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Chemistry of Photothermographic Imaging Materials. II

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The structural investigation is reported of the reactions between components utilized in photothermographic imaging systems, including toners, developers and silver with potential ligands such as triphenylphosphine, tribromomethylsulfonylbenzothiazole and 2-mercapto-benzimidazole. Depending on the complexing agent and silver counterion, various forms of silver complexes can be isolated and characterized. This report demonstrates the interactions, and characterizes the new compounds formed between various components in the photothermographic materials with emphasis on the formulation containing silver carboxylate, the toner system comprising phthalazine and phthalic acid and phenolic type developers.

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Introduction

Photothermographic imaging systems based on silver halide and silver carboxylates have been utilized for many years, however, very little has been reported on the details of the chemical reactions occurring between the imaging components before, during or after thermal processing.[1] We are continuing to investigate these reactions in order to understand the imaging chemistry, including the reaction between the silver carboxylate, from which the metallic silver image forms, and the various toners and developers. We now report that many interactions between various components not only are possible but result in compounds that can be readily isolated and characterised by normal techniques, including their solid state thermal and structural properties.

We have carried out a structural investigation of several of the key components in photothermographic imaging systems, and previously reported the first portion of this work[1] which revealed the molecular structures of several silver complexes, including the fundamental silver source on which these systems are based, silver stearate.[2] The continuation of this work has now shown that the interactions between many of the components incorporated within a thermal imaging construction are more complicated than might have been first predicted. The work reported here demonstrates the interactions between three separate groups of components which, once in the imaging construction, may affect the overall imaging properties. The three groups are toners, such as phthalazine (PHZ) and phthalic acid (PA), developers such as phenol based derivatives, and silver ion complexes, such as those formed with a development accelerator (triphenylphosphine, in this case). In addition, the latter group includes the first reported structure of silver bromide, the light sensitive component of photothermographic imaging systems, with the well known photographic stabilizer, 2-mercapto-benzimidazole (MBI).

Experimental

The 2:1 and 2:3 PHZ:PA ratio toner combinations and $[AgBr{\cdot}MBI(acetone)_{0.5}]_4$ complexes were obtained by the procedures described elsewhere.[3,4] DSC data were obtained on a TA Instruments 2200 Thermal Analyzer and 921 DSC dual sample cell under nitrogen flow, heating at 10.0°C/min.

Results and Discussion

The interactions between the basic components in a conventional photothermographic imaging formulation which we have investigated can be divided into three categories, interactions between toner components, hydrogen bonding interactions of phenolic based reducing agents, and the formation of silver complexes with available ligands. The structures of the components of these categories, PHZ/MPA, *bis*-catechol, and MBI, are shown in Fig. 1. Each group is discussed individually below.

Toners

Toner combinations such as phthalazine and phthalic acid are usually added as individual components,[5] however, we have found that they are not necessarily independent of each other. The acid-base interaction between them form at least two complexes, including the 2:1 and 2:3 ratios, which can be easily isolated and characterized. A simple change of crystallization conditions (evaporating acetone versus cooled water) produce these

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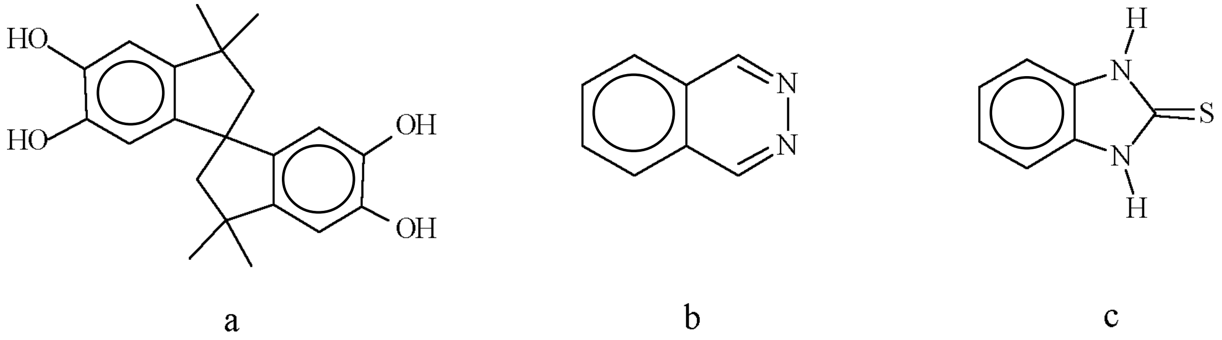


a b c

Figure 1. Classes of components of photothermographic imaging systems which interact with other components: a = developers, b = toners, c = stabilizers.

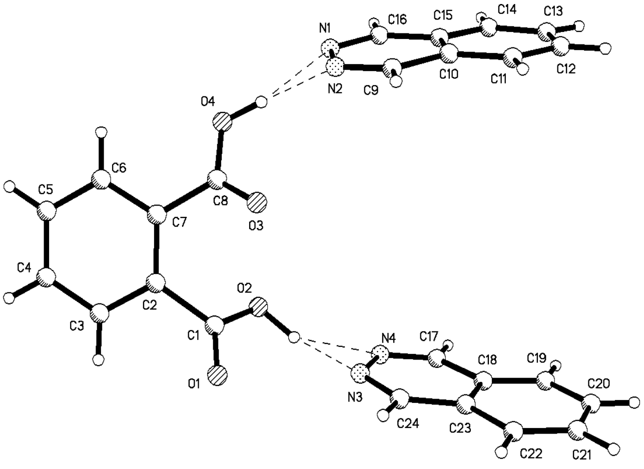


Figure 2. Structure of the $PHZ_2 \cdot PA$ complex (reprinted from R. D. Rogers, C. V. K. Sharma, D. R. Whitcomb, Molecular Tweezers: 2:1 and 2:3 Co-crystals of Phthalazine:Phthalic Acid, *Cryst. Eg.*, **1**, 255–262 (1998), with permission from Elsevier Science Ltd.).

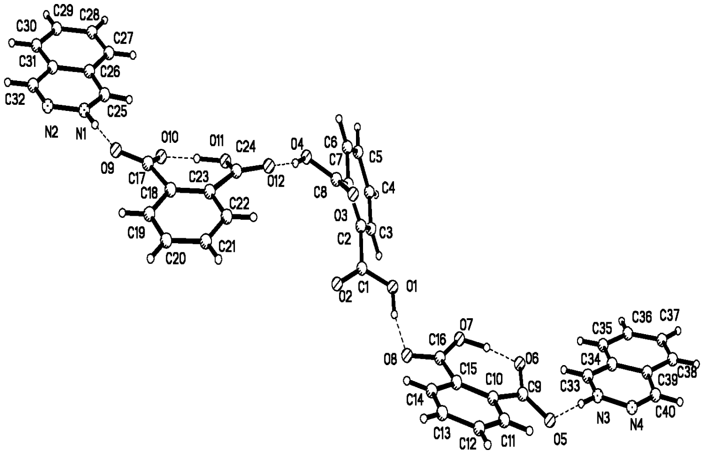


Figure 3. Structure of the $PHZ_2 \cdot PA_3$ complex (reprinted from R. D. Rogers, C. V. K. Sharma, D. R. Whitcomb, Molecular Tweezers: 2:1 and 2:3 Co-crystals of Phthalazine:Phthalic Acid, *Cryst. Eg.*, **1**, 255–262 (1998) with permission from Elsevier Science Ltd.).

compounds (2:1 and 2:3 respectively) which are very stable species. The crystal structures and thermal properties of these complexes have recently been determined.[3] In both compounds, the PHZ molecules were found to be bonded to the acidic hydrogen of the PA.

In the case of the $PHZ_2 \cdot PA$ compound the OH groups of the carboxylic acids are hydrogen bonding with the azo groups of two PHZ molecules and form a molecular tweezers structure. The interplanar separation between the PHZ units is ideal for binding the aromatic groups through stacking interactions. As a result of the aromatic interaction, the molecular tweezers are interdigitated *via* face-to-face stacking of PHZ units to form a close packed dimeric unit in the crystal lattice. The dimeric tweezers form an infinite 1D chain through complementary herringbone interactions and C-H···O hydrogen bonds, shown in Fig. 2. The proton of the acid remains associated with the carboxylate and is not salt-like, which is consistent with both the relatively low melting point (118.4°C) and good solubility properties of the $PHZ_2 \cdot PA$ complex in organic solvents.

The $PHZ_2 \cdot PA_3$ complex forms an interesting hydrogen bonded pentamer consisting of one neutral PA, two mono-deprotonated PA anions, and two mono-protonated PHZ cations, shown in Fig. 3. The hydrogen bonded PHZ-PA molecules result in a "Z-shaped" pentamer. In this case, the more salt-like nature of the hydrogen bonding results in a solid state material having a higher melting point (124.6°C) compared to the 2:1 ratio complex.

In a photothermographic construction, either the $PHZ_2 \cdot PA$ complex or the individual components added separately may be used to provide toning of the metallic silver image.

Developers

In the case of developing agents, phenolic compounds are used which have structural modifications that control their reactivity. We have found that one particular *bis*-catechol developer, 5,5',6,6'-tetrahydroxy-3,3,3',3',-tetramethyl-1,1'-spirobisindane,[6] Fig. 1, which has been used in thermal imaging materials based on ferric carboxylates[7] and on silver carboxylates,[8] exhibits an unusual crystal structure that is generated by combination of the spiro linkage between the catechols and the resulting juxtaposition of the hydroxy-hydrogens.[9] The spiro linkage between the aromatic rings forces the catechol rings to be perpendicular to each other. Consequently, the strong, interlaced hydrogen bonding between catechols generates a solvent tunnel comprised of stacked layers of (R) or (S) configurational pairs that

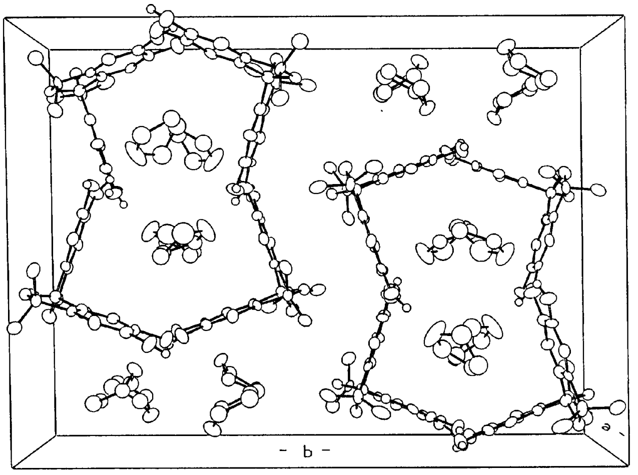


Figure 4. Solid state structure of 5,5',6,6'-tetrahydroxy-3,3,3',3',-tetramethyl-1,1'-spirobisindane (reprinted from J. A. Bjork, M. L. Brostrom, D. R. Whitcomb, *J. Chem. Cryst.*, **27**, 223–230 (1997), with permission from Kluwer Academic/Plenum Publisher).

is enhanced by extended hydrogen bonding to lattice solvent, shown in Fig. 4.

While hydrogen bonding in catechols is well known,[10] the spiro linkage based molecular structure of this particular catechol encourages an extended lattice effect which is reflected in its melting point. For example, while 3,5-di-*t*-butyl-catechol melts at 97°C, this spiro-catechol melts at 323°C. The difference in these melting points can be directly attributed to the spiro-linkage between the catechols and the resulting hydrogen bonding. A further practical consequence of this extensive hydrogen bonding may be its effect on the molecule's ability to diffuse within a coating containing residual solvent or other components having hydrogen bonding capability.

Silver Complexes

In addition to the silver complexation chemistry reported previously[1,2,11–14] we continue to find new complexes built from many of the components included in the photothermographic imaging formulation. For example, we have investigated three new complexes; the reaction between silver ions and tribromomethyl-sulfonyl-benzothiazole, published elsewhere,[15] between triphenylphosphine, a development accelerator[16] and silver stearate,[13] and between the conventional silver halide stabilizer, MBI, with silver in the form of silver bromide.[4]

In the case of triphenylphospine, this ligand has been cited as a development accelerator in thermal imaging systems containing silver carboxylate.[16] We have found that the reaction of silver stearate, the source of the silver ions for the metallic silver image in thermographic imaging materials, with triphenylphosphine converts the dimeric silver carboxylate structure, Fig. 5, to a monomeric silver complex, [AgSt·$(PPh_3)_2$].[13] In this complex, the original eight-membered silver carboxylate ring[2] has been completely disrupted and a new four-membered ring forms containing a chelating carboxylate and two phosphines that are mono-dentate, as shown in Fig. 6.

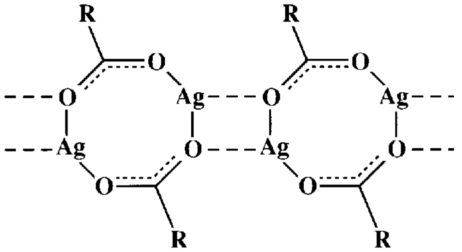


Figure 5. Structure of silver carboxylate dimers, $[Ag(O_2CR)]_2$: R = $C_{17}H_{35}$ for AgSt.

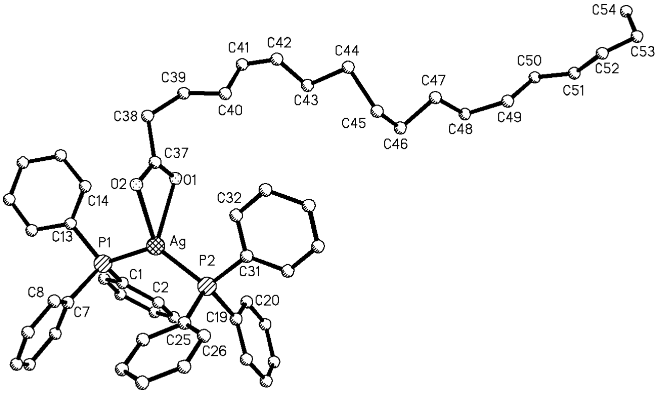
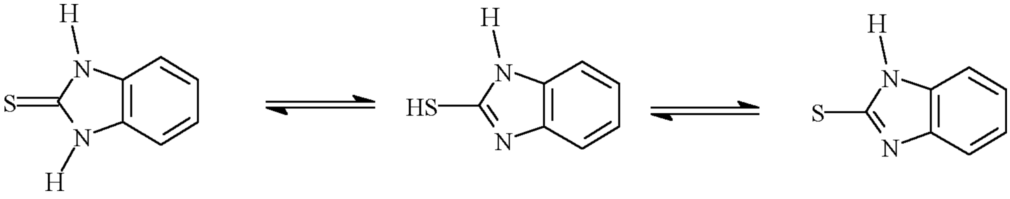


Figure 6. Structure of [AgSt·$(PPh_3)_2$] (reprinted from D. R. Whitcomb, R. D. Rogers, *J. Chem. Cryst.* **26**, 99–105 (1996), with permission from Kluwer Academic/Plenum Publisher).

The significance of the [AgSt·$(PPh_3)_2$] structure is the dramatic change in solubility compared to the starting silver carboxylate. While common silver carboxylates are quite insoluble in non-coordinating solvents, typically 10^{-5} M, this latter complex is about three orders of magnitude more soluble. A proposed mechanism for solubilization of silver carboxylates by these types of coordinating solvents, involving the disruption of the Ag···O interaction occurring between silver carboxylate dimers in the solid state, as seen in Fig. 5, is discussed elsewhere.[13] It is this solubility change that probably explains the ability of these types of ligands to be used as development accelerators.

Mercaptobenzimidazole, on the other hand, is an interesting complexing agent in that it is used extensively in photographic systems[17,18] but very little has been reported on the silver complex chemistry.[19–21] Unlike its apparent tendency to deprotonate under aqueous conditions with AgBr or Ag^+ to form AgMBI, we have found that the complex formed from MBI and AgBr in organic solvent has the stoichiometry $[AgBr \cdot MBI \cdot (acetone)_{0.5}]_4$.[4] This complex maintains a Ag-Br bonded silver bromide in the complex where the MBI is bonded *via* a bridging sulphur.

In addition to the coordination chemistry of MBI, this ligand is well known to exhibit a tautomeric equilibrium, as illustrated below, comprising the thione, thiol and deprotonated thiol. Each form could produce strikingly different coordination compounds. The thione form is apparently the preferred mode in solution.[19]



For discussion purposes, it is useful to view the MBI as a thiourea (TU) derivative. While no $AgBr\cdot MBI$ complexes have been structurally characterized, there are three known silver halide TU complexes[22,23,24]: $AgTU_2Cl$, $Ag(MeTU)_3Cl$ and $Ag(Et_2TU)_3I$. All three compounds are quite stable and the first exhibits a polymeric structure (due to the bridging thione TU) while the others are monomeric.

In the $[AgBr\cdot MBI]_4$ case, the crystal structure is comprised of an intricate network of interlocking ring systems, and contains non-coordinating acetone solvent. The fundamental building block of the crystal structure is shown below in Fig. 7. The $[AgBr\cdot MBI(acetone)_{0.5}]_4$ complex exhibits more similarities to the polymeric $AgTU_2Cl$ complex[22] than to the monomeric forms of $Ag(MeTU)_3Cl$ and $Ag(Et_2TU)_3I$.[23,24] A simple change in the TU substituents seems all that is necessary to create a polymeric or monomeric complex.

Most significant, however, is the fact that the molecular structure of this complex is similar to these TU complexes of AgBr in that the acidic proton of the MBI remains with the ligand. The retention of the acidic proton in the $[AgBr\cdot MBI]_4$ complex is quite different compared to the deprotonated AgMBI form prepared from AgBr under aqueous conditions.[19] While both complexes are poorly solvent soluble, which is the attractive feature of AgMBI for quantitative analysis purposes,[21] they begin to reveal their chemical differences visually in that the first is colorless while the second is yellow. These differences need to be taken into account in assessing their effect on the imaging properties of films made with these components. The complete details of the molecular and crystal structure of $[AgBr\cdot MBI(acetone)_{0.5}]_4$ are reported elsewhere.[4]

Summary

Interactions between various components in the formulation of photothermographic imaging materials have been clearly identified and can be rather extensive. Some of these interactions are predictable, such as simple acid-base interactions of toners and hydrogen bonding of developers. However, the extent of these reactions can be quite unexpected, including the more complicated formation of specific silver complexes. Silver complexes can form from the Ag^+ ions, the silver carboxylate, or even the relatively unreactive AgBr microcrystals present in the formulation. Unintended interactions may result among the various components of the imaging system, all of which may be considered to have an impact on the overall photographic properties of films prepared with these components.

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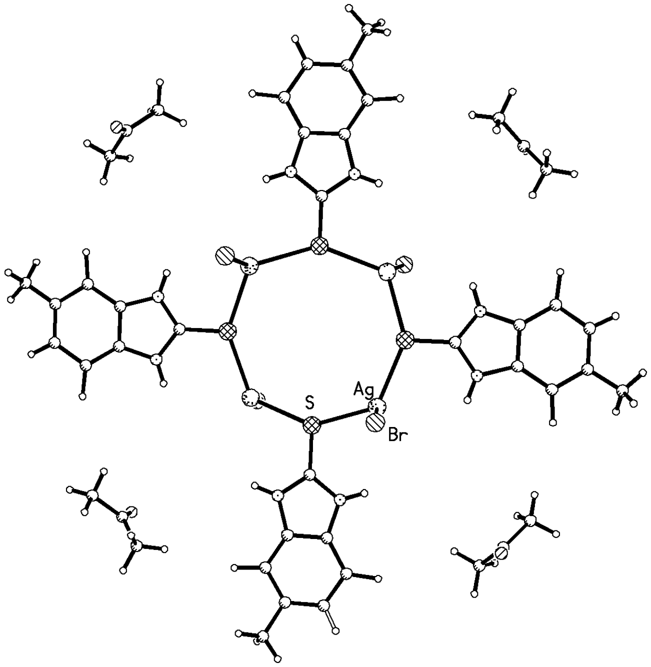

Figure 7. Structure of $[AgBr\cdot MBI(acetone)_{0.5}]_4$ (reprinted from *J. Imag. Sci. Technol.*, D. R. Whitcomb and R. D. Rogers, **43,** 498-502 (1999), with permission from the Society for Imaging Science and Technology).

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