

Photostabilization of Tetrahydro-2-(nitromethylene)-2H-1,3-thiazine Adsorbed on Clays

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The photochemical degradation of the insecticide tetrahydro-2-(nitromethylene)-2H-1,3-thiazine (NMH) adsorbed on montmorillonite, nontronite, and hectorite was studied. In all cases, a considerable photostabilization was observed in comparison with samples of the pesticide in its free form. NMH adsorbed on montmorillonite and nontronite decomposed more slowly than that adsorbed on hectorite, probably due to charge transfer from the excited pesticide to the Fe^{3+} ions in the clay lattice. Improvement of stabilization was achieved when the cationic dye 3,6-diamino-10-methylacridinium (AF) was coadsorbed with NMH on montmorillonite. Intermolecular interactions were studied by infrared and UV-vis absorption spectroscopy. The results of these measurements, and the relative position of the electronic absorption bands of NMH and AF, might indicate a deactivation mechanism via energy transfer between the two organic molecules adsorbed on the surface of the clay. Adsorption of the chromophore AF to montmorillonite takes place through a cation-exchange mechanism, whereas NMH interacts with the hydrophilic surface of the clay. Basal spacing measurements of the organo-clay complexes indicate a preferred planar orientation of the molecules.

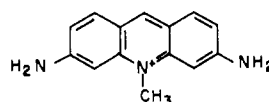
INTRODUCTION

Sensitivity to sunlight limits the use of some potential pesticides in agriculture. Classical approaches to overcome this obstacle have involved chemical modifications of the molecular structure of the pesticide or the use of UV-absorbing materials in the formulations. However, both methods suffer from serious drawbacks since chemical modification may affect the pesticidal activity of the compounds or their biodegradability and the large amount of UV screeners required to achieve acceptable photoprotection may introduce ecological problems related to soil and water pollution.

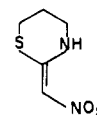
A new method for photostabilizing insect control agents, which is free from the above-mentioned disadvantages, was suggested by Margulies et al. (1985). The method is based on the adsorption of the photolabile bioactive compound on the surface of clays to which a selected organic chromophore has been previously attached. This chromophore, with specific spectroscopical and charge properties, is adsorbed at concentrations similar to those of the pesticide. The surface properties of the clay determine the orientation and distances between the two organic molecules so that intermolecular interactions can take place. The chromophore can either absorb light and prevent photoexcitation of the pesticide or accept the excess energy from already excited pesticide molecules by different energy-transfer or charge-transfer mechanisms (Forster, 1959; Dexter, 1953; Kavarnos and Turro, 1986). As a result, substantial extension of the pesticide's lifetime can be achieved. Using bioassays, we have already shown that the method can be applied to extend the biological activity under sunlight exposure of the insecticides bioresmethrin (Margulies et al., 1987) and tetrahydro-2-(nitromethylene)-2H-1,3-thiazine (NMH) (Margulies et al., 1988a). The latter is an extremely potent insecticide with low acute mammalian and fish toxicity (Soloway et al., 1978; Johnston et al., 1986; Ross and Brown, 1982), but its high photolability prevented its practical use. Pho-

tochemical studies have shown that the toxophoric nitrovinyl group is involved in the photochemical reaction, suggesting that photostabilization should be tried by making improvements in the formulation (Kleier et al., 1985).

In the present work we report results (obtained using analytical techniques) on the kinetics of the photochemical degradation of NMH adsorbed on three different clays and on a clay-chromophore complex, as well as the study of the intermolecular interactions at the clay surface. The organic chromophore selected as potential photostabilizer of NMH was 3,6-diamino-10-methylacridinium (AF).



AF



NMH

MATERIALS AND METHODS

Materials. The clays used were sodium montmorillonite SWy-1 (Mont) and hectorite SHCa-1 obtained from the Source Clays Repository, Clay Minerals Society, and nontronite type H-33a obtained from Ward's Natural Science Establishment. NMH (Shell SD 35651) was supplied by L. O. Ruzo of the University of California. AF was purchased from Fluka AG. These materials, except hectorite, were used without further purification. Hectorite was shaken overnight with buffer acetate solution (pH 5) to remove calcite, and the state of purification of the clay was monitored by measuring the IR spectrum.

Adsorption Isotherms. To measure the adsorption isotherm of AF to montmorillonite, aliquots of an aqueous solution containing 1×10^{-2} M of the dye were added dropwise to 10 mL of a 0.5% w/w suspension of sodium montmorillonite in distilled water, under continuous stirring. The final volume was brought to 40 mL. After 6 days at room temperature, the suspension was centrifuged in an ultracentrifuge for 30 min at 60000g. The concentration of the dye in the supernatant was determined by UV-vis spectrophotometry measuring the absorption at 450 nm ($\epsilon = 30\,000\text{ M}^{-1}\text{ cm}^{-1}$).

The adsorption of NMH to the different clays and to the montmorillonite-AF complex was done by shaking overnight 0.15 g of the clay or clay-dye complex with 25 mL of a solution of NMH

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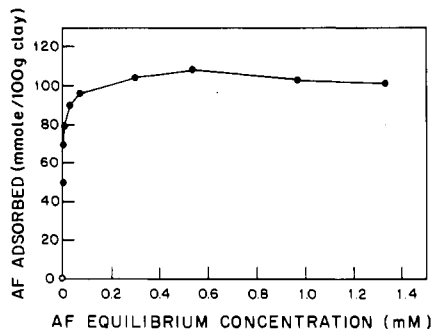


Figure 1. Adsorption isotherm from water of 3,6-diamino-10-methylacridinium (AF) on sodium montmorillonite.

in toluene in the appropriate concentration. After the precipitation of the clay, the concentration of NMH in the supernatant was measured by UV-vis spectrophotometry at 350 nm ($\epsilon = 25\,000\text{ M}^{-1}\text{ cm}^{-1}$).

Preparation of Clay-Organic Complexes. Samples of montmorillonite adsorbed with AF (Mont-AF) at concentrations of 20, 50, and 80 mmol of AF/100 g of clay were prepared by adding dropwise aliquots of a 1×10^{-2} M aqueous solution of the dye to a 0.5% w/w aqueous suspension of the clay under continuous stirring. After 30 min of centrifugation at 16000g, the precipitate was washed three times with distilled water, freeze-dried, and ground to $<50\ \mu\text{m}$. In all cases the adsorption was complete since no traces of the dye were present in the supernatant, as indicated by UV-vis spectroscopic measurements.

The clay complexes containing NMH were prepared by adsorbing the pesticide from toluene solutions as described above (under Adsorption Isotherms). After separation of the precipitated clay-organic complex, the samples were kept at reduced pressure until no traces of toluene could be detected by IR spectrophotometry.

Irradiation. For irradiation treatment, 5 mg of the powdered clay-organic complex was spread homogeneously on the bottom of Petri dishes (5 cm in diameter). To irradiate the free insecticide, NMH dissolved in methanol was applied to the Petri dish and the solvent subsequently evaporated. The NMH-AF mixture was prepared by evaporating a methanol solution of the two organic compounds. The samples were exposed to irradiation at 350 nm for various time periods by using a Rayonet RPR100 photochemical reactor. Dishes covered with aluminum foil served as controls. After irradiation, the samples were extracted with distilled water and the concentration of unreacted NMH was determined by high-performance liquid chromatography (HPLC) in a HP1090 instrument with a diode array detector and a Li-chrospher 100 RP18/10 μ (125 mm \times 4 mm i.d.) column: gradient elution, 30% methanol in water up to 100% methanol; 15 min; detection at 350 nm.

Spectroscopic and X-ray Powder Diffraction Measurements. UV-vis absorption spectra of aqueous solutions of NMH and AF and of aqueous suspensions of Mont-AF complexes were measured in a Uvikon 820 spectrophotometer. The complexes Mont-NMH and Mont-AF-NMH were measured by using a HP8451 diode array spectrophotometer.

Fourier transform infrared (FTIR) spectra of the pure compounds and of the complexes were measured in KBr pellets by using a Nicolet MX-S spectrophotometer interfaced to an Elite Star 16-bit PC and a Goerz SE 284 digital plotter.

X-ray powder diffraction measurements were carried out in a Philips PW-720 diffractometer using the Co K α line.

RESULTS AND DISCUSSION

The adsorption isotherm of AF to sodium montmorillonite is shown in Figure 1. The data presented indicate that for amounts of added dye less than or equal to the cation-exchange capacity (CEC) of montmorillonite (~ 80 mmol/100 g of clay) practically all the added dye was taken up by the clay. For larger amounts of added AF, the adsorption increases until a maximum of about 100 mmol/100 g of clay (i.e., 130% of the CEC) is reached.

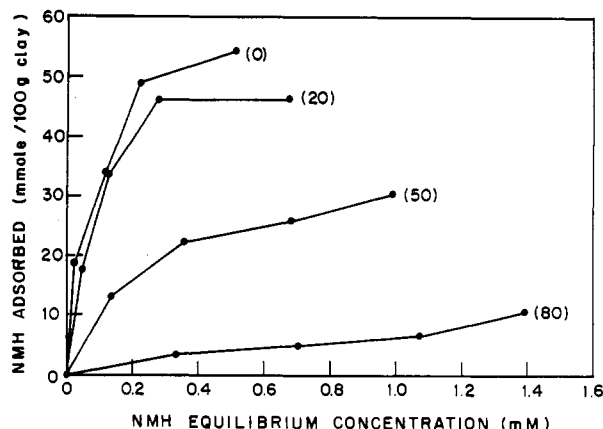


Figure 2. Adsorption isotherm from toluene of tetrahydro-2-(nitromethylene)-2H-1,3-thiazine (NMH) on complexes of montmorillonite and 3,6-diamino-10-methylacridinium (AF). Numbers in parentheses refer to the concentration of AF on the clay (in millimoles per 100 g of clay).

Such an adsorption beyond the CEC of the clay was shown to occur also with other organic cations (De et al., 1974; Margulies and Rozen, 1986; Narine and Guy, 1981) and a theoretical model describing this effect was previously reported (Margulies et al., 1988b).

In Figure 2 the results of the adsorption of NMH from toluene to montmorillonite and to Mont-AF complexes having different concentrations of AF are presented. The adsorption of the pesticide increases as its concentration in the equilibrium solution is increased. The adsorption decreases with increasing coverage of the clay surface by the organic cation.

A possible explanation for this result may be related to the molecular structure of the pesticide. Being a highly polar molecule, NMH strongly interacts with the hydrophilic surface of the mineral, either with the exchangeable inorganic cations or directly with the clay surface. As the mineral surface is covered by another large organic molecule it becomes more and more hydrophobic and, consequently, the NMH adsorption decreases. Such a partition of molecules between hydrophilic and hydrophobic adsorption sites at clay surfaces was previously observed by Mortland et al. (1986) and Boyd et al. (1988) for adsorption of phenol and chlorophenols to organo-clay complexes. When both the number of chlorine substituents in the phenol ring (which decreases its polarity) and the hydrophobicity of the complex increased, their adsorption from aqueous solutions became more significant.

Adsorption to clay surfaces considerably affects the stability of NMH to ultraviolet radiation. In Figure 3 the results obtained in a photochemical experiment aimed at evaluating different clays as potential photoprotectors of NMH are shown. When the pesticide was adsorbed to montmorillonite or nontronite, about 30% of the initial amount of NMH remained unreacted after 16 h of irradiation, whereas control samples of free NMH were almost completely degraded (5% recovery) following 1 h of exposure to the ultraviolet light. Some photostabilization was also observed in samples of NMH adsorbed on hectorite, although the degree of stabilization was lower than with the two other clays (only 5% recovery after 16 h of irradiation).

We have previously reported that the ultraviolet absorption of NMH adsorbed on montmorillonite was red-shifted as compared to the absorption of the free pesticide in aqueous solutions, indicating that the interactions of NMH molecules with the clay were stronger in the excited

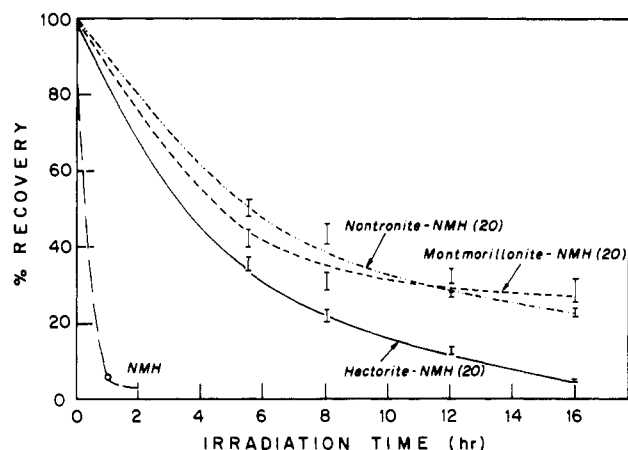


Figure 3. Photodegradation kinetics of tetrahydro-2-(nitromethylene)-2H-1,3-thiazine (NMH) adsorbed on different clays. Numbers in parentheses refer to the concentration of 3,6-diamino-10-methylacridinium (AF) on the clay (in millimoles per 100 g of clay).

Table I. Iron Content of Clay Samples

clay	% Fe ₂ O ₃
hectorite SHCa-1	0.26 ^a
sodium montmorillonite SWy-1	3.72 ^a
nontronite H-33a	29.46 ^b

^a Ben-Dor and Banin (1990). ^b Van Olphen and Fripiat (1979).

state than in the ground state (Margulies et al., 1988a). Such clay-NMH interactions are probably involved in the photostabilization observed for the three clay-NMH complexes shown in Figure 3. The lower degree of photostabilization obtained by using hectorite as compared to montmorillonite and nontronite might be related to their different contents of lattice iron (Table I). It is well documented that efficient charge-transfer processes can take place between adsorbed species and the structural iron ions. Using fluorescent probes, several authors have reported the observation of such processes for both inorganic (Bergaya and Van Damme, 1983) and organic (Habti et al., 1984; Krenske et al., 1980; DellaGuardia and Thomas, 1983; Schoonheydt et al., 1984) adsorbates. We suggest that charge-transfer processes between NMH molecules and lattice iron might be responsible for the enhanced photostabilization of the insecticide observed with montmorillonite and nontronite, whose iron concentrations are above a certain minimum. Similar conclusions were reached by Villemure et al. (1986) when studying the fluorescence behavior of methylviologen adsorbed on hectorite, montmorillonite, and nontronite.

A considerable improvement in the photostabilization of NMH was obtained when the cationic dye AF was coadsorbed to montmorillonite in two different concentrations (20 and 50 mmol/100 g of clay) while the concentration of the pesticide (20 mmol/100 g of clay) was kept constant (Figure 4). The two complexes gave similar results, although a slightly better stabilization can be observed for the sample with the higher AF:NMH ratio. In both cases, however, the recovery of unreacted pesticide after 12 h of irradiation was much higher (50–55%) than for samples without AF as protecting chromophore (30%).

The data obtained in this work are not sufficient for elucidating the details of the photostabilization mechanism. However, some general conclusions can be drawn. From the results obtained by using hectorite as adsorbent (Figure 3) it is clear that light scattering by the clay particles does not play an important role in the observed photostabilization. Also, the possibility of a trivial UV

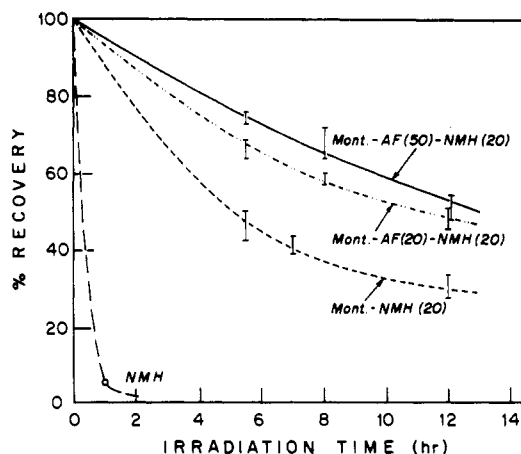


Figure 4. Photodegradation kinetics of tetrahydro-2-(nitromethylene)-2H-1,3-thiazine (NMH) adsorbed on complexes of montmorillonite and 3,6-diamino-10-methylacridinium (AF). Numbers in parentheses refer to the concentrations of the organic compounds on the clay (in millimoles per 100 g of clay).

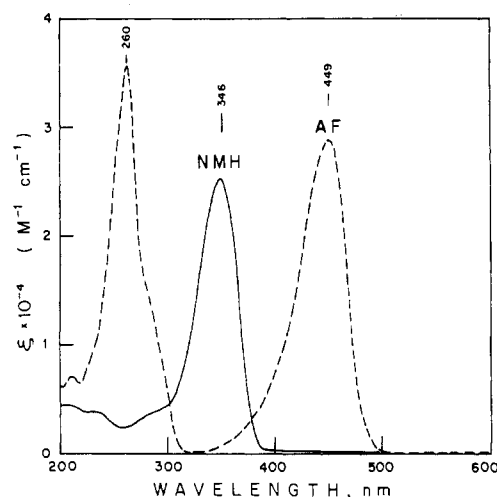


Figure 5. Electronic absorption spectra of tetrahydro-2-(nitromethylene)-2H-1,3-thiazine (NMH) and 3,6-diamino-10-methylacridinium (AF) in aqueous solutions.

screening effect by AF on NMH can be dismissed since the absorption intensity of AF at the irradiation wavelength (350 nm) is much lower than that of NMH (Figure 5). Moreover, increasing the dye concentration on the clay by a factor of 2.5 resulted in very little improvement of the recovery of NMH from the irradiated samples. Therefore, we believe that more specific interactions should be responsible for the observed photostabilization in the clay-organic system. The relative positions of the strong absorption bands of NMH and AF (Figure 5) are adequate (at least from energetic considerations) for a possible energy-transfer process between the two molecules. The efficiency of such a process could be enhanced on the surface of the clay, where the organic molecules are forced to adopt certain orientations. However, the possibility of other intermolecular deactivation mechanisms such as charge transfer cannot be excluded.

Some information on intermolecular interactions in the complexes of montmorillonite with AF and NMH was obtained by using UV-vis and FTIR spectroscopy. In Figure 6 the electronic absorption spectra of Mont-AF complexes dispersed in water with two different concentrations of adsorbed dye are presented. Pronounced differences are observed between the two spectra: two absorption maxima at 446 and 470 nm are measured for the low dye concentration complex (20 mmol/100 g of

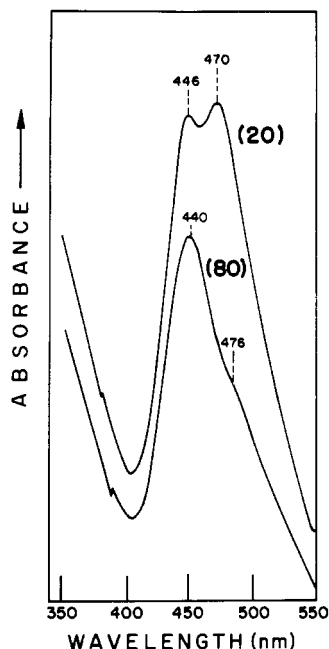


Figure 6. Electronic absorption spectra of complexes of montmorillonite and 3,6-diamino-10-methylacridinium (AF) in aqueous suspension. Numbers in parentheses refer to the concentration of AF on the clay (in millimoles per 100 g of clay). The increasing absorption toward wavelengths shorter than 400 nm is due to light scattering by the clay particles.

clay), whereas in the spectrum of the clay whose surface had been completely covered with the organic dye (80 mmol/100 g of clay) the relative intensities of the two bands are drastically changed, the longer wavelength band appearing only as a shoulder around 476 nm. The small differences in peak wavelengths between the two spectra are probably due to a different extent of overlap of the two bands. It is noteworthy that for aqueous solutions of AF the spectrum in this range (not shown) has a single absorption band whose wavelength ($\lambda_{\max} = 449$ nm) and intensity do not change when the concentration is increased by 2 orders of magnitude.

A small blue shift (~ 15 nm) of the NMH band was observed when the absorption spectrum of the pesticide incorporated in a Mont-AF-NMH complex (20 mmol of each AF and NMH/100 g of clay) was compared with the spectrum of the pesticide adsorbed on the clay in the absence of the cationic dye (Margulies et al., 1988a). This may indicate intermolecular interactions between the pesticide and the dye.

More details on the interactions at the surface of the clay were obtained by using vibrational spectroscopy. The FTIR spectra of AF adsorbed on montmorillonite and in its free state, in the 1150–1750- cm^{-1} range, are shown in Figure 7. We note the absence of a band which in the spectrum of the free dye appears at 1171 cm^{-1} and which corresponds to an in-plane bending vibration and the shift of the band at 1587 cm^{-1} which is assigned to a ring vibration (Nakanishi and Solomon, 1977).

The interactions between NMH and the clay surface as revealed from the FTIR spectra were discussed previously (Margulies et al., 1988a). The FTIR spectrum of a clay-organic complex containing both AF and NMH (20 mmol each/g of clay) showed a strong overlap between the absorption bands of AF, NMH, and water in the 1300–1700- cm^{-1} region. This made it difficult to detect small changes in the position and intensity of the bands corresponding to the different components of the complex as a result of the coadsorption. In the case of larger

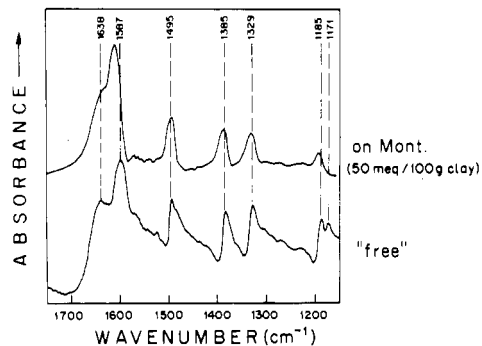


Figure 7. Fourier transform infrared absorption spectra of 3,6-diamino-10-methylacridinium (AF): free; adsorbed on montmorillonite (Mont) (after subtracting the spectrum of Mont).

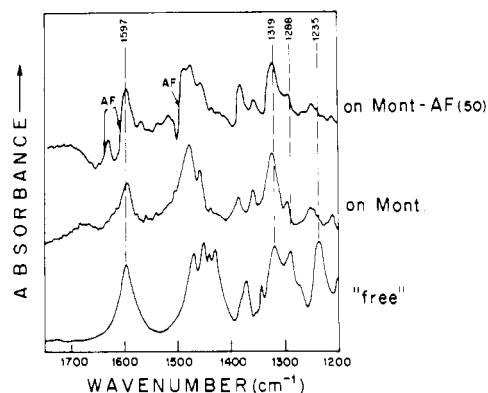


Figure 8. Fourier transform infrared absorption spectra of tetrahydro-2-(nitromethylene)-2H-1,3-thiazine (NMH): free; adsorbed on montmorillonite (Mont) (after subtracting the spectrum of Mont); adsorbed on a complex of montmorillonite and 3,6-diamino-10-methylacridinium (AF) (after subtracting the spectrum of Mont-AF). The concentrations of NMH and AF were 20 and 50 mmol/100 g of clay, respectively.

Table II. Basal Spacing of Clay Complexes

sample ^a	c spacing, Å	sample ^a	c spacing, Å
Mont	12.21	Mont-AF(20)-NMH(20)	13.50
Mont-NMH(20)	12.51	Mont-AF(50)	13.50
Mont-AF(20)	13.50	Mont-AF(50)-NMH(20)	14.25

^a Heated at 60 °C. Numbers in parentheses refer to the concentrations of NMH and AF on the clay (in millimoles per 100 g of clay).

concentrations of AF the NMH absorptions became almost completely masked by the strong absorption of the dye. To facilitate the analysis, difference spectra were obtained by subtracting from the spectra of the complexes containing NMH the spectra of the corresponding materials without NMH.

In Figure 8 the difference spectra of NMH adsorbed on Mont and Mont-AF are presented, together with the spectrum of NMH in its free state. Adsorption to the clays is revealed by the disappearance of the two strong bands at 1288 and 1235 cm^{-1} and the changes in positions and intensities of the peaks between 1350 and 1500 cm^{-1} . These spectral changes are observed in both Mont-NMH and Mont-AF-NMH, indicating that the interactions between the insecticide and the clay are similar in the two complexes. In addition, sharp discontinuities appear in the difference spectrum of NMH adsorbed on Mont-AF, at the position of the strong absorption bands of the dye (1495, 1610, and 1638 cm^{-1}). These discontinuities are the result of small shifts in the frequencies of the vibrations of AF upon coadsorption of NMH, indicating intermolecular interactions between the two organic molecules at the clay surface.

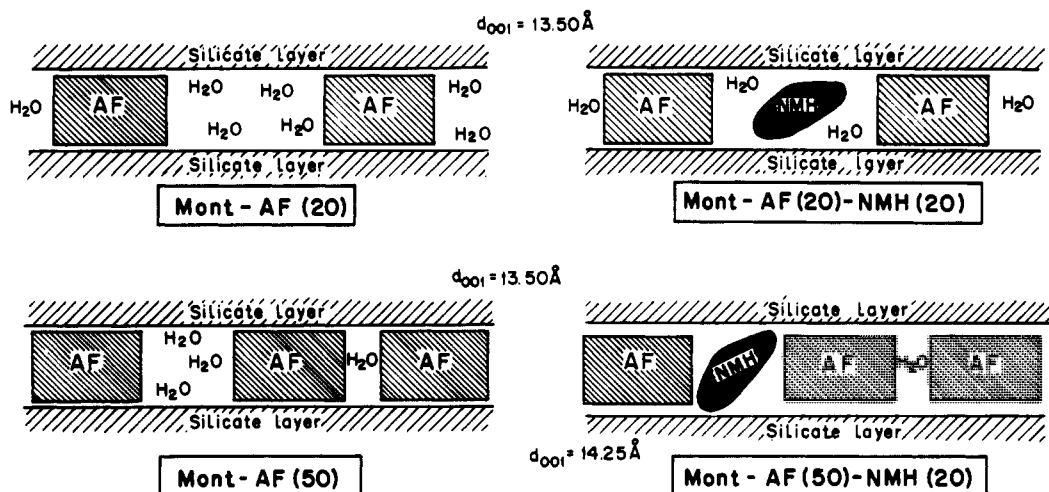


Figure 9. Schematic representation of the orientation of tetrahydro-2-(nitromethylene)-2H-1,3-thiazine (NMH) and 3,6-diamino-10-methylacridinium (AF) in the interlayer space of montmorillonite. Numbers in parentheses refer to the concentrations of NMH and AF on the clay (in millimoles per 100 g of clay).

It is worth noting that the FTIR absorptions corresponding to the symmetric and antisymmetric stretching of the nitro groups at 1319 and 1597 cm^{-1} , respectively (Nakanishi and Solomon, 1977; Pouchert, 1981), and the UV absorption spectrum of NMH are only slightly affected by adsorption of the pesticide to the clay (Margulies et al., 1988a). This suggests that the relative amounts of possible tautomers of NMH (including those having an endocyclic double bond) are not significantly changed upon adsorption.

The relative orientations of the adsorbed organic molecules play an important role in the efficiency of the deactivation process that occurs in the clay-organic system. Powder X-ray diffraction (XRD) is a powerful tool for elucidating the orientation of the organic molecules in the interlayer space (Lagaly, 1982). The basal spacing measured for the Mont-AF complexes containing either 20 or 50 mmol of AF/100 g of clay was 13.5 Å (Table II), indicating that the planar aromatic AF molecules are oriented parallel to the clay surface. If a perpendicular orientation was preferred, a much larger basal spacing would be observed. Addition of NMH to the Mont-AF-(20) complex does not modify the basal spacing, whereas in the case of higher dye concentration (50 mmol/100 g of clay) the basal spacing is increased by 0.75 Å. It is tempting to speculate that in the low dye concentration complex the NMH molecules are oriented with their ring parallel to the clay surface but when the surface is covered by larger amounts of dye, steric impediments force the pesticide molecules to become tilted with respect to the surface, thus increasing the basal spacing. A schematic representation of the molecular orientations in the interlayer space is shown in Figure 9.

It may be concluded that several factors contribute to the efficiency of the photostabilization of NMH incorporated in clay-organic complexes. Adsorption to clays containing a minimal concentration of lattice iron was found to slow down the photoinactivation, probably due to charge-transfer processes occurring between the insecticide molecules and the Fe^{3+} ions. When the cationic dye AF was coadsorbed, intermolecular interactions between it and the pesticide resulted in a considerable improvement of the photostabilization yield. As pointed out, the clay-NMH complexes retain their biological activity under sunlight exposure (Margulies et al., 1988a), but the possible application of these complexes in the field might be limited to low-humidity environments, due to

the high solubility of NMH in water. It is expected that the biological activity of many other photolabile pesticides can be extended by an appropriate choice of clays and chromophores. The clay is not merely a carrier but rather an active factor in the stabilization process.

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