

Ultraviolet Absorbers. The Protective Ability of Aromatic Nitro Compounds in Plasticized Poly(vinyl Chloride)

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Synopsis

Investigated were three types of aromatic nitro compounds: (a) a derivative of *o*-nitrophenol capable of forming an intramolecular hydrogen bond, (b) simple aromatic nitro compounds, and (c) the intramolecular charge transfer complexes, i.e., compounds incorporating in a single molecule the donor and the acceptor moieties, the latter substituted with the nitro groups. Samples of plasticized poly(vinyl chloride) were stabilized with these compounds and tested in an Atlas Weatherometer. The extent of degradation was determined by measuring the tensile strength, elongation, and the blue light reflectance before and after 270 and 500 hr of exposure. Samples without the stabilizers and samples containing 2,4-dihydroxybenzophenone were used as standards for comparison. Little protection was provided by simple nitro compounds. The derivative of *o*-nitrophenol and the donor-acceptor compounds were either better or comparable to 2,4-dihydroxybenzophenone in preserving the tensile strength and elongation. It appears that the protective ability of the derivative of *o*-nitrophenol was associated with the hydrogen-bonded six-membered ring whereas the protection rendered by the donor-acceptor compounds was determined by the extent of the contribution of the charge transfer states and the number of benzylic hydrogens capable of undergoing photochemical reactions. However, the mechanistic interpretation of the protective ability of the donor-acceptor compounds was complicated by the color changes occurring during the exposure.

INTRODUCTION

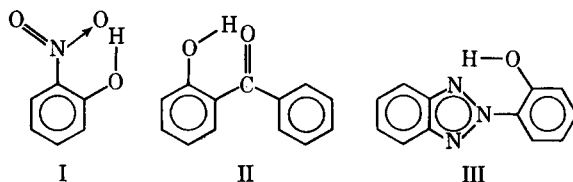
It is a common practice to protect organic matter from the light-induced degradation by incorporation of small quantities of "light stabilizers." We report the results of our investigation of such a protective ability of three types of aromatic nitro compounds.

The first investigated type represented a derivative of *o*-nitrophenol (I). It was related to a widely used class of light stabilizers, known as ultraviolet absorbers, and exemplified by various derivatives of 2-hydroxybenzophenone (II) and of 2-(2'-hydroxyphenyl)benzotriazole, (III).

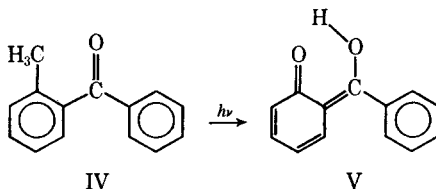
(The commonly used nomenclature in the field of stabilizers is based on the current understanding of the degradative mechanism. Degradation of organic matter is a multistep process that can be initiated either thermally

or by light, ultraviolet light in particular. Except for the specific initiation steps, the subsequent steps appear to be common for both types of degradation. Compounds that interfere with the specific light-induced step are called *light* or *ultraviolet stabilizers*, as opposed to *thermal stabilizers* and *antioxidants*. The light stabilizers either absorb light and efficiently convert it into thermal energy or they quench the active centers, produced by light, that otherwise would initiate the degradative sequence. Light stabilizers of the first type are commonly known as *light* or *ultraviolet absorbers* and for the second type the name *light protective agents* is frequently used.)

Compounds of types I, II, and III apparently can undergo a light-induced,



intramolecular and reversible hydrogen abstraction, analogous to the experimentally verified photoenolization of $IV \rightarrow V$,¹ that renders their excited states chemically inactive and presumably is related to a facile conversion of electronic excitation into thermal energy.



(The conversion of electronic excitation into thermal energy could proceed by a direct crossover from a higher electronic state to the isoenergetic level of a lower-lying electronic state or it could involve the intermediacy of a thermodynamically unstable isomer. Alternatively, other molecules, e.g., the impurities or the medium, could participate in the primary step of the conversion. By referring to "conversion of electronic excitation into thermal energy" we use the most general terminology devoid of any mechanistic implications.)

The second investigated type was represented by simple aromatic nitro compounds. It is well known that substitution of a fluorescent aromatic molecule with a nitro group quenches, as a rule, the fluorescence.²⁻⁴ It is conceivable that the nitro substituent provides the molecule with a new pathway for an efficient nonradiative transition. The parallelism between the quenching constants of fluorescence of pyrene and anthracene, and the electron affinities of the quenchers suggested that the charge transfer interaction plays an important part in the quenching mechanism.⁵ However, another mechanism also has been encountered. The absence of fluorescence in 5-nitro-8-quinolinol, in contrast to 8-quinolinol, has been attributed to

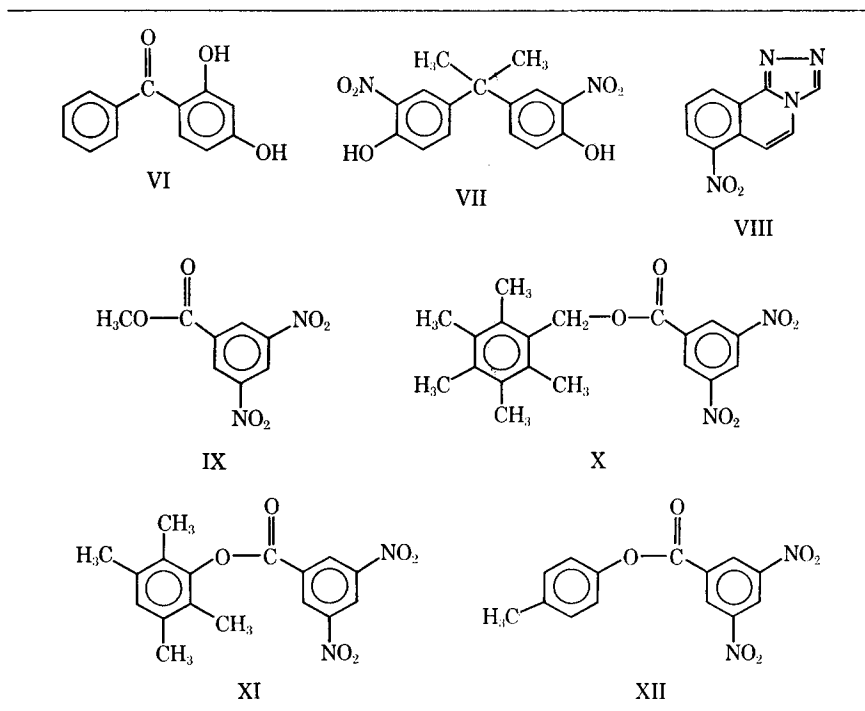
the increased acidity of the nitro compound in the excited state that prevented formation of the protonated fluorescent species.⁴

If this nonradiative transition could also effectively compete with the chemical reactions in the excited states, and with the photosensitization processes, then simple aromatic compounds should act as ultraviolet absorbers.

The third type was represented by *o*-dinitrobenzene that was linked to an aromatic ring substituted with electron-donating groups. Such donor-acceptor compounds were expected to present systems suitable for an intramolecular electron transfer⁶⁻¹⁰ and their selection was based on our study of photochemical reactions of the maleic anhydride-hexamethylbenzene charge transfer complex that suggested the presence of a deactivation mechanism efficiently competing with the formation of the products.¹¹ Since this mechanism presumably was a consequence of the donor-acceptor interaction it was interesting to test its value in protection of the organic matter from degradation. In order to increase the probability of this interaction, both moieties were incorporated in a single molecule.

The structures of the investigated compounds are given in Table I. They include the commercial ultraviolet absorber 2,4-dihydroxybenzophenone (Uvinul 400, GAF Corp.) that was used as a standard for com-

TABLE I
Investigated Compounds



parison. (The patent literature contains claims of 2-nitrophenol and its derivatives as light stabilizers,¹²⁻¹⁵ methyl 4-nitrobenzoate as a thermal stabilizer,²⁰ and various nitro compounds as light stabilizers,^{12-16, 19, 22, 24} thermal stabilizers,^{16, 17, 20-22} antioxidants,^{18, 24} and stabilizers in general.^{23, 25})

EXPERIMENTAL

The resin used in the tests consisted of pure poly(vinyl chloride) (100 g, Union Carbide Corp.), Flexol Plasticizer DOP (50 g, bis(2-ethylhexyl) phthalate, Union Carbide Corp.), thermal stabilizer Mark M (3.0 g, organic salts of barium and cadmium, Argus Chemical Corp.), and the investigated compounds. The latter, either obtained from the commercial sources or synthesized by the standard procedures, were carefully purified by repeated crystallizations and incorporated in the concentration approximating the ROC figures (vide infra). Parallel tests were performed with samples containing 2,4-dihydroxybenzophenone and without any light stabilizer.

The components were mixed under standardized conditions that included heating to 160°C for 10 min. The plaques of approximately 9-mil thickness were exposed in an Atlas XW Weatherometer. Their tensile strength, elongation, and the blue light reflectance were measured before and after 270 and 500 hr of exposure. Tensile strength and elongation were measured with a Model TM Instron apparatus (Instron Corp., Canton, Mass.), and the blue light reflectance was measured with a Photovolt Reflection Meter, Model 610 (Photovolt Corp., New York, N. Y.). The meter was equipped with a Wratten C-5 blue filter and adjusted to indicate 100% blue light reflectance from a white calibration surface. A carbon arc with a Corex D filter was used as the light source in the Weatherometer. Maximum emission occurred at 380 nm with the cut-off at about 280 nm. This differs from the energy distribution in the solar spectrum which is more flat, starts at about 290 nm, and reaches the maximum at about 500 nm.

For each investigated compound the "relative optimum concentration" (ROC) was determined indicating the amount, in weight units, that absorbed the same number of light quanta, in the region from 365 nm to the end of the long-wavelength absorption (about 400 nm), as one weight unit of 2,4-dihydroxybenzophenone:

$$\text{ROC} = \frac{I_b}{I_i} \times \frac{MW_i}{MW_b}$$

where I_b and I_i are the integrated absorption intensities, within the aforementioned limits, of 2,4-dihydroxybenzophenone and of the investigated compound, and MW_b and MW_i are the respective molecular weights. The limit of 365 nm was selected arbitrarily.

RESULTS AND DISCUSSION

The protective ability of ultraviolet absorbers depends on their absorbance and their efficiency in the conversion of electronic excitation into ther-

mal energy. The obviously advantageous separate evaluation of these two factors is difficult because under normal conditions the degradation is caused by polychromatic light whereas both the sensitivity of organic media to light and the absorbance of the protective agents are wavelength dependent. Thus, unless monochromatic light is used, the evaluation of the protective ability per one quantum of the absorbed light, rather than per unit weight of the incorporated absorber, requires knowledge of the energy distribution in the light source, the absorption spectrum of the protective agent, and the not easily accessible activation spectrum of the medium. Another complication would arise if the energy conversion were also wavelength dependent.

Our simplified procedure, that involved incorporation of the investigated compounds in concentrations approximating the ROC figures, was based on the assumption that the protective ability was principally determined by two factors: (a) the integrated absorption intensity in the long-wavelength region, and (b) the efficiency in the conversion of electronic excitation into thermal energy. Thus, by introducing corrections for variation in the long-wavelength absorbance, the experimental results were expected to give a measure of the conversion efficiency, provided that the absorbance remained constant during the exposure.

In Table II are listed the molecular weights, the ROC figures determined in cyclohexane, isopropyl alcohol, and, in four cases, in acetonitrile, and the concentrations at which the investigated compounds were actually incorporated. (Compound XI was insoluble in cold isopropyl alcohol yielding, on warming, a red solution probably indicative of the formation of a Mesenheimer type compound.^{26, 27}) The ROC figures for 2,4-dihydroxybenzophenone were taken as unity in all three solvents. However, the I_b figures in cyclohexane, isopropyl alcohol, and acetonitrile were related as 1.0:4.1:0.9, respectively. No data were available on the absorbance of the investigated compounds in plasticized poly(vinyl chloride). For this reason, the figures obtained in cyclohexane and in acetonitrile were taken as an approximate concentration guide.

The results obtained before the exposure were characterized by considerable dispersion but no effect of the amount of the added compound and of its nature was discernible. The arithmetic means and the standard deviations of the initial tensile strength and elongation were, respectively, 2810 ± 128 psi and $248 \pm 20\%$. These data are based on 155 samples that contained, in addition to the nitro compounds, other stabilizers not discussed in this report. Changes in tensile strength and elongation that occurred during the exposure are summarized in Table III.

Incorporation of 2,4-dihydroxybenzophenone (VI) at the 0.5 wt-% concentration level produced virtually no improvement in the deterioration in tensile strength and elongation, as compared with samples that contained no stabilizer. However, VI at the 1.0 wt-% level clearly demonstrated its good protective ability. A better preservation of tensile strength, after 270 and 500 hr of exposure, was obtained with compounds (the concentra-

TABLE II
Molecular Weight, Relative Optimum Concentration in Cyclohexane, Isopropyl Alcohol,
and Acetonitrile, and Concentration at which the Compounds were Incorporated in Poly(vinyl Chloride)

Compd.	Name	Mol wt	Rel. Opt. Concn.				
			C ₆ H ₁₂	i-PrOH	CH ₃ CN	Concn in PVC, wt-%	
VI	2,4-dihydroxybenzophenone	214.21	1.00	1.00	1.00	0.5	1.0
VII	2,2-bis(3'-nitro-4'-hydroxyphenyl)propane	318.28	0.062	0.24	—	0.3	1.0
VIII	s-triazolo[3,4-a]-6-nitroquinoline	201.16	insol.	0.58	—	—	1.0
IX	methyl 3,5-dinitrobenzoate	226.14	3.1	11.5	2.6	—	2.0
X	pentamethylbenzyl 3,5-dinitrobenzoate	372.37	3.6	insol	—	—	3.5
XI	2,3,5,6-tetramethylphenyl 3,5-dinitrobenzoate	344.31	—	—	2.0	1.0	2.0
XII	4-methoxyphenyl 3,5-dinitrobenzoate	318.24	insol	insol	2.1	1.0	2.0

TABLE III
Changes in Tensile Strength and Elongation of Plasticized Poly(vinyl Chloride) with
and without the Investigated Compounds after 270 and 500 Hours of Exposure in an Atlas XW Weatherometer^a

			Tensile strength, psi						Elongation, %					
			270 hr			500 hr			270 hr			500 hr		
Compd	Concn	Change	Compd	Concn	Change	Compd	Concn	Change	Compd	Concn	Change	Compd	Concn	Change
VII	1.0	-60	XII	2.0	-110	VII	1.0	-14	XII	2.0	-3			
XII	2.0	-130	VII	1.0	-190	X	3.5	-15	X	3.5	-40			
X	3.5	-320	VI	1.0	-410	XII	1.0	-17	XI	2.0	-40			
VI	1.0	-350	X	3.5	-430	VII	0.3	-32	VI	1.0	-43			
VII	0.3	-360	VII	0.3	-540	VI	1.0	-33	VII	1.0	-44			
XII	1.0	-520	XI	2.0	-650	VIII	1.0	-48	VII	0.3	-52			
VIII	1.0	-530	XII	1.0	-730	XII	2.0	-53	XII	1.0	-67			
XI	2.0	-580	IX	2.0	-980	IX	2.0	-62	XI	1.0	-114			
IX	2.0	-700	XI	1.0	-1000	XI	2.0	-76	IX	2.0	-135			
XI	1.0	-90	VIII	1.0	-1050	VI	0.5	-76	VI	0.5	-157			
—	0	-1030	VI	0.5	-1600	XI	1.0	-90	VIII	1.0	-158			
VI	0.5	-1100	—	0	-1790	—	0	-123	—	0	-187			
—	0	-1430	—	0	-1920	—	0	-193	—	0	-231			

^a Concentrations of compounds expressed in wt-%.

tions are given in the parentheses) XII (2.0) and VII (1.0), virtually the same with X (3.5) and VII (0.3), and a somewhat worse with XI (2.0) and XII (1.0). The remaining compounds represented a gradually declining quality. Changes in elongation after 270 hr of exposure followed a continuous sequence, but changes after 500 hr permitted separation of the com-

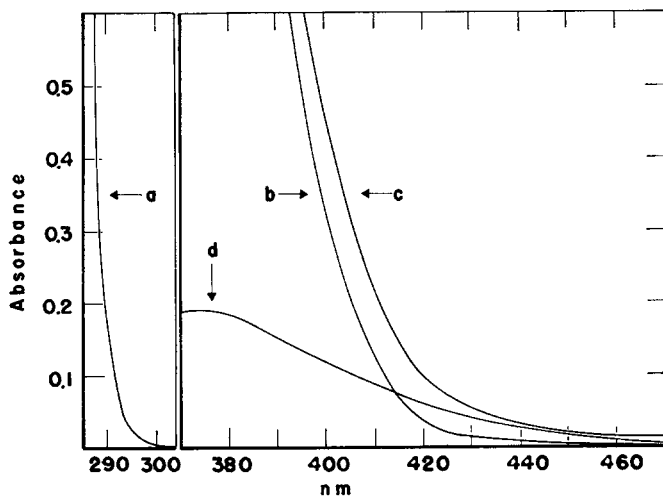


Fig. 1. Ultraviolet spectra in acetonitrile, 5-cm cell length: (a) hexamethylbenzene, 6.08 mM, acetonitrile in the reference cell; (b) methyl 3,5-dinitrobenzoate (IX), 6.10 mM, acetonitrile in the reference cell; (c) mixture of hexamethylbenzene, 6.08 mM, and of IX, 6.10 mM, acetonitrile in the reference cell; (d) mixture of hexamethylbenzene, 6.08 mM, and of IX, 6.10 mM, a solution of IX, 6.10 mM, in the reference cell.

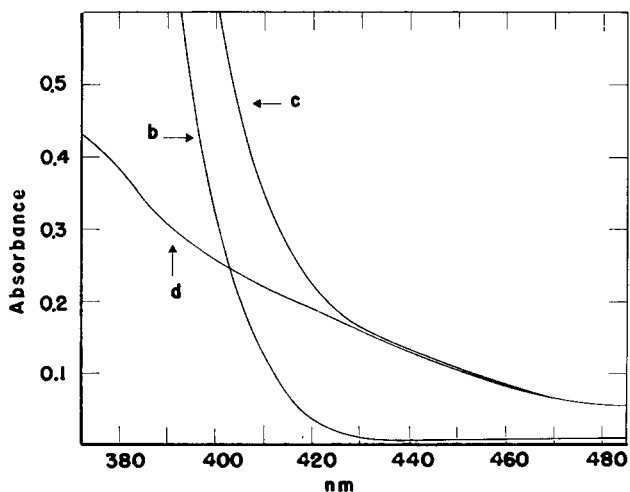


Fig. 2. Ultraviolet spectra in acetonitrile, 5-cm cell length: (b) methyl 3,5-dinitrobenzoate (IX), 6.10 mM, acetonitrile in the reference cell; (c) 2,3,5,6-tetramethylphenyl 3,5-dinitrobenzoate (XI), 6.08 mM, acetonitrile in the reference cell; (d) XI, 6.08 mM, a solution of IX, 6.10 mM, in the reference cell.

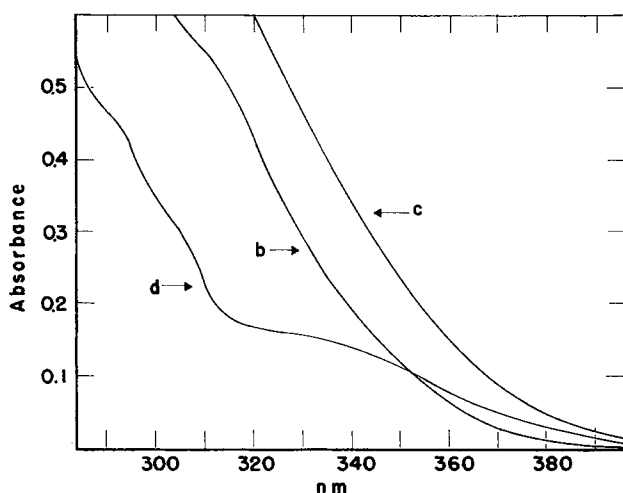


Fig. 3. Ultraviolet spectra in acetonitrile, 1.0-mm cell length: (b) methyl 3,5-dinitrobenzoate (IX), 6.12 mM, acetonitrile in the reference cell; (c) 4-methoxyphenyl 3,5-dinitrobenzoate (XII), 6.11 mM, acetonitrile in the reference cell; (d) XII, 6.11 mM, a solution of IX, 6.12 mM, in the reference cell.

pounds into three groups. Compound XII (2.0) again performed better than VI (1.0). Virtually the same results as with VI (1.0) were given by VII (1.0), VII (0.3), X (3.5), XI (2.0), and XII (1.0). The rest of the compounds were worse than VI (1.0).

The good protective ability of VII and VI confirmed our expectation that a hydrogen-bonded six-membered ring represents a system capable of an efficient conversion of electronic excitation into thermal energy. (This observation, and other of our results not discussed here, illustrate the uniqueness²⁸ of the six-membered rings. The analogous five-membered rings, e.g., in tropolone, do not protect organic matter from the detrimental effects of light.) Better results obtained with VII (0.1) than with VI (1.0) in preserving the tensile strength can be explained by the difference in the ROC figures. At equal concentration, VII absorbs more light than VI.

The results obtained with X, XI, and XII clearly indicate the good protective ability of the intramolecular charge transfer complexes. Aside from the concentration effect, the variation in the results can be explained by the concurrence of the two opposing factors: (a) the contribution of the charge transfer states, determined by the proximity and conformation of the acceptor and the donor, as well as the ionization potential of the latter, and (b) the number of benzylic hydrogens capable of undergoing photochemical reactions.

The occurrence of the charge transfer interaction is demonstrated in Figures 1 to 3. Figure 1 illustrates the spectrum of a typical donor (hexamethylbenzene), an acceptor (compound IX), and their equimolar mixture. The donor has virtually no absorption above 300 nm, but its addition to the

acceptor results in a red shift, apparently by a formation of a charge transfer complex. By placing a solution of the acceptor in the reference cell of the spectrophotometer and a mixture of the donor and the acceptor of the same concentration in the measuring cell, an approximate spectrum of the complex was obtained (Fig. 1, curve *d*). (Since the concentration of the *free* acceptor in the measuring cell was lower than the concentration of the acceptor in the reference cell, the recorded absorbance of the complex was lower than the actual values.) Comparison of this spectrum with an analogous spectrum of XI (Fig. 2, curve *d*) indicates the expected substantial increase in the absorbance of the intramolecular complex. Even a greater increase is observed in the spectrum of XII (Fig. 3, curve *d*; note a 50-fold decrease in the cell length).

By analogy to the photochemical reactions of the maleic anhydride-hexamethylbenzene charge transfer complex,¹¹ the benzylic hydrogens could either participate in the rearrangement of X and XI to some new species or they could serve as centers initiating the degradation of poly(vinyl chloride).

The protective ability of the intramolecular charge transfer complexes cannot be ascribed to the presence of the nitro substituents or the donor moiety per se. This is evidenced by the relatively poor results obtained with the simple nitro compounds VIII and IX and no absorption of light by the free donors above 300 nm.

Unfortunately the development of color during the exposure does not permit to make a clear separation between the effect of the increased absorbance and the efficiency in the energy conversion. The measurements of the blue light reflectance, although somewhat uncertain because of the usually nonuniform distribution of color, confirmed the visual observation that before the exposure only the samples containing VII and VIII had a slight amber-like appearance. After 500 hr in the Weatherometer, all samples, except for those with VI and one sample without the stabilizer, developed yellow color of varying intensity. However, no correlation between the blue light reflectance and the preservation of tensile strength and elongation was noted.

The development of color represents certain limitation in practical applications of the investigated compounds and suggests the advisability of a study of other donor-acceptor systems with different electron-withdrawing substituents replacing the nitro group.

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