



Figure 2 Energy diagrams for the photoisomerization of 1,2-disubstituted ethenes. **a**, In free solution. **b**, In the context of a photoreceptor. The energy profile of the excited (π, π^*) state (shown in red) is different than that for the thermal isomerization. Genick *et al.*¹ have observed that early-state photoreceptor intermediates of the photoactive yellow protein resemble this 'p-state' intermediate.

similar strategy, a 1.9-Å structure of the late, blueshifted I_2 PYP intermediate has been obtained⁴, several milliseconds after excitation. In this intermediate, the *pCA* chromophore flips its double bond to a *cis* configuration by swinging the phenolic ring like a tennis racket. This large movement causes a considerable reorganization of surface-exposed protein residues nearby, and might enable PYP to interact with other signalling molecules. The chromophore is not planar, and the authors supposed this to be the molecular spring for completion of the photocycle.

An absorbed photon supplies more than enough energy to generate such late intermediates. But how is the energy that is initially localized in a 'hot' chromophore converted to the gross structural changes of the protein environment? And how can a photoreceptor catalyse a single reaction pathway, avoiding the unwanted side reactions that are well known to photochemists? The answer might be found in the structures of very early intermediates. However, these are formed too rapidly to be studied by the time-resolved approach, which operates on a nanosecond timescale⁶.

Genick *et al.*¹ offer a simple but elegant solution to these problems. They excited crystals of PYP at liquid-nitrogen temperatures, and assumed that the degrees of freedom that were frozen out were those responsible for the slower thermal relaxations towards the I_2 intermediate. Their 0.85-Å structure of such an early PYP photocycle intermediate shows, for the first time, a chromophore that has started a *trans*-to-*cis* isomerization around its C7–C8 double bond, but has become trapped halfway between.

What does the orthogonal conformation of the double bond tell us about a mechanism for photoreceptors? Consider, as the simplest model, 1,2-disubstituted ethenes in free solu-

tion. When they are excited by light, they form a transient (π, π^*) state in which there is effectively no π bond. Subsequent rotation around the bond gives a staggered, lower-energy conformer in which the adjacent *p*-orbitals are perpendicular to one another (Fig. 2a). This relaxed 'p state' can decay, without emitting radiation, to a *cis* or *trans* isomer with almost equal probability, by crossing to the ground-state energy curve⁷.

Genick *et al.* observe that, in their 0.85-Å structure, the chromophore looks similar to such a *p*-state intermediate. One could speculate that photoreceptors maximize

their quantum efficiencies by selectively stabilizing *p*-state-like intermediates. This is analogous to the way in which enzymes are efficient catalysts — by selective stabilization of the transition state. For PYP, the non-uniform protein environment means that photoisomerization is unidirectional, because the energetic barriers for returning to the original configuration or progressing through the reaction are not equal (Fig. 2b).

To understand the small, structural changes in early photocycle intermediates, we certainly need more sub-ångstrom structures like that presented by Genick *et al.* Unfortunately, it will probably be a long time before we have such an eagle-eyed view of rhodopsins or phytochromes — the quality of these crystals is a long way behind that of PYP. But the new results on PYP mean that crystallographers, quantum chemists and spectroscopists have got good reasons to chat to one another. □

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Meteoritics

Diamonds in the dust

Primitive meteorites are time capsules, containing dust that may have remained virtually unchanged since the earliest days of the Solar System. The dust is often peppered with tiny diamonds, which probably condensed from a stellar outflow before the birth of the Sun. But uncertainty surrounds the types of star involved.

Anja Andersen and colleagues (*Astron. Astrophys.* **330**, 1080–1090; 1998) have investigated the matter by extracting diamonds from the 1969 Allende meteorite, shown here in greatly magnified clusters. They then analysed the diamonds' spectral and absorption characteristics at various wavelengths, and predict the spectrum of a plausible candidate star (in this case, a type of carbon-rich red giant). With a template against which to compare real stellar spectra, the origin of the diamonds could in principle be revealed.

Things are not so simple, however, for diamonds have a comparatively weak influence on stellar spectra. But other lines



of approach may open up because these microscopic gems can act as seeds, and may have become covered with coats of other dust grains. Andersen *et al.* suggest such coatings might be retained and their composition revealed by sensitive extraction techniques — offering further clues to the diamonds' history.

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