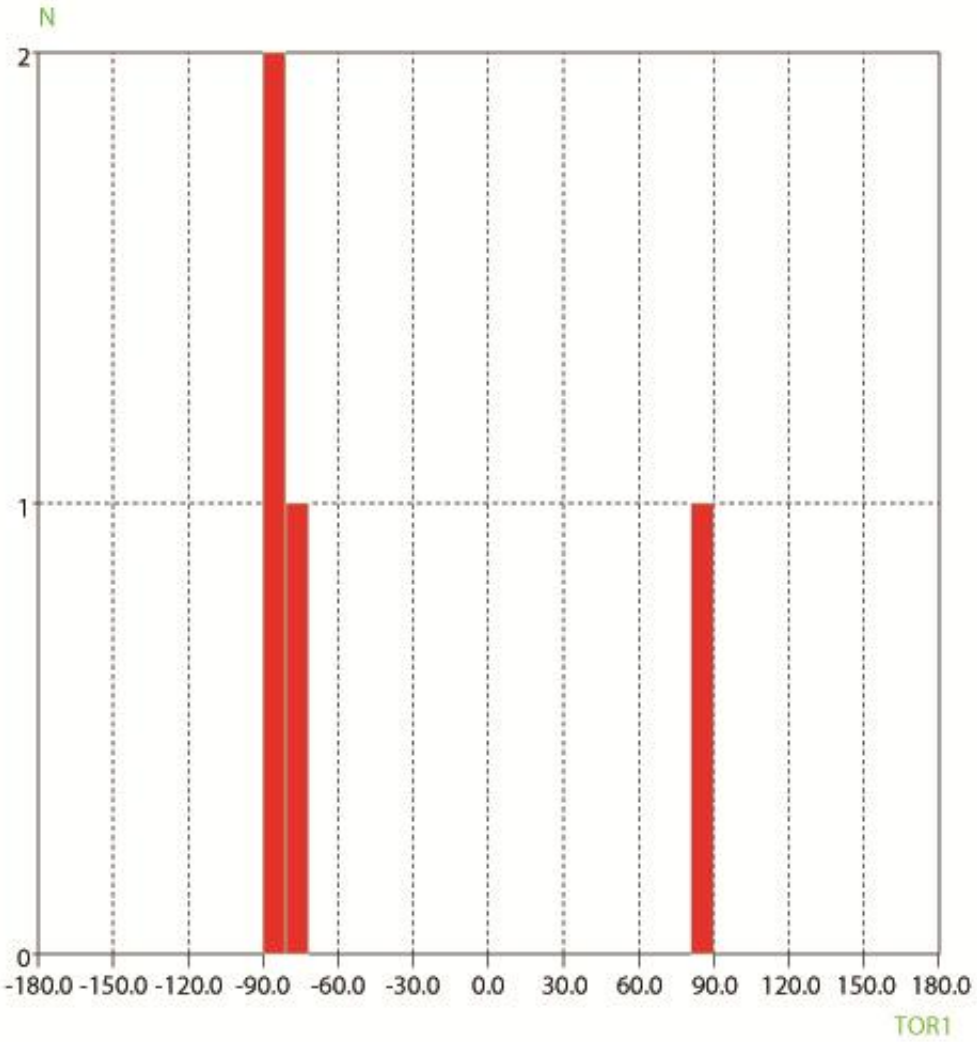


180°
vdW radius Me: 1.85 Å
132 occurrences

Question 1F



F



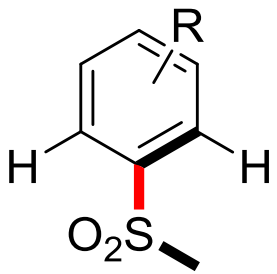
90°

vdW radius Me: 1.85 Å

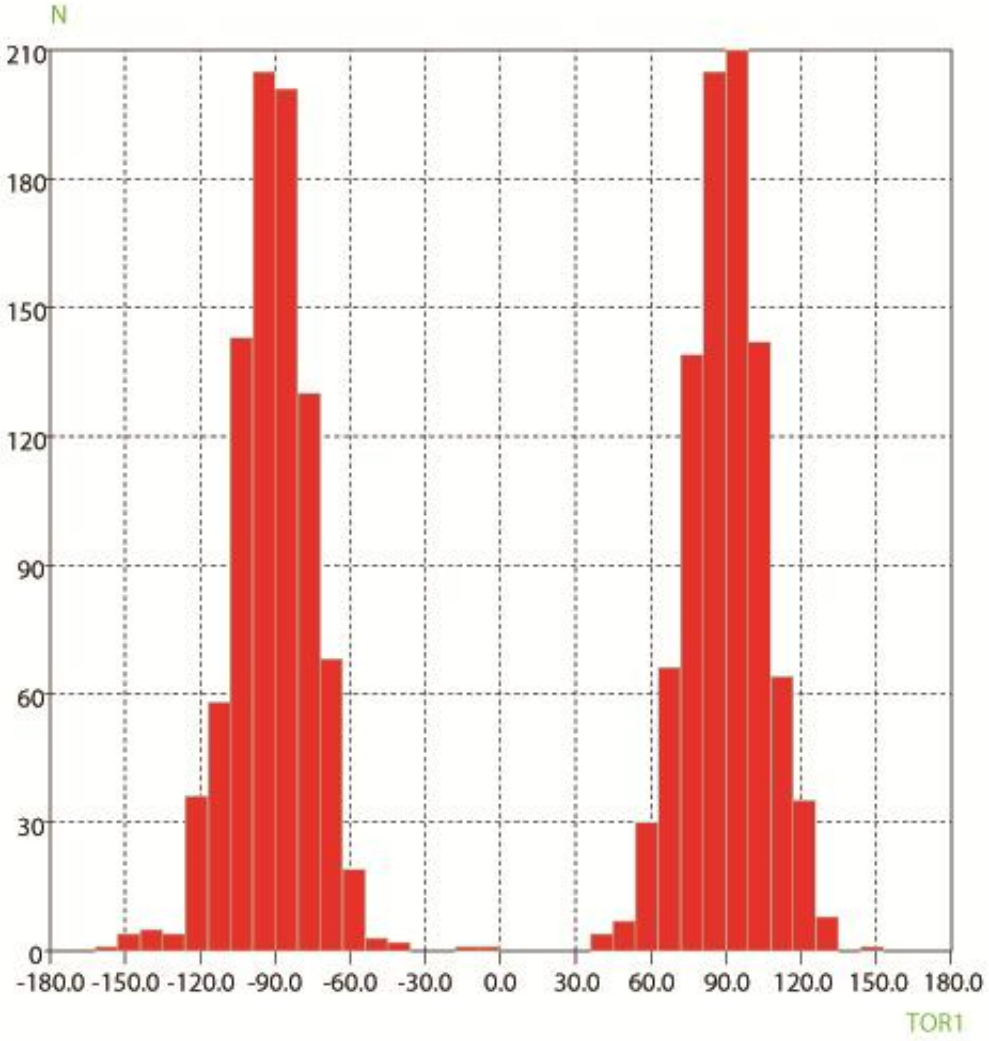
vdW radius Cl: 1.75 Å

4 occurrences

Question 1G

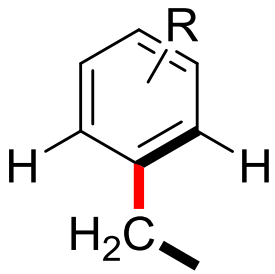


G

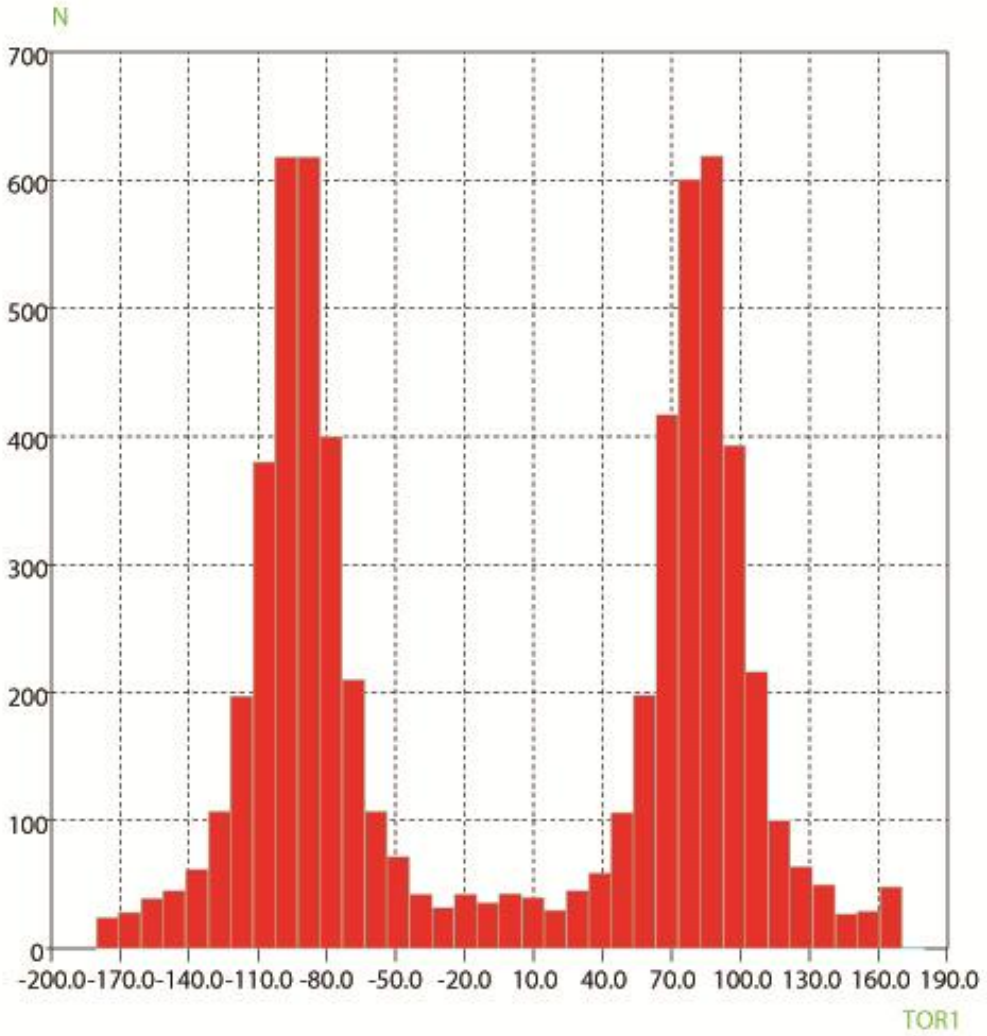


90°
1796 occurrences

Question 1H

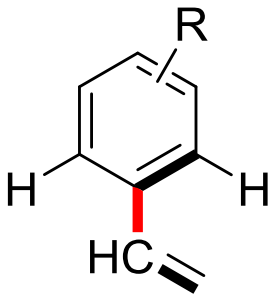


H

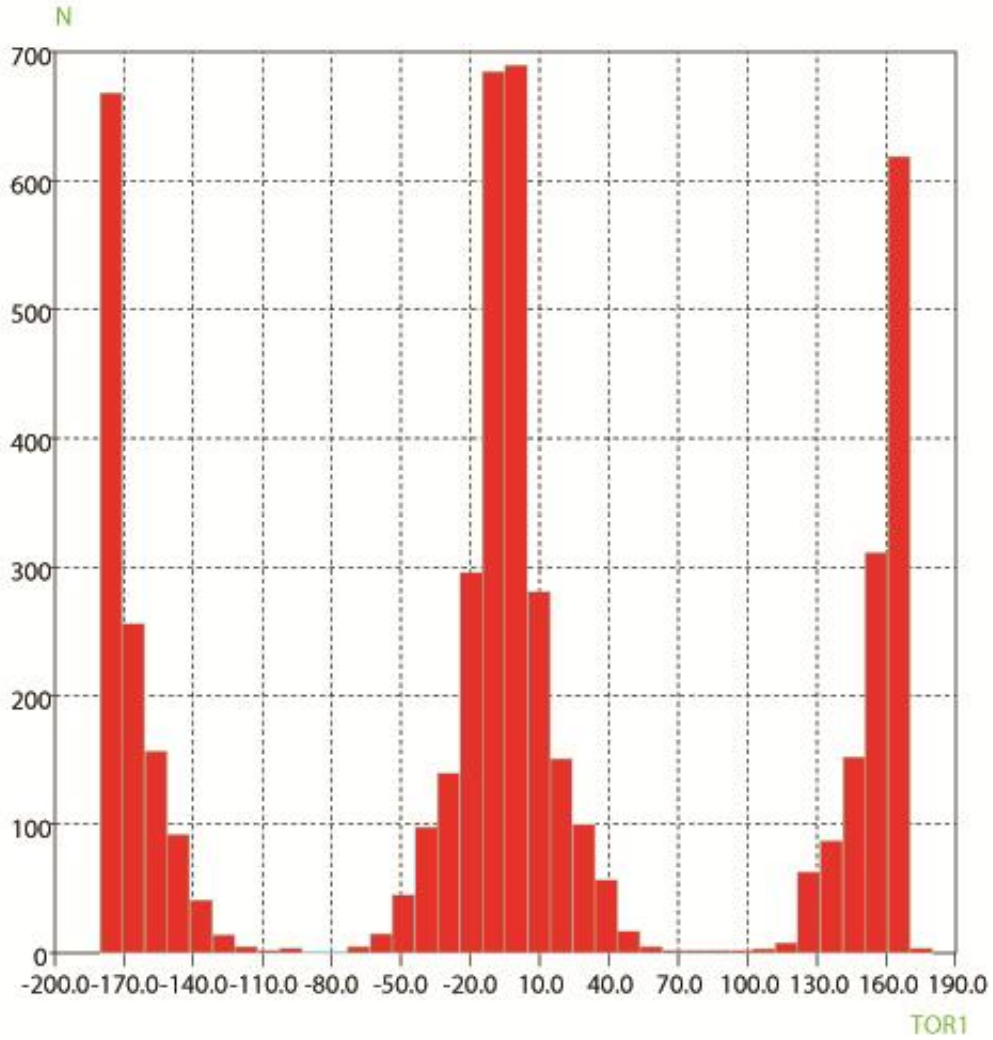


90°
6145 occurrences

Question 1I

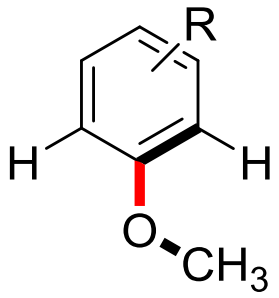


I

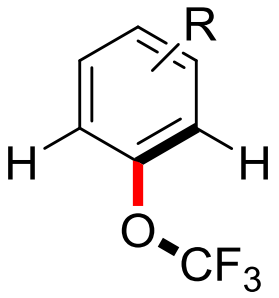


0°
5081 occurrences

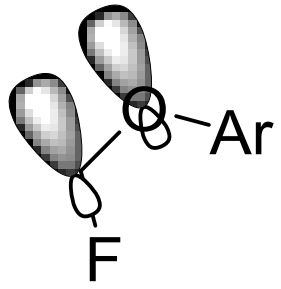
Question 2 A



J

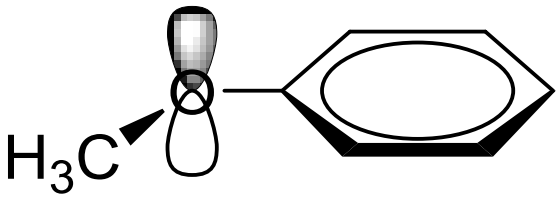


K

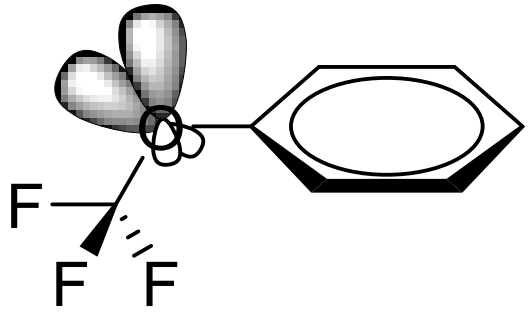


$n_O \rightarrow \sigma^*_{C\text{-}F}$

O: sp^2-hybridized



O: sp^3-hybridized



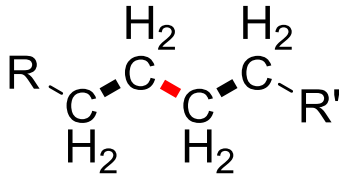
- C–F bond weakend and lengthened
- Increased steric congestion
- n -> π overlap reduced

lone pairs of O antiperiplanar to $\sigma_{C\text{-}F}$ bond

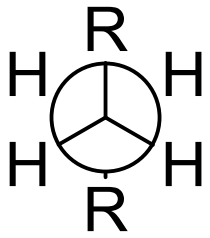
References: *J. Chem. Inf. Model.* **2008**, *48*, 1–24; *Science* **2007**, *317*, 1881–1886.

Question 2 B

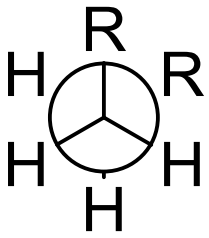
Gauche effect



L



anti

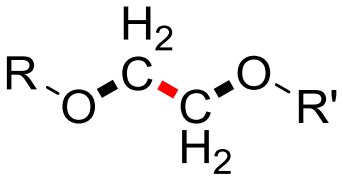


gauche

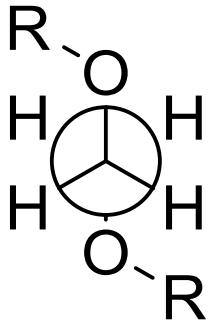
ΔE = 0.9 kcal mol^{-1}

for butane

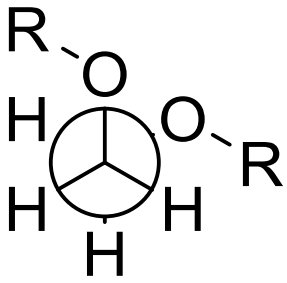
K = 0.2



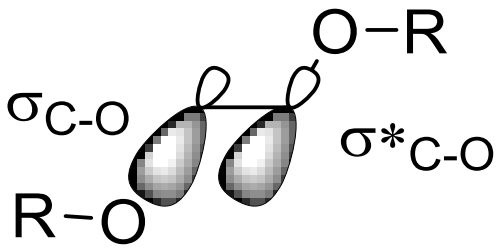
M

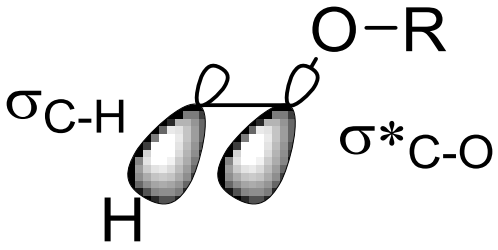


anti



gauche

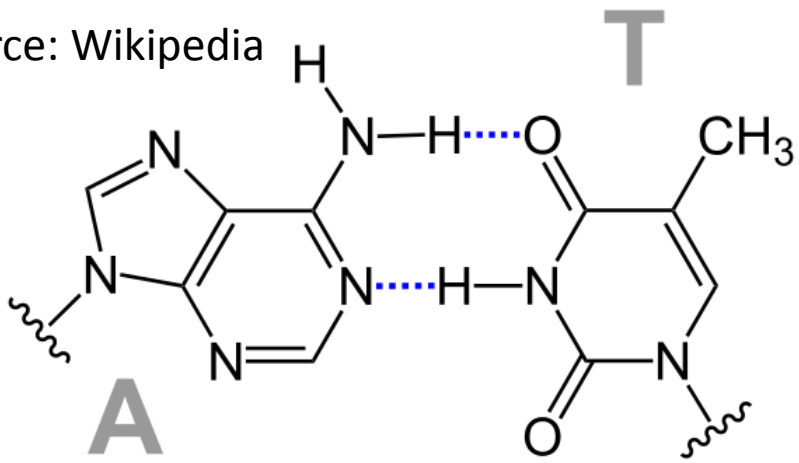




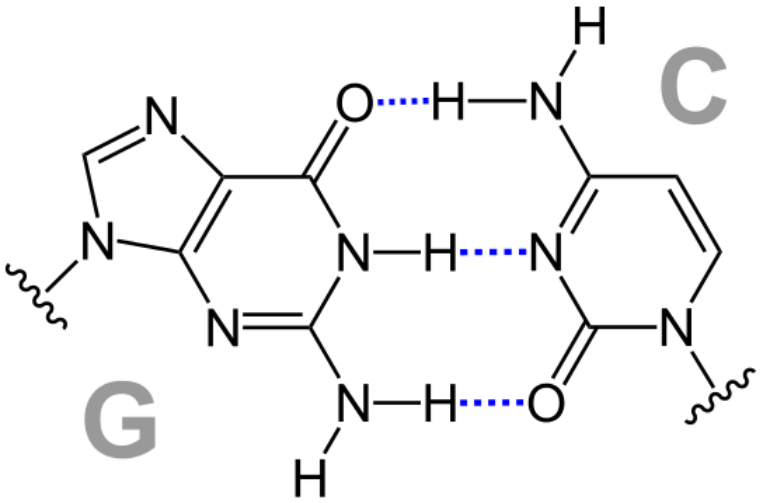
Reference: *J. Chem. Inf. Model.* **2008**, *48*, 1–24.

Question 3

Source: Wikipedia



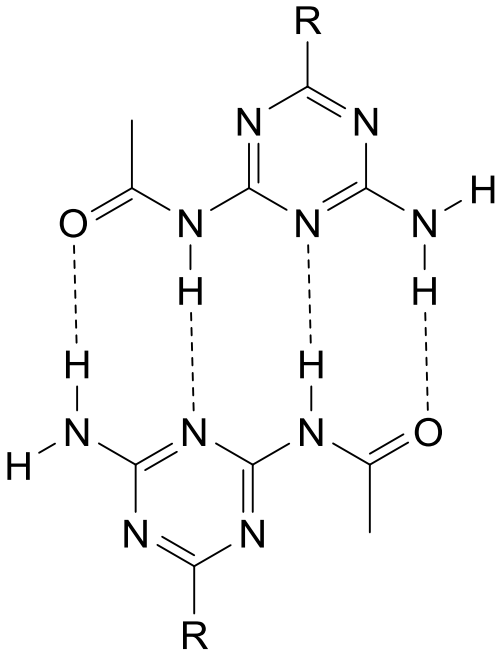
2 H-bonds
Melting point of ds poly[AT]: 50.9 °C



3 H-bonds
Melting point of ds poly[GC]: 103.8 °C

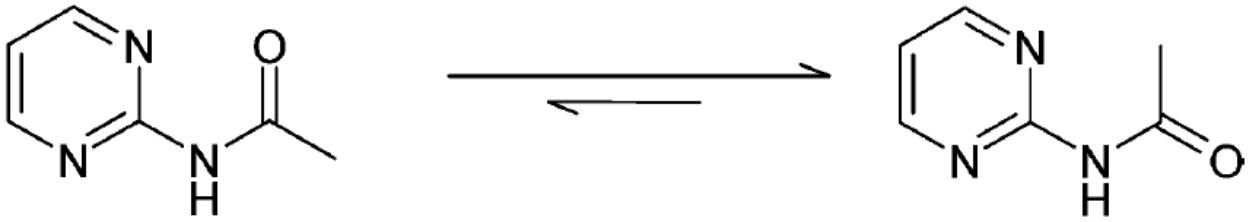
Reference: *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 7853–7858.

Question 4



O*O: K = 530 M^{-1}

$-\Delta G = R*T*\ln K = -15$ kJ mol^{-1}

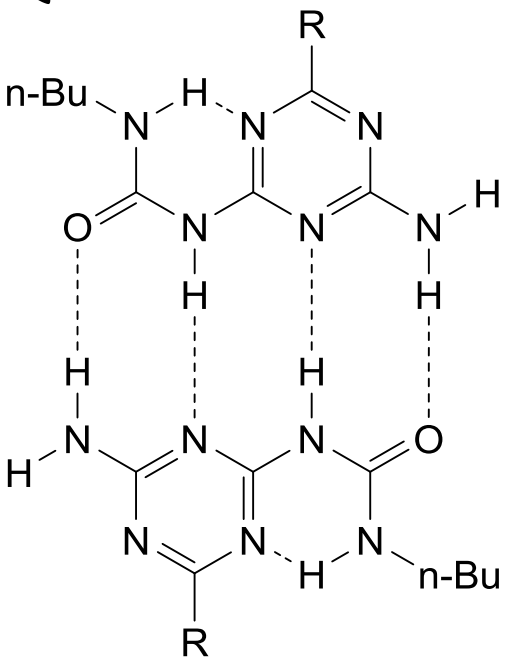


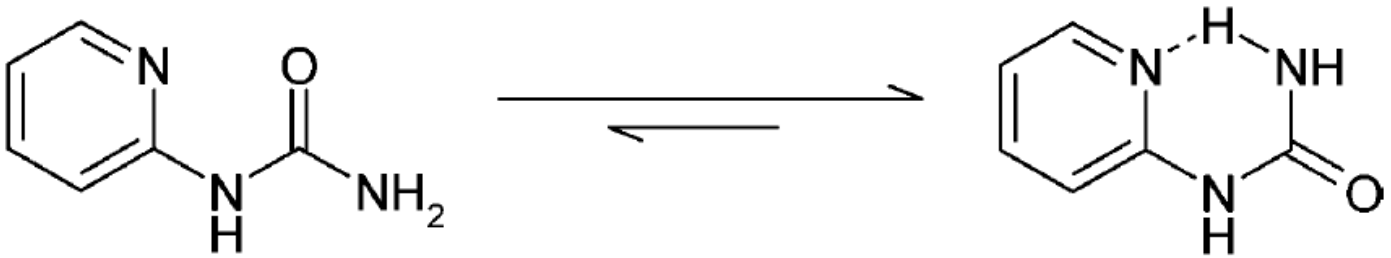
Reference: *Angew. Chem. Int. Ed.* **1998**, *37*, 75–78.

Question 4

N*N: $K = 2*10^4$ м$^{-1}$

$-\Delta G = R*T*\ln K = -25$ kJ mol^{-1}



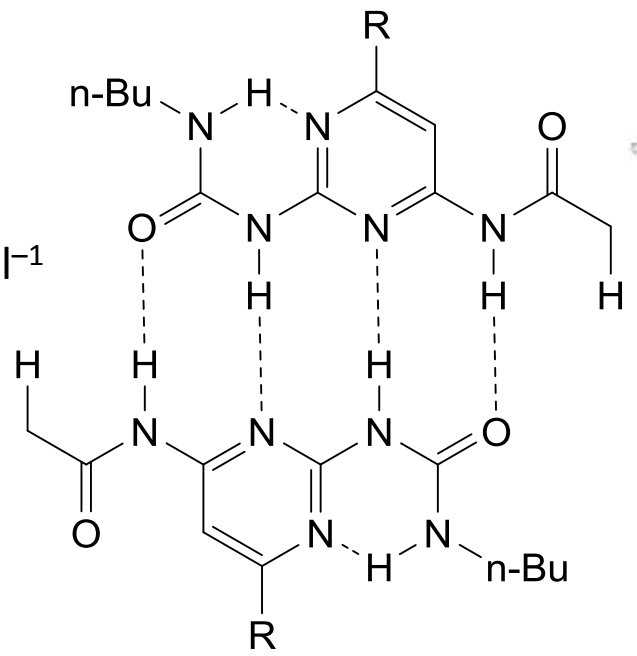


Reference: *Angew. Chem. Int. Ed.* **1998**, *37*, 75–78.

Question 4

N*N: $K = 2*10^5\ M^{-1}$

$-\Delta G = R*T*\ln K = -30\ kJ\ mol^{-1}$



Amides are better H-bond donors than aromatic amines

cis conformation of amide entropically and enthalpically desifavored

Reference: *Angew. Chem. Int. Ed.* **1998**, *37*, 75–78.

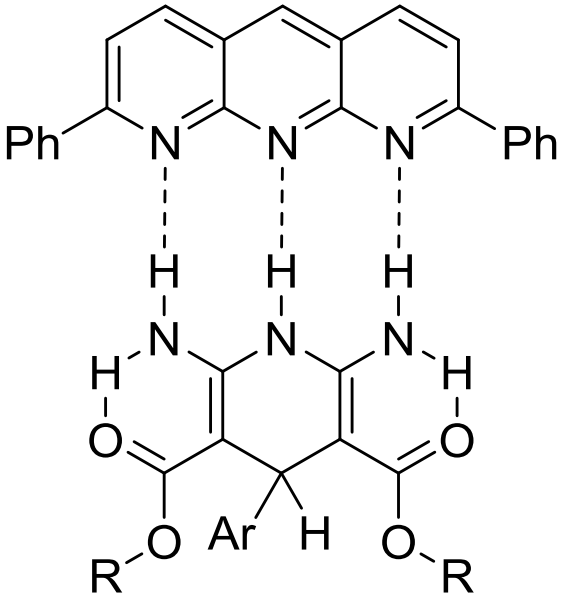
Question 4 - Bonus

Hydrogen bonds	OH	NH
Carbonyl/sulfonyl O	2.7 - 3.0	2.8 - 3.1
Heteroaromatic N	2.7 - 3.0	2.8 - 3.2
Carboxylic acid O	2.6 - 2.8	2.7 - 3.0

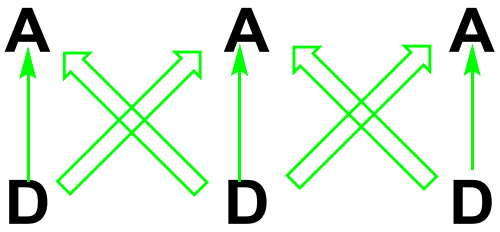
Reference: *J. Med. Chem.* **2010**, *53*, 5061–5084.

Question 5

Q



U

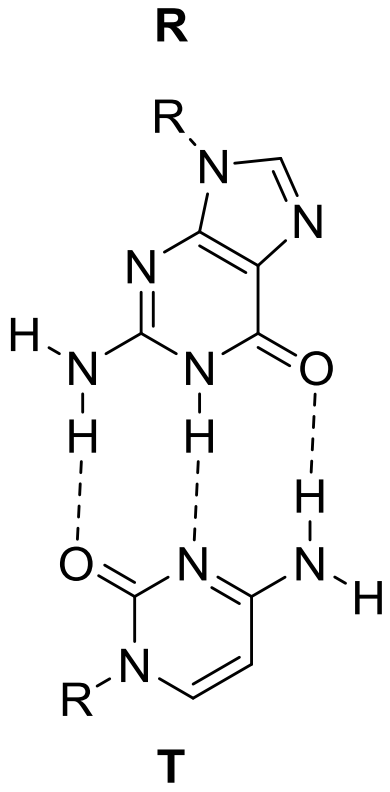


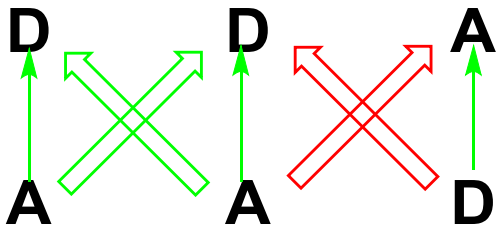
–3*7.9 kJ mol^{-1} = –23.7 kJ mol^{-1}
–4*2.9 kJ mol^{-1} = –11.6 kJ mol^{-1}
Total: –35.3 kJ mol^{-1}

Q*U: K = ≥10^5 M^{-1}

Reference: *J. Am. Chem. Soc.* **1992**, *114*, 4011–4013; *Chem. Eur. J.*, **1996**, *2*, 1446–1452.

Question 5





–3*7.9 kJ mol^{-1} = –23.7 kJ mol^{-1}
–2*2.9 kJ mol^{-1} = –5.8 kJ mol^{-1}
+2*2.9 kJ mol^{-1} = +5.8 kJ mol^{-1}
Total: –23.7 kJ mol^{-1}

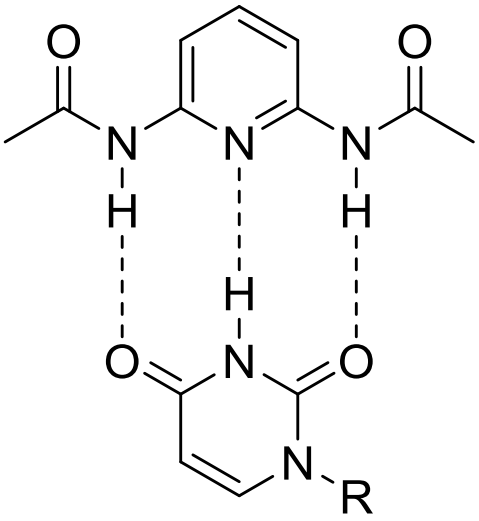
R*T: $K = 10^4$ M^{-1}

Compare G*C base pairing in DNA.

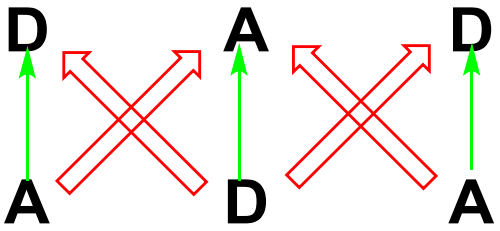
Reference: *J. Am. Chem. Soc.* **1992**, *114*, 4011–4013; *Chem. Eur. J.*, **1996**, *2*, 1446–1452.

Question 5

S



V



–3*7.9 kJ mol^{-1} = –23.7 kJ mol^{-1}
+4*2.9 kJ mol^{-1} = +11.6 kJ mol^{-1}
Total: –12.1 kJ mol^{-1}

S*V: K = 90 M^{-1}

Reference: *J. Am. Chem. Soc.* **1992**, *114*, 4011–4013; *Chem. Eur. J.*, **1996**, *2*, 1446–1452.