61. Triplet-State Energy of the Photostabilizer Tinuvin P

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Electron-energy-loss spectroscopy shows that the lowest triplet level of the photostabilizer molecule *Tinuvin P* (= 2-(2'-hydroxy-5'-methylphenyl) benzotriazole) is at ca. 3.0 eV. *Tinuvin P* acts as a photostable inner filter rather than as a quencher of excited impurity sites.

The mechanism of action of the polymer photostabilizer *Tinuvin P* (2-(2'-hydroxy-5'-methylphenyl)benzotriazole; 1), has been the object of recent controversy [1][2]. Since the original work of *Heller* and *Blattmann* [3] some twenty years ago, the photostability of 1 has been attributed to very fast reversible intramolecular proton transfer, the stabilising action towards polymers then being explained by its inner filter affect. Against this generally accepted model, it was suggested recently that this molecule had a very low lying triplet state beyond 800 nm (below 1.5 eV) which would account for its quenching action on the carbonyl groups present in the polymer [1]. This suggestion was supported by some quantum chemical calculations but lacked experimental support.



We have now measured the triplet state energy of *Tinuvin* P by the method of electron-energy-loss spectroscopy [4]. The spectra obtained at 20 eV and 3 eV residual energy are shown in the *Figure*. The selection rules corresponding to the high-energy spectrum are equivalent to those of light absorption and this spectrum is, therefore, practically the same as the optical absorption spectrum of the molecule.

In the low-residual-energy spectrum, these selection rules are relaxed, and triplet states can be observed as well. The lowest triplet level is found at ca. 3.0 eV, as expected for a molecule of this type. Only the vibrational levels of the ground state can be observed at lower energies, so it must be concluded that calculations which predict a triplet level around 1.5 eV are likely to be mistaken.



Figure. Electron-energy-loss spectra of Tinuvin P at ca. 3.0 eV and 20 eV residual energy

Since the energy of the lowest triplet state of 1 is now established, it can be concluded that quenching does not play a significant role in the photostabilizing action, and that the original model of *Heller* and *Blattmann* remains a valid explanation.

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REFERENCES

- J. Catalan, F. Fabero, M. Soledad Guijarro, R. M. Claramunt, M. D. Santa Maria, M. de la Conception Foces-Foces, F. H. Cano, J. Elguero, R. Sastre, J. Am. Chem. Soc. 1990, 112, 747.
- [2] D. Noukakis, P. Suppan, J. Photochem. Photobiol. A: Chem. 1991, 58, 393.
- [3] H.J. Heller, H.R. Blattmann, Pure Appl. Chem. 1972, 30, 145.
- [4] M. Allan, J. Electron Spectrosc. Relat. Phenom. 1989, 48, 219.