Absolute configurations established for persistent organic pollutants DDT and DDD

Polychlorinated hydrocarbons such as hexachlorocyclohexane, hexachlorobenzene, heptachlor and chlorodane have long been known as effective and durable pesticides. Dichlorodiphenyltrichloroethane (or 1,1,1-trichloro-2,2-bis(chlorophenyl)ethane, DDT) has also been used widely and is still used in a few countries to control malaria and typhus vectors. Less chlorinated DDD (1,1-dichloro-2,2-bis(chlorophenyl) ethane) and DDE (1,1-dichloro-2,2-bis(chlorophenyl)ethene) are metabolites of DDT and contaminants in technical-grade DDT. Interestingly, *o,p'*-DDD has been used medically to treat adrenal gland cancer, while the exposure to *p,p'*-DDD increases the risk of breast cancer.

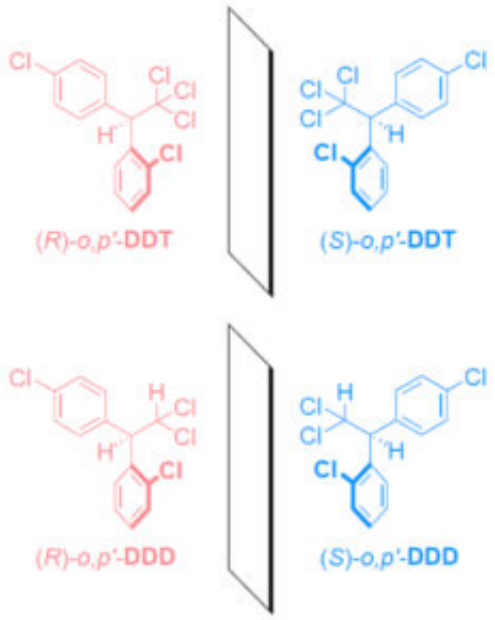

Fig. 1.

For this reason, it is imperative to monitor the uptake and degradation of these legacy persistent organic pollutants (POPs) in biological and environmental samples. Some congeners of these POPs (i.e., *o,p'*-DDT and *o,p'*-DDD, see Figure 1) are chiral and their enantiomeric enrichment through biodegradation is regarded as an additional measure of risk assessment and accumulation of such POPs in environment. Although the absolute configurations of these chiral POPs were tentatively assigned quite a long time ago with superior refinement parameters on one of the enantiomers in the X-ray diffraction analysis, some uncertainties still remain, due to the lack of heavy atom(s) in the molecules. Recently, the absolute configuration determination using

chiroptical properties has been widely recognized as an alternative and/or complementary method. By direct comparison of the theoretical versus experimental chiroptical properties such as circular dichroism, the absolute configurations have been determined for a number of natural and synthetic chiral molecules. More recently, the chiroptical methods have been also applied to more complex molecular and supramolecular systems.

In this study, we performed combined experimental and theoretical studies on the circular dichroisms of *o,p'*-DDT and *o,p'*-DDD. to unambiguously assign their absolute configurations. Applying a chiroptical method to DDT and DDD was thought to be a challenge, as the Cotton effects reported for point-chiral molecules are much weaker in general than those for axially chiral ones. It turned out, however, that DDT and DDD enantiomers exhibit intense Cotton effects arising from the excitonic coupling of *o*- and *p*-chlorophenyl chromophores, facilitating the absolute configuration determination. The first-eluted enantiomers of both *o,p'*-DDT and *o,p'*-DDD exhibited a weak negative Cotton effect for the lowest energy transition. Interestingly, much stronger exciton coupled CEs with a characteristic negative-positive-negative pattern were also observed in the high energy region (200-250 nm), which allowed us to unambiguously determine the absolute configurations of *o,p'*-DDT and *o,p'*-DDD by direct comparison with the results of theoretical computations at the approximate coupled cluster calculations. Accordingly, the enantiomers of *o,p'*-DDT and *o,p'*-DDD that elute earlier from a Chiralcel OJ-H column were assigned to (*S*)-(+)-DDT and (*S*)-(-)-DDD, reaffirming the previous tentative assignments, which will contribute to reliable monitoring of the biodegradation processes of these legacy POPs.

Tadashi Mori
Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Japan

Publication

Absolute configuration determination through the unique intramolecular excitonic coupling in the circular dichroisms of o,p'-DDT and o,p'-DDD. A combined experimental and theoretical study.
Tanaka H, Inoue Y, Nakano T, Mori T
Photochem Photobiol Sci. 2017 Apr 12