Question 1. NMR Coupling of an AB\textsubscript{n} System. (12 points)

Two simulations are shown of an AB\textsubscript{n} system, one at 60 MHz and one at 600 MHz.

(a) Write into the above boxes whether the simulation refers to the 60 (left) or 600 MHz (right) case. (2 points)

(b) Determine the value of “n”: \( n = 2 \). (2 points)

(c) Which J value(s) can be extracted from the spectrum on the top-right (\( \frac{3}{2} J_{AB1}, \frac{3}{2} J_{AB2}, \frac{1}{2} J_{B1B2} \))? (4 points)

\[ \frac{3}{2} J_{AB1} = \frac{3}{2} J_{AB2} = \frac{3}{2} J_{AB}; \text{ not } \frac{1}{2} J_{B1B2} \]

(d) Briefly explain why the spectra look so very different when recorded at the two field strengths. (4 points)

The ratio of the difference in absorption frequencies and the coupling constants is small on the 60 MHz machine and first-order rules do not apply.

Higher field strength increases the absorption frequencies without changing the coupling constants.

The ratio of the difference in chemical shifts and the coupling constants is larger on the 600 MHz machine and first-order rules do apply.
Question 2. NMR Coupling of an “ABₙ System”. (13 points)

Three simulations are shown of an ABₙ system, one at 300 MHz, one at 600 MHz, and one at 900 MHz.

(a) Write into the above boxes whether the simulation refers to the 300, 600 or 900 MHz case. (3 points)

(b) Determine the value of “n”: \( n = 2 \). (2 points)

(c) Which J value(s) can be extracted from the spectrum on the top-right \( (^{3}J_{AB1}, ^{3}J_{AB2}, ^{2}J_{B1B2}) \)? (4 points) 

\[ \text{all three} \]

(d) Briefly explain why the spectra of Questions 2 looks so very different from the spectra of Question 1. Use the appropriate language to describe relations between nuclei. (4 points)

The B nuclei are diastereotopic!

Each H is magnetically unique and each H couples to two others.

Each H results in a doublet of doublets.
Question 3. UV/Vis Spectroscopy of Hexatriene. (17 points)

(a) Write into the above boxes which MO is shown. It is understood that “HOMO” means ____highest occupied MO____ and that “LUMO” means ____lowest unoccupied MO______. (5 points)

(b) The three MOs all are p-MOs, that is, they feature a “horizontal node plane” that contains the hexatriene. In the above boxes indicate for each MO (i) the number of “vertical node planes” and (ii) draw those “vertical node planes” schematically. (3 points)

(c) Draw a schematic energy level diagram that shows the ground state singlet state $S_0$ and the excited singlet states $S_1$ and $S_2$ that result form the HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1 transitions. There also are two triplet states $T_1$ and $T_2$ that are slightly more stable than the respective singlet states $S_1$ and $S_2$. Indicate the levels of these triplet states schematically in your diagram. Indicate intersystem crossings as dashed lines. Draw “down arrows” to show the possibilities for phosphorescence. (9 points)
Question 4. UV/Vis Spectroscopy of Dimethylaminobenzonitrile. (8 points)

(a) In dimethylaminobenzonitrile, the HOMO is MO#39 and the LUMO is MO#40. (2 points).

(b) Since the value of the electron density equals the square of the orbital value, the knowledge of the MOs that characterize the transition informs about the electron density shift associated with the excitation. Inspection of the HOMO and LUMO suggests that the HOMO → LUMO excitation moves electrons away from the amino group. Considering the frontier MOs shown, where is the electron density moved to? (2 points).

Looks like the electron density in the benzene ring increases.
Looks like there will not be all that much change on the cyano group at all.

(c) Draw resonance structures of dimethylaminobenzonitrile and indicate which resonance structures are important for the ground state and which are important for the HOMO → LUMO excited state. (4 points).

GS: lots
ES: little
GS: little
ES: lots
GS: little
ES: little