

Replacement of Mercury Antifoggants for Photothermographic Imaging Materials

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Abstract

Addition of mercury salts to photothermographic imaging materials was discovered many years ago to dramatically affect the overall photographic characteristics of these materials. One particular advantage is the antifoggant property exhibited by the mercuric ion in silver halide/silver carboxylate systems. Various approaches have been undertaken to improve the antifoggant properties of these materials, as well as to eliminate the incorporation of heavy metals in the formulation. Tribromomethyl substituted organic compounds have been found to be very effective antifoggants, although the toxicity of these materials must also be considered prior to their use. The mechanism of action of these materials is not completely understood, although incorporation of groups within the antifoggant which enable it to coordinate with the silver halide surface may also increase their effectiveness. We have developed the technology to generate novel tribromomethyl compounds which are useful antifoggants, but also pass the required toxicity tests. Computational modeling of the target molecules, in combination with calculated partition coefficients, enables effective screening of new compounds for toxicity testing prior to actual animal tests that are expensive and time consuming. This presentation will discuss the overall technology of this class of compounds.

Introduction

Imation and other companies have been investigating and using photothermographic imaging systems for decades. Hence, there is a large body of chemical, physical and engineering data on these systems. As with most complex systems, there are opportunities for more insight into the mechanisms behind the data.

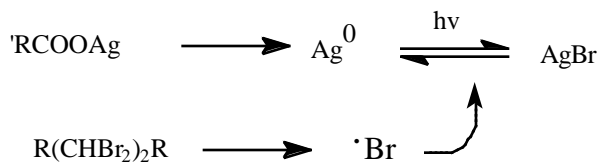
Mercury compounds are the traditional antifoggants in these systems,¹⁻³ however, these compounds are environmentally undesirable. The elimination of heavy metals as antifoggants has led to the development of new antifoggants, but these compounds have to be acceptable for both health and environmental reasons. Tribromomethyl substituted compounds have been found to be useful antifoggants and stabilizers in silver halide photographic constructions.⁴ In addition to the antifoggant properties these compounds must pass either mutagenic or carcinogenic testing. The key step

was to find compounds having antifoggant and image stability properties for photothermographic materials that exhibit low mutagenicity and sensitization of human skin.

Discussion and Results

Polybrominated organic compounds have been used as antifoggants and image-stabilizers for photothermographic materials because they can oxidize reduced silver (fog centers) back to silver bromide thermally (acting as an antifoggant) and photochemically (as image stabilizer).

The theory for the activity of tribromomethyl compounds has resulted from the investigation of various tribromomethyl substituted compounds.⁴ These tribromomethyl compounds were tested and ranked according to their activity. The mechanism proposed is shown below.



Alternatively, tribromomethyl containing compounds having the ability to coordinate silver, such as 2-tribromomethylsulfonyl-benzothiazole (1) which could bind to coordinately unsaturated silver ions on the surface of silver halide, may be advantageous. The close proximity of the tribromomethyl group to the fog centers could then easily lead to silver atom cluster oxidation and to bromide transfer.⁵ Hence this process would provide antifoggant properties⁵.

Emphasis on replacing toxic heavy metals in photothermographic imaging materials led to the generation of novel tribromomethyl compounds. To accomplish this, we had to develop the technology to prepare these compounds as well as a method to predict their mutagenicity. This concern led to an emphasis on the understanding and prediction of the mutagenicity of various tribromomethyl compounds.

To address these concerns, it was important to answer the questions of mutagenicity computationally as well as experimentally. This would lead to a better understanding of the correlation of various antifoggants to mutagenicity. Computational results are of value only after they have been

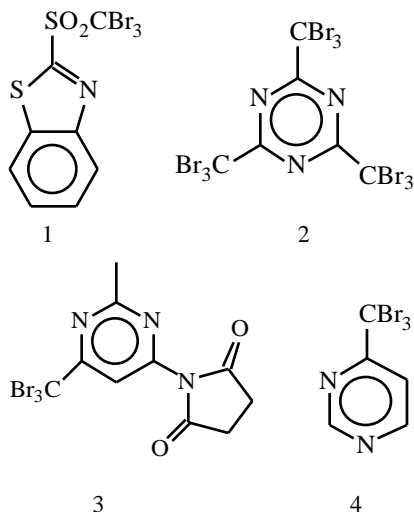
correlated to known experimental results. In the area of tribromomethyl compounds, mutagenicity assessments are made from the "Ames" and Mouse Lymphoma tests.

A detailed examination of the Ames test, rather than just looking at the "pass" or "fail" test summary is important for two reasons, to understand the complex biochemical processes involved and to suggest improved compounds. The pass or fail results are adequate for excluding specific tribromomethyl compounds from future use, however, to understand why certain molecules fail, and suggest modifications that will produce nonmutagenic alternatives, we need to understand the details of what has occurred during the experiments.

In order for any molecule to have biochemical activity it must first be transported into living cells and then it must have chemical reactivity inside the cell. A good way to model the transport based activity of molecules is through the octanol/water partition coefficient. This is simply the logarithm of the ratio of molecular solubility's in octanol and water log(P).

Statistical methods of Quantitative Structure Activity Relationship (QSAR)⁶⁻⁷ computations gave the log(P) values⁸ for a variety of molecules. The log(P) values were determined either experimentally or from calculations. The program used to compute the log (P) value summed parameterized atomic values. The computed log (P) result for the whole molecule is a sum of log (P) values for its constituent atoms. Chemical reactivity is modeled using standard methods, such as MOPAC⁹ and NBO¹⁰⁻¹¹ analysis. These produce chemical descriptors, for example, ionization potential and electron affinity.

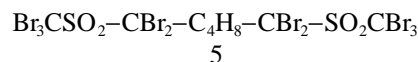
Tribromomethyl compounds were tested experimentally as well as computationally. A valid correlation of calculation and experiment gives an improved mechanistic understanding of the chemical process involved. Calculations then can be done on suggested but untested compounds to screen them for applicability as ingredients in alternative product formulations. Four compounds, of the compounds tested, are seen below.¹¹⁻¹³



Compound #	Log (P) Value	Mutagenicity
1	5.68	Pass
2	4.40	Pass
3	1.19	Fail
4	2.20	Fail

A correlation between the mutagenicity and the log (P) value showed that when these tribromomethyl compounds had a $\log(P) \geq 3.8$, then they were non-mutagenic. When the tribromomethyl compounds had $\log(P) \leq 2.5$, then they were mutagenic. For intermediate log (P) values, the mutagenicity depended on computed ionization potential: ionization potentials between 10.0 and 10.8 eV corresponded to non-mutagenic tribromomethyl compounds. Correlations between experimental data and computed molecular descriptors of mutagenicity could now be used to screen suggest molecules for use as antifogants.

Using these results, we are able to computationally examine suggested but unsynthesized tribromomethyl compounds. These calculations suggested several possibilities that should have good antifogant ability and also be nonmutagenic. An example of this approach led to the synthesis of compound (5) which has log (P) value of 7.35. When tested in a photothermographic system the results showed excellent antifogant properties.¹⁴



Summary

An initial understanding of the correlation of the tribromomethyl compounds properties to mutagenicity, coupled with experimental data, has led to a method of screening untested compounds for utility in alternative product formulations. Based on this work we can better suggest compounds to be synthesized with improved product performance.

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