1. Which species has the smallest bond angle? How can you tell?

[Br-I-Br]- [F-I-F]- Br-Te-Br F-Te-F

Based on the “how can you tell” prompt, students would be expected to:

* Select the correct answer: F-Te-F
* Identify the warrant to distinguish I and Te complex bond angles:

I complexes have steric number of 5 and will form a trigonal bipyramidal electron geometry with Br in axial positions (exactly 180º bond angles), while Te complexes have steric number of 4 and will form tetrahedral electron geometries (approximately 109.5º bond angles)

* Identify the warrant to distinguish Br and F complex bond angles:
  + Br more similar in electronegativity to Te than is F. Trend is that less electronegative ligands give larger bond angles.

Common errors were to either cite only one of the two warrants, or to cite warrants that exposed misconceptions.

2. The compound 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile, also known as ROY, exhibits remarkable behavior in that it forms different polymorphs with different colors due to *twisting* about angle θ shown below.

|  |  |  |
| --- | --- | --- |
| Color of Crystal | Color Absorbed | Angle θ (°) |
| **Red** | **Green** | **21.7** |
| Orange-red | Blue-green | 39.4 |
| Orange | Blue | 52.6 |
| **Yellow** | **Violet-blue** | **105** |



ROY

Provide an explanation for why the crystals with θ = 21.7° (almost flat) are red, while the crystals with θ = 105° are yellow. Make the logical connections between color and angle clear and include the fundamental physical basis.

Based on this prompt, students would be expected to trace the logical connections between molecule flatness and color absorbed using the particle-in-a-box model, the most applicable model introduced in lecture. This would include in some logical pathway connecting the following ideas:

* The “data” is that smaller θ angles (flatter conformations) correlate with colors due to absorption of lower energy photons.
* The “backing” comes from the particle-in-a-box model: From the calculated energy level spacings, it is predicted that species in which electrons are delocalized over larger lengths have closer energy level spacings.
* One “warrant” would relate the conformation and electron delocalization: Flatter conformations of ROY provide greater electron delocalization (a larger electron box) due to better p-orbital overlap, and therefore flatter conformations have closer energy levels.
* Another necessary “warrant” relates the energy level spacings and light absorption: Closer energy levels require absorption of lower energy photons in the color-causing energy level transition.
* A last “warrant” relates color absorbed and energy of the photons: Of the absorbed colors observed, green has the smallest energy photons.

Common errors were to skip warrants or describe them in ways that revealed misconceptions. Students tended to add, perhaps unnecessarily, the relation between photon energy and wavelength. I think this revealed that students were thinking about colors in terms of wavelengths rather than photon energies.

Here is an exemplary student response:

Based on the quantum mechanical “particle-in-a-box” model, the longer the length of the a box containing an electron, the closer the spacing of energy levels the electron may exist at. (Quantitatively, ΔE = (Δn)2h2/(8mL2), so ΔE ∝ 1/L2) In ROY, when θ = 21.7º and the molecule is nearly planar, the electrons in the π system can effectively delocalize across the nitrophenyl and thiophene moieties, creating a long “box”. This happens because the π electrons can more easily spread over the orbitals when the molecule is more planar. Since the “box” is long, the energy spacing is close together, and the low energy (green) photons can excite electrons. Since green light gets absorbed, ROY (θ = 21.7º) appears red. In contrast, the π e- in ROY when θ = 105º cannot delocalize to the same extent because the aromatic moieties containing the π system are twisted away from each other. The resulting short “box” has high energy spacing, requiring more energetic (violet-blue) photons to excite electrons. Absorbance of such photons gives ROY (θ = 105º) a yellow appearance.