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ESR spectra of triplet carbenes

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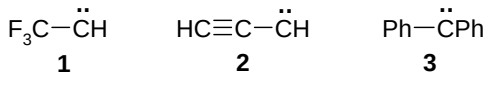
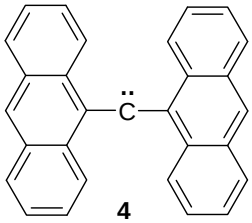
Unpaired electrons give rise to electron spin resonance (ESR) signals. As all electrons in singlet carbenes are (spin) paired, they cannot be observed using ESR spectroscopy. Triplet carbenes, on the other hand, possess two unpaired electrons (with a spin S = 1/2 each) in two different orbitals, with a total spin of 1 and magnetic quantum numbers (M_S) of –1, 0 or +1. While all three states are ideally degenerate, a zero-field splitting is observed already in the absence of an external magnetic field, i.e., the energy of the ±1 states is raised over that of the 0 state. In addition, in most triplet carbenes –1 and +1 states are also split at zero-field due to the difference in energy between sp^2 and p-type orbitals. The energy of the spin 0 state is not affected by an external magnetic field, whereas that of the –1 state is lowered and that of the +1 state is raised. This energetic splitting gives rise to two allowed transitions (–1 to 0 and 0 to +1), at different field strength for a given energy. The zero-field parameters D and E are determined from the absorption spectra, where the size of D gives information on the degree of delocalization and that of E allows for a determination of the bond angle at the carbene carbon.[1]

I will discuss the determination of the geometry at the carbene carbon of carbenes such as **1**-**4** from the observed zero-field parameters.



1 **2** **3**



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Reference

1. Moss, Platz, Jones, Reactive Intermediate Chemistry, Wiley-Interscience, 2004.