Triplet State Zero-field Splitting Parameters of a Carotenoid determined by Optically Detected Magnetic Resonance

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Triplet state zero-field splitting parameters for a carotenoid as measured by optically detected magnetic resonance in a carotenoporphyrin have been unambiguously determined.

Recently, a new class of compounds has been synthesized in which a carotenoid unit is covalently linked to a tetra-arylporphyrin.[1] These carotenoporphyrins have been shown to exhibit interesting energy transfer characteristics. Singlet–singlet (carotene to porphyrin) energy transfer relies on a high fluorescence quantum yield of the donor carotenoid (Förster mechanism) or a close physical approach of the two units (exchange mechanism).[2] For triplet–triplet (porphyrin to carotene) energy transfer to be observed, a geometrical stacking of these two units must be effected, as only the latter mechanism can operate.[3] Carotenoids are known to have a vanishingly small intersystem crossing from their photoexcited singlet to the excited triplet state. The triplet state of a carotenoid can thus be studied only in the presence of a sensitizing molecule. The ideal molecular system for investigating a carotenoid triplet state then is a carotenoporphyrin. We have obtained zero-field splitting (ZFS) parameters of the excited triplet state of a carotenoid polyene of six double bonds which was covalently linked in the *ortho* position of a phenyl group in the tetra-arylporphyrin† [molecule (**3**) in ref. 2, with R_1 and R_2 switched]. In this molecule, the triplet state of the carotenoid must then necessarily lie at a lower energy than that of the porphyrin.

We have utilized optically detected magnetic resonance in which an optical parameter associated with the triplet state changes when two of the three sublevels are connected *via* an applied microwave field of the appropriate frequency. In particular, we have monitored the triplet–triplet absorption intensity[3] at 535 nm; a shift in sublevel dynamics accompanying the resonance condition changes the overall triplet state population, and therefore the triplet absorption.[4] Signals were detected in the 'single beam' configuration in which one source, a xenon arc lamp system, serves as both the excitation and the probe beam. The sample (10^{-5} M in toluene) was suspended in a liquid helium Dewar flask, with the helium pumped down to 1.8 K. The transmitted light was detected by a cooled phototube after passing through a monochromator set at the triplet–triplet absorption wavelength of the carotenoid.

The porphyrin unit, as a molecular entity free of polyene, was found to yield the ZFS parameters listed in Table 1. These values are in essential agreement with those published for tetraphenylporphyrin.[5] For our carotenoporphyrin a new

Table 1. Triplet state sublevel resonance frequencies (in MHz) for the two chromophores in the carotenoporphyrin.[a]

	ν_1	ν_2	ν_3	$\|D\|$	$\|E\|$
Porphyrin	459	888	1347	0.0372	0.0076
Carotenoid	410	1840	2250	0.0682	0.0068
TPP	502	839	1341	0.0363	0.0083

[a] ZFS parameters $|D|$ and $|E|$, which are calculated from the frequencies, are expressed in cm^{-1}. The values for tetraphenyl porphyrin (TPP) are taken from ref. 5 for comparison.

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set of transitions appeared, which are therefore assigned to the six-double-bond polyene.

The only earlier references to carotenoid triplet state ZFS parameters were studies on various photosynthetic bacteria.[6] In biological preparations of this type, however, many different chromophores, in various states of aggregation, ligation, or configuration are present. An unambiguous assignment is therefore difficult, and in fact triplet-state e.s.r. spectra that were observed were similar to those in which a possible assignment to pheophytin was made.[7] Our optically detected magnetic resonance experiments, on the other hand, were performed on a sample containing only the porphyrin and the polyene chromophores, removing any ambiguity. It should be noted, however, that our values are in agreement with the trend found in the bacterial carotenoid ZFS parameters; our very short polyene exhibits ZFS parameters that are much larger than those of the various-length, but longer, carotenoids in the bacteria studied.

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