

For decades the observation of P was impossible because of a short lifetime τ_P in combination with slow population flow over a barrier (A_1 or B_1 in the figure). But these limitations can be overcome by ethylenic substitution.

Comparing stilbene and 1,2-dimethyl-stilbene with precision transient absorption spectroscopy in the range 250-800 nm, we determine the electronic properties of P.

By substitutions – also at the phenyl moieties - the excited *trans*, *cis*, and *perpendicular* forms are stabilized on a >10 ps timescale. Their excited-state absorption bands (ESA in the figure) are used for resonance in fs stimulated Raman spectroscopy. In this way we find several new phenomena during the photoreaction.

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