SPIN DENSITY DISTRIBUTION IN ORGANIC BIRADICALS

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INTRODUCTION & SCOPE OF THE WORK

Organic biradicals are carbon-based molecules with two unpaired electrons. Each electron has a spin, causing unpaired electrons to behave like tiny magnets, unlike paired electrons [1]. This makes the molecule paramagnetic and highly chemically reactive. Molecules with similar properties are used in MRI, electronics, and as catalysts. Our study focuses on three such molecules, which have potential applications as photoswitches for renewable energy technologies (Figure 1).
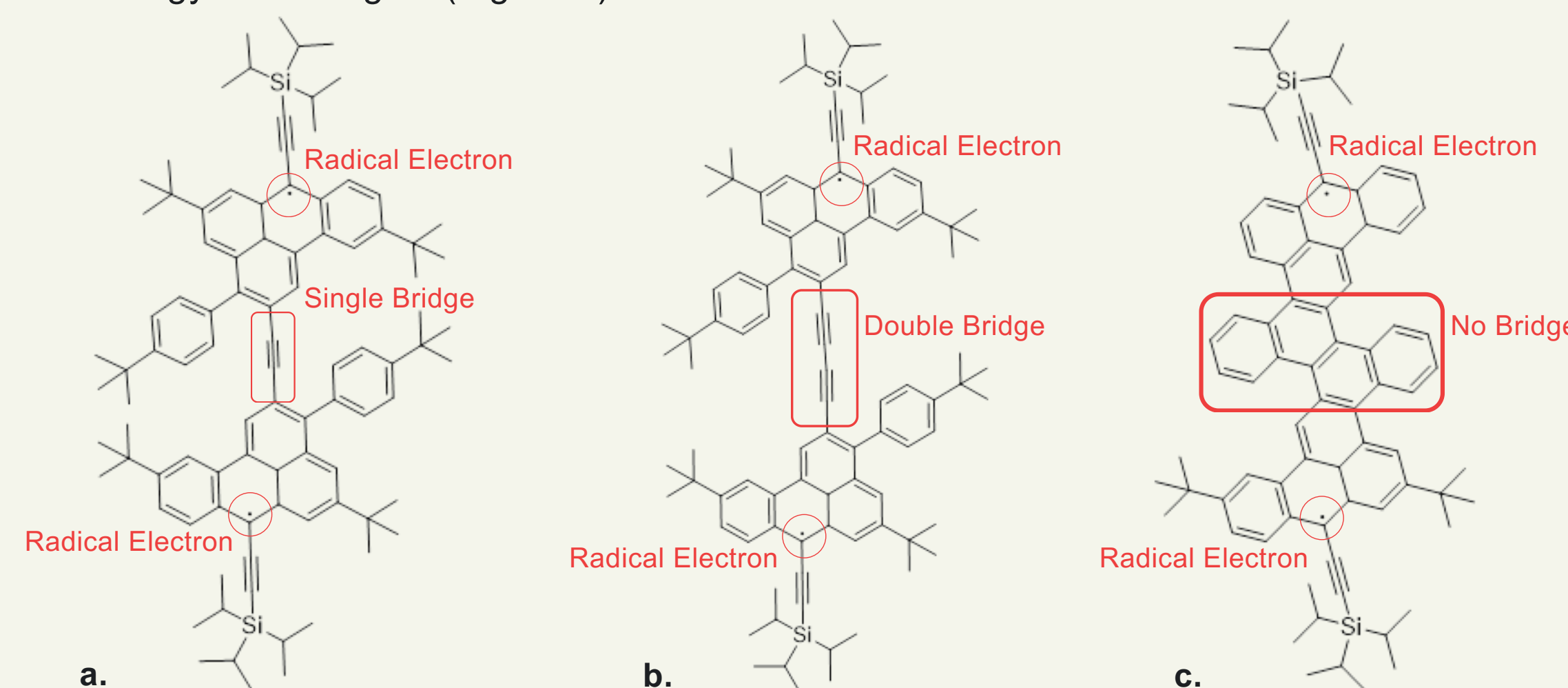
Figure 1. Structures of the molecules investigated in this study. The two radicals are connected by different carbon bridges: (a) Single alkyne bridge; (b) Double alkyne bridge; (c) Closed diketone bridge. Free radical electrons are denoted as single dots.

Our aim is to reconstruct the electron spin properties of the molecules above by using experimental EPR spectroscopy and quantum chemistry simulations.

METHODS

Unpaired electron spins can be probed directly with a spectroscopy method called Electron Paramagnetic Resonance (EPR), which offers insights into the electron spin density distribution, and gives valuable information on the molecule structure and function.

What's the important parameter?

The hyperfine coupling or A_{iso} value is the energy of the magnetic interaction between an unpaired electron and a nucleus nearby [2]. The greater magnitude, the more this electron can be found near this atom. Typical values range between a few MHz to 1 GHz for nuclei in organic radicals.

How do we calculate A_{iso}?

1. Molecule is built in 3D with Avogadro
A molecule built in Avogadro is only crudely optimized, meaning the molecule is less likely to be in its natural most stable state at this stage

**2. Geometry optimization with xtb and ORCA [3]**
A Geometry optimization analyzes possible conformations (bond angles, distance between atoms) to find the structure that is most likely the natural state

3. Calculation of A_{iso} value with ORCA
ORCA takes this optimized molecule and simulates the full electronic structure. This program records near which atoms the electrons can be found the most and presents them in an output file.

How do we measure A_{iso}?

EPR is a measure of microwave radiation absorption. Each unpaired electron gives one line. When the electron is coupled to N nuclei with nuclear spin 1/2, thumber of lines to 2N + 1, where N is the number of equivalent nuclei. The peak separation corresponds to the A_{iso} value.
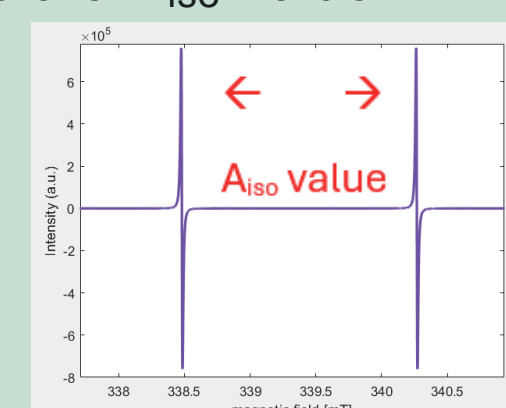
EPR Spectrum with 1 coupled N
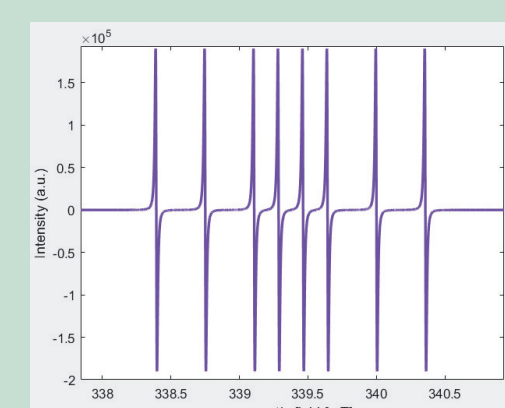
EPR Spectrum with 3 coupled N

Hyperfine couplings interact with each other. The more nuclei the radical electron interacts with, the greater the N, forming multiple peaks. (See above)

Quantum chemistry → **Calculated A_{ISO}** → **SIMULATED EPR SPECTRUM** ≈ **EXPERIMENTAL EPR SPECTRUM** ← **Sample synthesis**

What are we looking for?

Spin density is the difference between spin up and spin down electrons in an area of the molecule. We expect, then, for spin density to be greater in the areas of the molecule where the radical electrons are, since they have a magnetic moment that aligns electrons in one direction.

Since three very similar molecules are being analyzed, we are searching for differences in A_{iso} values caused by the different carbon bridges.

RESULTS

Calculated A_{iso}

When running a hyperfine calculations, we considered only hydrogen atoms (H) because of their spin 1/2. Carbon (C) and silicon (Si) have spins of 0 and do not couple to the electron. Electron spin maps of each biradical are shown in Figure 3, simulated with ORCA and modeled with Avogadro. Each A_{iso} value shown is greater in magnitude than 1MHz, which is large enough to give a detectable splitting in an EPR spectrum. We found that there are sixteen H coupled to the electron in the single alkyne molecule, with A_{iso} ranging from 1 MHz to 9.3 MHz. The double alkyne molecule has fourteen coupled H atoms, with 1 MHz < A_{iso} < 9.3 MHz. The closed diketone molecule also has sixteen coupled H atoms 1 MHz < A_{iso} < 7.9 MHz.
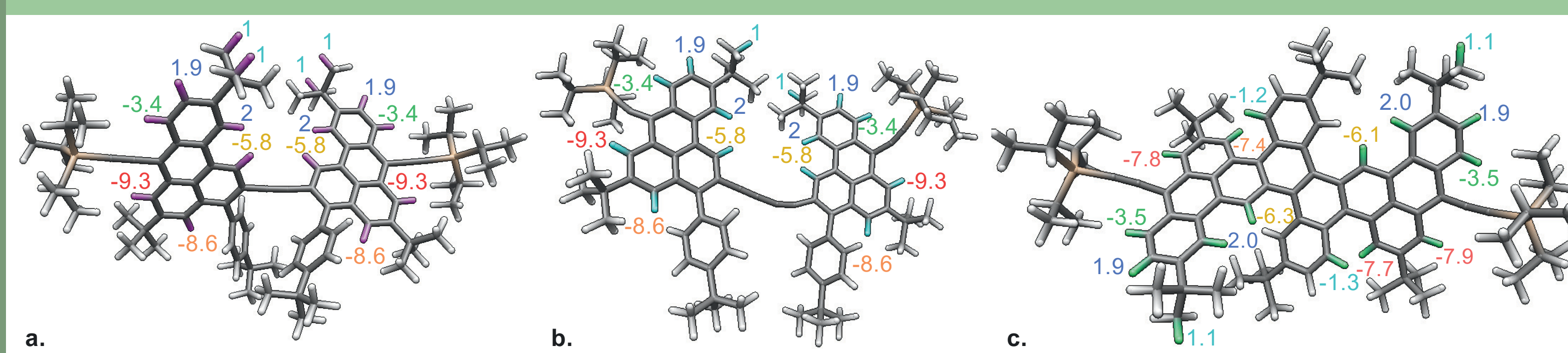
Figure 2. Geometry optimized structures. (a) Single alkyne; (b) Double alkyne; (c) Closed diketone. Color code: H white, C gray, Si yellow. Highlighted H atoms have an A_{iso} > 1 MHz, and the value is presented next to the atom. The color of the value represents its magnitude, ranging from lowest, light blue, to highest, red.

### Simulated EPR vs. Experimental EPR
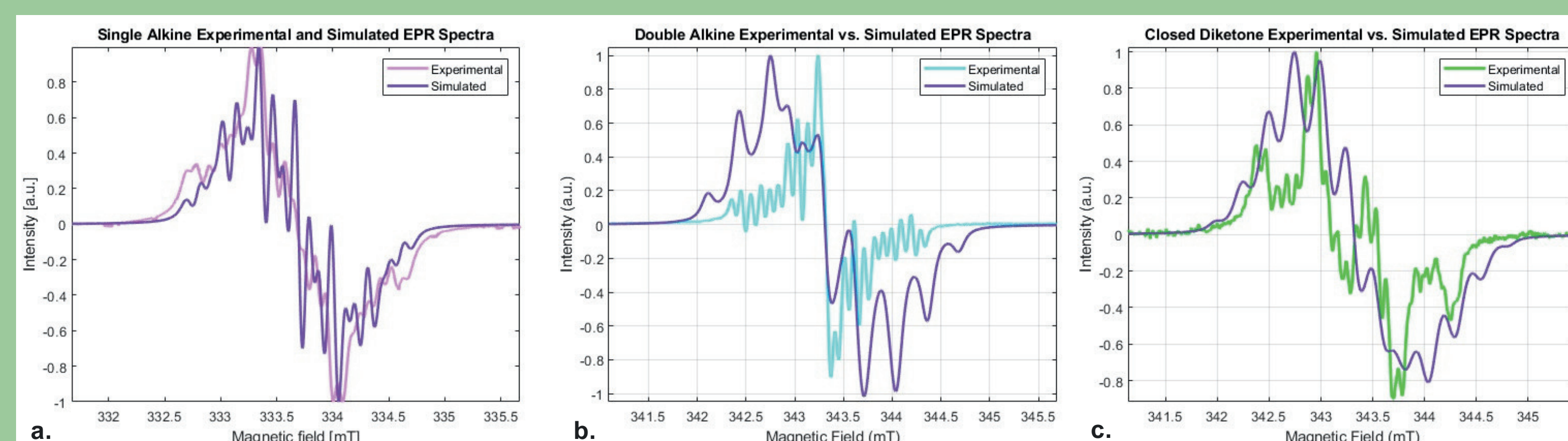
Figure 3. Experimental and simulated CW-EPR spectra of the investigated molecules. (a) Single alkyne; the simulation was performed with 8 H atoms coupled to the electron with hyperfine coupling values -9.3, -9.3, -8.6, -8.6, 5.8, 5.8, -3.4, -3.4 in MHz. (b) Double alkyne; the simulation considers 4 H atoms with A_{iso} -9.33, -8.62, -9.33, -8.62 MHz. (c) Closed diketone; the simulation considered 6 H atoms with A_{iso} -7.9, -7.8, -7.7, -7.4, -6.1, -6.3 MHz. Simulated and experimental spectra are normalized on the y-axis so that they could be properly overlayed. These experimental EPR spectra were measured using a Bruker EMX Nano.

Hyperfine coupling values obtained from quantum chemistry calculations were used to simulate the EPR spectra. Pepper, an EasySpin command function, was used to generate all simulated EPR spectra in this work. Figure 4 shows the best fit of the simulated spectra to the experimental EPR spectra, with slightly adjusted A_{iso} values to achieve a closer match. Since EPR is a spectroscopic technique, the key parameters to look at include the number of lines, their distribution, and their relative intensities.

Radical Stability Over Time

The best fits of the simulated spectra to experimental spectra show a few discrepancies. Therefore, we decided to monitor the radical decay over time, which could reveal any contaminants present in the samples.
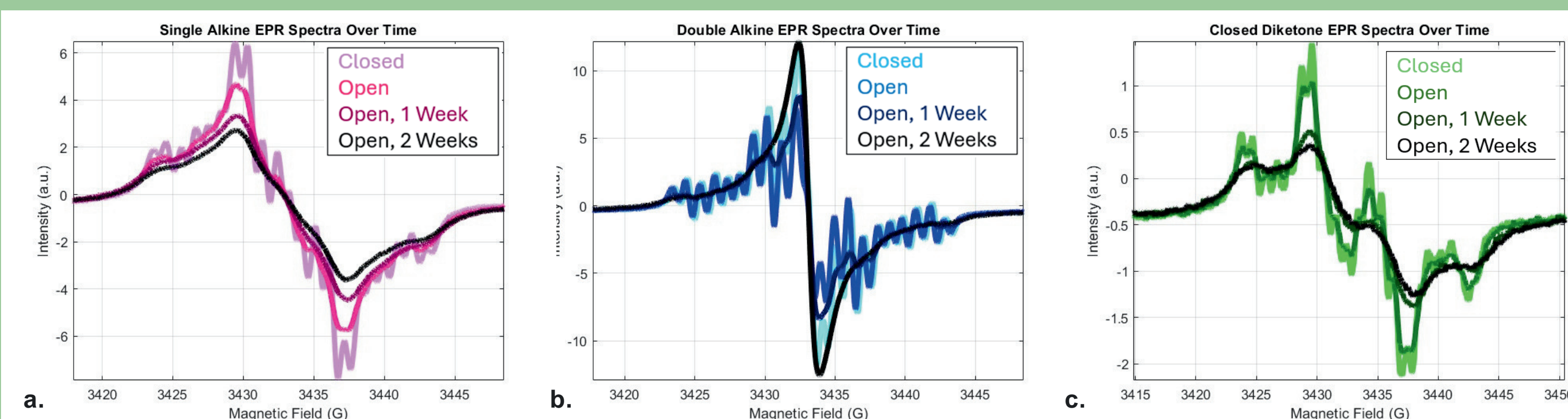
Figure 4. radical EPR decay over time. (a) Single alkyne; (b) Double alkyne; (c) Closed diketone. Sample was measured when the tube containing the sample was closed, just opened, opened for one week, and open for two weeks sitting in the freezer and making contact with the air, eroding the delicate biradicals.

The biradicals are very sensitive to air, so by breaking the tubes open they begin to decay. This decay is measured over the span of two weeks and is shown in figures 5a-c. The radical decay graphs are displayed with the magnetic field, in Gauss, on the x-axis, and intensity, in arbitrary units, on the y-axis. For all three figures, general trends of decreasing intensity can be seen the longer the tubes are left open. There are no drastic changes in the EPR spectra width that might arise from an emerging remaining molecule in the sample after the decay of the biradical.

DISCUSSION

Does the simulation agree with the experimental EPR?

The purpose of overlaying the simulated spectrum with the experimental spectrum is to check if our simulation correctly represents the electron spin density distribution of the biradicals. If that's the case, the line width, relative intensity of the peaks, and overall width of the spectrum would match closely with the experimental ones. This is not the case with our spectra (Figure 4). For the single alkyne, the line width is well reproduced, while the relative intensities are inaccurate. For the double alkyne and closed diketone, neither line width nor relative intensities are a close match for their experimental spectra.

This indicates that the A_{iso} values calculated might not be representative of the real ones.

This could be due to shortcomings of the simulation software (poor geometry optimization, inaccurate hyperfine calculation), possibly caused by the presence of the unpaired electrons. Another reason could be the presence of additional radical species as a byproduct of the synthesis, which overlays with the spectrum of the biradical. For this reason, we have started to investigate the decay of the biradicals, for which the analysis is still ongoing.

Does the carbon bridge affect the biradical's properties?

The single and double alkynes are nearly identical in their spin density maps (Fig. 3). Many hyperfine coupling values such as -5.8, 2, and -8.6 MHz seem to be located on the same hydrogens between the single alkyne and double alkyne molecules.

This indicates that the length of the carbon bridge does not impact the radical electron distribution.

However, without the presence of the bridge (closed diketone), the hyperfine values are differently distributed when compared to those of the single and double alkynes. On average, the A_{iso} values are also smaller in magnitude than those calculated for the single and double alkyne structures.

Are there impurities in our samples?

The presence of a contaminant is not immediately obvious. With typical cases of decay, we would expect the signal to go flat after two weeks. For all three, the spectra intensities decrease over time but not at the predicted rate. Furthermore, the double alkyne's intensity increases at week two, whereas the single alkyne and closed diketone continue to decrease. We would also expect the peaks to get broader but these peaks get sharper, especially with the double alkyne. More analysis must be done on these graphs to draw any conclusive results from them.

CONCLUSIONS AND FUTURE RESEARCH

Conclusion

- We developed a process by which to analyze complex biradicals
- Our simulations do not fully reproduce the experimental data
- The spin density distribution is affected by the presence of the carbon bridge

Future Research

These organic radicals still need more simulations to fully understand their paramagnetic systems. We have much more work to do to find the proper parameters to perfectly replicate the experimental EPR spectra. In the coming weeks we will attempt to:

- Take the differences of the closed tube from each of the later times to more clearly view differences in the EPR spectra.
- Refine our quantum chemistry methods
- Refine our EPR simulation methods

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