



50 Years Ago

The Acting Administrator of the National Aeronautics and Space Administration ... shows every sign of confidence that two Americans will tramp about on the surface of the Moon some time next year. The last flight of a team of three astronauts in October seems enormously to have cheered up those responsible for the Apollo programme. Even the accident this weekend which destroyed one of the machines being used to test the rocket system for descending the last few hundred feet to the surface of the Moon seems to have left them unmoved ... Plans are now well advanced for the journey around the Moon of the Apollo 8 spacecraft, now assembled at Cape Kennedy, due to begin some time during the week of December 21.

From *Nature* 14 December 1968

100 Years Ago

A writer in the *Times*, directing attention to the fact that a large number of Royal Air Force officers will shortly be demobilised, suggests that they might profitably be employed in making an aerial photographic survey of the British Isles. He believes that this would prove useful to surveyors, architects, engineers, and others. While fully endorsing this writer's opinion that it would be unfortunate to lose the expert services of these flying officers ... we cannot agree that a series of aerial photographs could be of great service to surveyors and engineers. Such photographs show the landscape from a new point of view, but they naturally lack the accuracy of carefully drawn topographical maps. On the other hand, such a survey might be of considerable value in the progress of flying for commercial and other purposes. Many attempts have been made to devise suitable maps for airmen, but even the best available leave much room for improvement.

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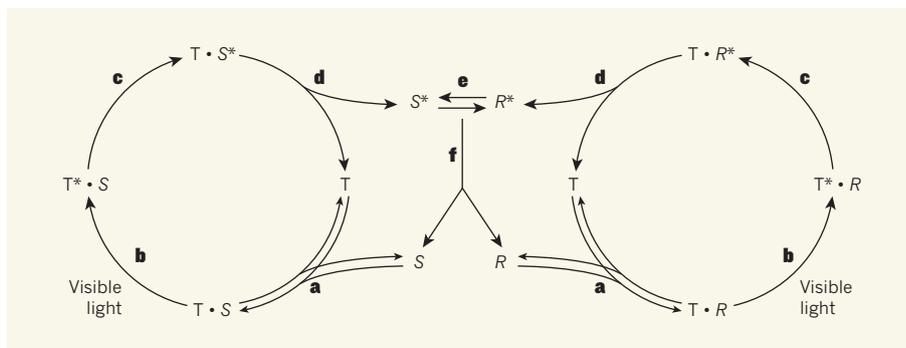


Figure 2 | A plausible mechanism for light-activated deracemization. **a**, T reversibly forms a complex with either S or R. **b**, Visible light excites T to generate an excited 'triplet' state (T^*). **c**, Energy from T^* is transferred to S or R, which enter triplet states (S^* or R^* , respectively), and T returns to its ground state. **d**, The $T \cdot S^*$ (or $T \cdot R^*$) complex comes apart, releasing T and S^* (or R^*). **e**, **f**, The excited molecules can interconvert (**e**), and eventually relax to their ground states (**f**). However, thermodynamic factors in step a and kinetic factors in step c ensure that most of the molecules end up as R, rather than S.

that are difficult or tedious to prepare when in their ground states, but more easily made using light-induced (photochemical) reactions that proceed through electronically excited states.

Nevertheless, achieving highly enantioselective photochirogenesis is not a trivial matter, because excited molecules are short-lived and highly reactive, and because it is difficult to precisely control the stereochemistry — the geometrical arrangement of groups in a molecule — of products formed from reactions of excited molecules. The control problem has been overcome using a supramolecular approach², in which a 'guest' molecule is fixed into a particular position and orientation within a chiral 'host' environment to enable better stereochemical control of the guest's reactions. Hölzl-Hobmeier and co-workers have developed a new take on supramolecular photochirogenesis that they apply to allenes.

Allenes are organic molecules in which one carbon atom (designated C2) forms a double bond to both of its neighbouring carbon atoms (C1 and C3; Fig. 1). These molecules can assume a type of chirality known as axial chirality if two different groups are attached at each of C1 and C3. In their study, Hölzl-Hobmeier and colleagues used axially chiral allenes that have a lactam group attached at C1. The enantiomeric form of these allenes is fixed when they are in their ground states, but they spontaneously interconvert between the two enantiomers when excited to a state known as a triplet³.

The lactam group is designed to form pairs of hydrogen bonds with a molecule known as an enantiomeric photosensitizing template (T), which was developed previously by workers from the same research group⁴. T forms complexes with the allene, within which it can absorb visible light and transfer the energy to the allene, exciting the latter to a triplet state⁵.

So how does T induce the conversion of a racemic mixture of allenes into a single enantiomer, a process known as deracemization? The

process begins with the formation of a complex of T with either of the two enantiomers (which are known as the S- and R-enantiomers, hereafter referred to simply as S and R; Fig. 2). Irradiation of the resulting complex $T \cdot S$ (or $T \cdot R$) by visible light excites T into a triplet state (T^*), which then transfers energy to S (or R). The excited molecule S^* (or R^*) is then released from the complex, regenerating free T for another catalytic cycle. The liberated excited molecules then undergo racemization, and — in the absence of any factors that discriminate between the two enantiomers — eventually relax to form both S and R products in the ground state in equal quantities.

However, the overall deracemization process can be enantioselective depending on two things: one is how strongly T binds to S to form a complex compared with how strongly it binds to R; the other is the relative rate at which energy is transferred from T^* to S and from T^* to R. For an allene that carries an extremely bulky group known as a *tert*-butyl, Hölzl-Hobmeier and colleagues' experiments show that T binds to S about five times more strongly than it does to R. This makes sense in the context of the authors' computational simulations, which show that S and R stack above T in their respective complexes, but that S stacks more closely to T than R does (see Fig. 4a of the paper¹) — which suggests that $T \cdot S$ is thermodynamically more stable than $T \cdot R$.

Moreover, the enantiomeric excess (e.e.) — a measure of the ratio of enantiomers in a sample of a chiral compound, where 100% indicates the presence of just one enantiomer — reported by Hölzl-Hobmeier *et al.* for the deracemized allene is 96% in favour of R. The rate of energy transfer for T^* to each of the two enantiomers can therefore be calculated, and it emerges that the rate of energy transfer to S is about ten times the rate of transfer from T^* to R.

The chiral environment generated by T for the allene in the complex therefore has dual, synergistic roles that lead to the extraordinarily high e.e.: when T is in its ground state,