

The Photochemical Ionization of the Triarylmethane Leuconitriles

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Abstract: Upon irradiation in ethanol, the triarylmethane leuconitriles generally undergo a heterolytic cleavage to form dye cation and cyanide ion. The absorption and emission spectra have been obtained for a series of these leuconitriles along with the quantum yields of the cleavage. Complete transfer of the excitation energy to the methylene-insulated chromophore with the lowest singlet energy leading to the photoionization (cleavage) with varying degrees of efficiency was observed. Whether the excited molecule photoionizes, fluoresces, or decays to its ground state is dependent on the nature of the particular excited singlet state. The efficiency of the photoionization is reduced either with chromophores which competitively undergo intersystem crossing, such as the halogen-, carbonyl-, or nitro-substituted leuconitriles, or with those which exhibit increased fluorescence, such as the naphthyl-substituted leuconitrile.

The use of Malachite Green Leuconitrile **2a** (MGLN) as an actinometer is well established.^{1,2} Its use for this purpose depends upon a photoionization, which occurs with high quantum efficiency in polar solution forming a highly colored dye cation (**2b**). This photochemical reaction takes place throughout the entire spectral absorption range of the compound,³ independent of light intensity⁴ and temperature.⁵ For these reasons, this leuconitrile provides a sensitive molecular system easily adapted for making actinometric measurements, especially at low light intensities. Although numerous studies of the photochromism of the triarylmethane leuconitriles have been reported, a photochemical mechanism for the photocoloration reaction has yet to be postulated. Toward this end, we have measured the spectra and photoionization efficiencies for a series of substituted triarylmethanes (**1-14**). The compounds selected have the same skeletal structure, and thus lend themselves to the study of structure-activity relationships. It was also anticipated that elucidation of the pertinent photochemistry might lead to compounds useful as actinometers into the visible region of the spectrum.

The quantum yield of photoionization (φ_c) in ethanol for

the leuconitrile derivatives of the triarylmethane dye cations can be measured using a solution of Malachite Green Leuconitrile (**2a**) as the actinometric reference. The value for the quantum efficiency of this photoionization has been reported most recently at 0.91,² compared with the earlier reported value at 1.00.¹ Since this difference is due to an error in the value used earlier for the extinction coefficient of the dye form, the use of the more recent value of 0.91 in our work did not affect our results.

Results

Preparation of the Triarylmethane Dyes and Leuconitriles. The substituted Malachite Green dyes were prepared either by the addition of the appropriate aryllithium⁷ or sodium^{8a} salt to Michler's ketone, or by the condensation of the appropriately substituted benzaldehyde with *N,N*-dimethylaniline to give the dye leucobase, which was then oxidized with excess chloranil to give the desired dye.⁶ For most of the compounds studied, the carbinol produced by either route was then recrystallized until the melting point, and the extinction coefficient of the dye form in the visible spectrum remained unchanged. The conversion of the dye

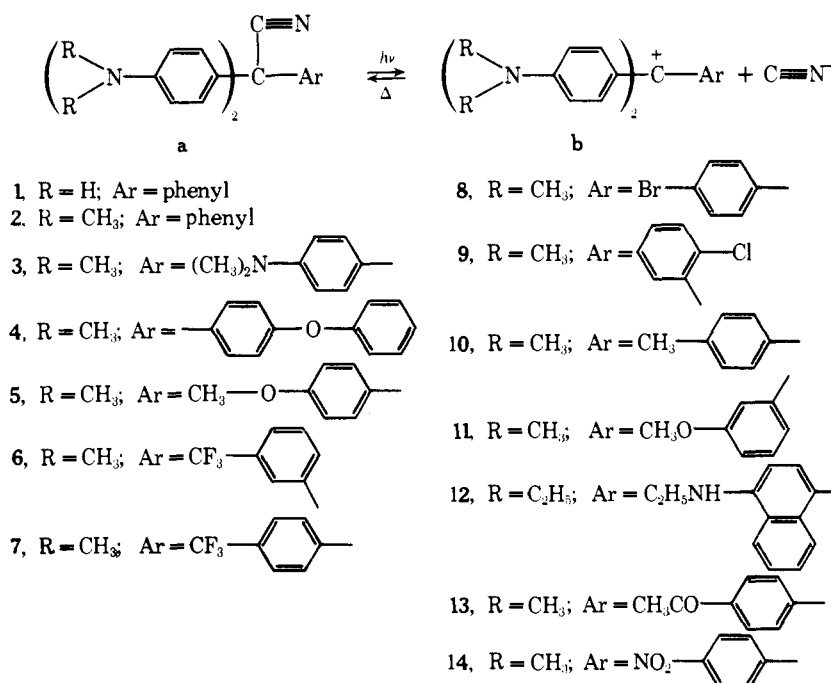


Table I. Uv-Visible Absorption in 95% Ethanol

Triarylmethane		Leuconitrile ($\epsilon \times 10^{-4}$)	Dye cation ($\epsilon \times 10^{-4}$)
Doebner's Violet	(1)	251 (2.54), 292 (0.355)	564 (10.2), 400 (2.35) ^d
Malachite Green	(2)	272 (4.06), 307 (0.538)	622 (10.63), 428 (2.08) ^b
Crystal Violet	(3)	272 (6.12), 305 (0.835)	589 (11.3), ^d 590 (11.) ^c
<i>p</i> -Phenoxy-MG	(4)	272 (4.73), 304 (0.628)	616 (10.3), 455 (3.08) ^a
<i>p</i> -Methoxy-MG	(5)	270 (3.88), 303 (0.514)	610.5 (9.89), 464 (2.90) ^a
<i>m</i> -Trifluoromethyl-MG	(6)	272 (3.67), 308 (0.585)	634 (9.66), 423.8 (1.57) ^e
<i>p</i> -Trifluoromethyl-MG	(7)	271 (3.73), 308 (0.656)	636 (9.93), 423 (1.60) ^a
<i>p</i> -Bromo-MG	(8)	272 (3.44), 308 (0.505)	628.5 (10.1), 433 (2.15) ^a 628.5 (10.2), 433 (2.28) ^e
<i>o</i> -Chloro-MG	(9)	272 (3.80), 307 (0.543)	640 (12.6), 410 (1.84) ^d
<i>p</i> -Methyl-MG	(10)	272 (3.64), 304 (0.509)	618 (10.6), 438 (2.74) ^a
<i>m</i> -Methoxy-MG	(11)	272 (4.28), 299 (0.611)	637 (9.89), 434 (1.47) ^a
Basic Blue 7	(12)	267 (s, 4.49), 275 (4.64), 324 (1.38) 259 (1.92), 341 (1.08)	586 (14.7) ^d
<i>p</i> -Acetyl-MG	(13)	273 (3.93), 308 (0.847)	629 (9.31), 432 (2.16) ^a
<i>p</i> -Nitro-MG	(14)	271.5 (4.97), 309 (0.731) 351 (0.159)	646 (7.88), 428 (1.61) ^a

^a By acidification of the leuocarbinol. ^b From ref 2. ^c From A. MacLachlan, *J. Phys. Chem.* 71, 718 (1967); L. Michaelis and S. Granick, *J. Am. Chem. Soc.* 67, 1212 (1945). ^d By irradiation of leuconitrile. ^e By chloranil oxidation.

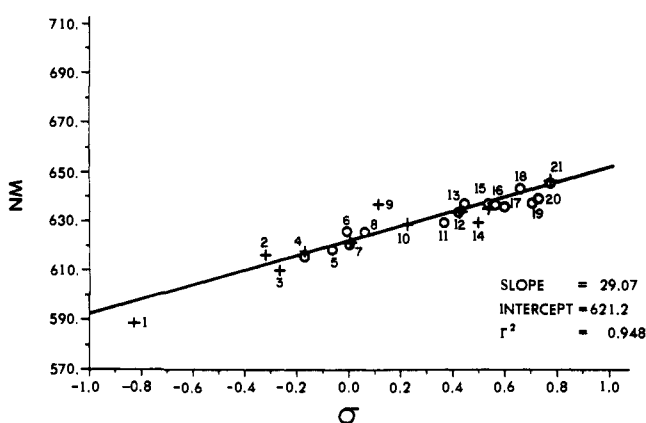


Figure 1. A plot of Hammett σ against ν_{\max} for the substituted Malachite Green dyes from this work (+) and from other work⁷ (O). The substitution as numbered in the figure are: (1) *p*-N(CH₃)₂; (2) *p*-PhO-, (3) *p*-CH₃O; (4) *p*-CH₃; (5) *m*-CH₃; (6) *p*-Ph; (7) H; (8) *m*-Ph; (9) *m*-CH₃O; (10) *p*-Br; (11) *m*-CO₂CH₃; (12) *m*-CF₃; (13) *p*-CO₂CH₃; (14) *p*-CH₃CO; (15) *p*-CF₃; (16) *m*-CN; (17) *m*-SO₂CH₃; (18) *p*-CN; (19) *m*-NO₂; (20) *p*-SO₂CH₃; (21) *p*-NO₂.

leuocarbinols to their leuconitriles was carried out in dimethyl sulfoxide containing excess potassium cyanide.⁹

Spectral Characterization of the Triarylmethane Dyes. Since the dye form of the compounds could be purified only with extreme difficulty, it was necessary to use one of three alternative methods to obtain accurate values for the extinction coefficients of the carbocations. The most straightforward technique involved the conversion of the dye leuocarbinol to its cation by treatment with a slight excess of hydrochloric acid. In the one case where the pure carbinol was not available (i.e., *m*-CF₃, 6) and the pure triphenylmethane could be quantitatively converted to the dye cation,¹⁰ a chloranil oxidation reaction solution was assumed to contain the desired pure cation and was used to determine the extinction coefficient. In both these methods, the initial solutions were diluted further and the absorbances were measured to demonstrate conformation of these dyes to Beer's law under the conditions of this study and to permit calculation of extinction coefficients from these linear regression lines.

For those dyes which could be best purified by conversion to their leuconitrile [i.e., Doebner's Violet (DV) (1); Basic Blue 7 (BB7) (12); and the *o*-Cl dye Rhoduline Blue (9)], it was necessary to use the irradiation technique of Fisher.² The absorption peaks found and extinction coefficients calculated for the entire series of dyes in ethanol are given in

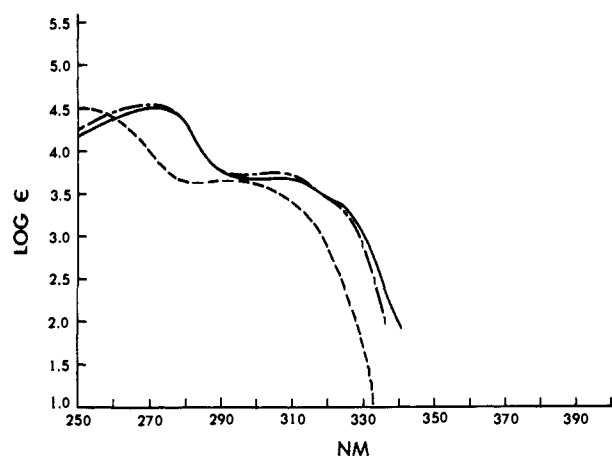


Figure 2. The ultraviolet spectra of the leuconitriles of (---) Doebner's Violet; (—) *p*-CH₃ Malachite Green, and (- · - ·), Malachite Green.

Table I. Our values for the intensities of the major absorption bands (the "x" bands) are in very good agreement with the extinction coefficients found by Ritchie⁶ in methanol and by Hallas et al.^{7,12} in acetic acid.

As anticipated from the earlier work,^{6,7,11} the wavelengths of the maximum absorption peaks in the visible spectrum have been found to correlate well with the Hammett substituent constants. Our results support the generality of these findings and extend the range of results well into the region of electron donating substituents. These results measured in acidified 95% ethanol are shown in Figure 1, along with the earlier results measured in 98% acetic acid.⁷

Spectral Characteristics of the Triarylmethane Leuconitriles. Since the triarylmethane leuconitriles are composed of three separate aryl moieties separated by a central insulating carbon atom, their ultraviolet spectra resemble the sum of the spectra of the individual aryl chromophores²⁸ (see Figures 2-6 and Table I). The leuconitrile compounds which were studied contain the equivalent of two toluidine rings and a third aromatic ring system. The third ring in most cases is substituted with a group that is not a strong auxochrome and its effect on the phenyl absorption is hidden by the amine chromophore. It is important to note that, as a result, most of the compounds have spectra almost identical with those of the leuconitrile of Malachite Green.

The three exceptions are those leuconitriles which have chromophores that absorb in the near ultraviolet region

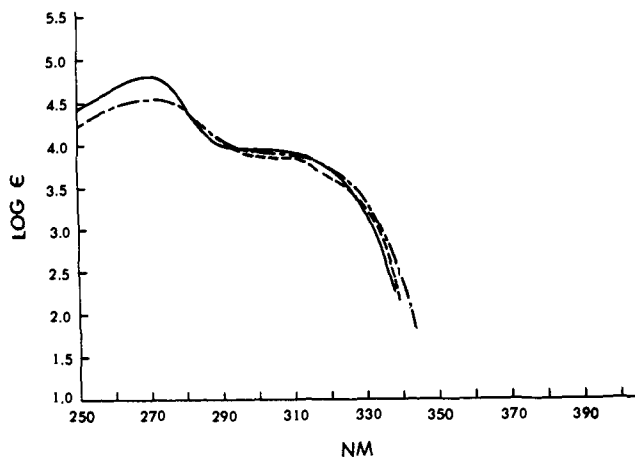


Figure 3. The ultraviolet spectra of the leuconitriles of (---) *m*-CF₃ and (- - - -) *p*-CF₃ Malachite Green; and (—) Crystal Violet.

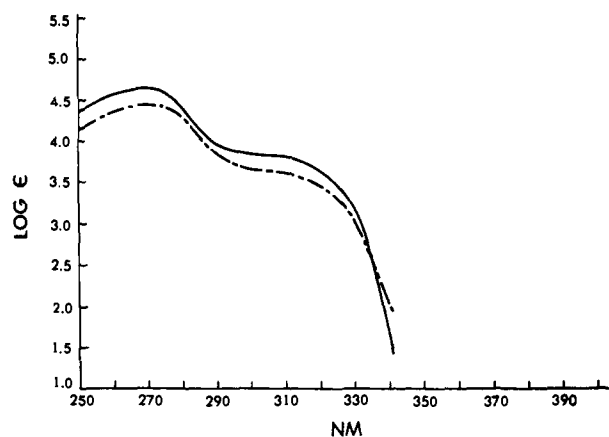


Figure 4. The ultraviolet spectra of the leuconitriles of (—) *p*-Br and (- - - -) *o*-Cl Malachite Green.

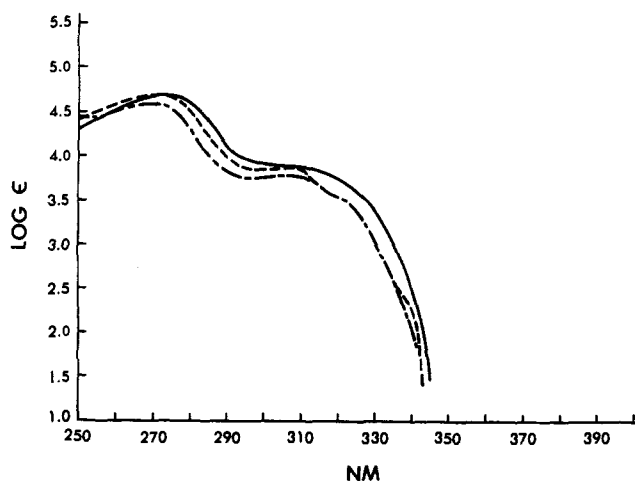


Figure 5. The ultraviolet spectrum of the leuconitriles of (- - - -) *p*-CH₃O; (- . - .) *p*-PhO; and (—) *m*-CH₃O Malachite Green.

(i.e., aminonaphthyl in **12a**, acetylphenyl in **13a**, and nitrophenyl in **14a**) and exhibit absorption bands attributable to the $n-\pi^*$ transition of these chromophores as well as the shorter wavelength absorptions attributable to the arylamine chromophore (Figure 6).

Similarly, the emission spectra of the leuconitrile compounds both at room temperature and at 77 K are characteristic of that insulated aromatic ring system in each molecule having the lowest singlet and triplet excited state energies. This can be seen in Figures 7–13 and in Table II in

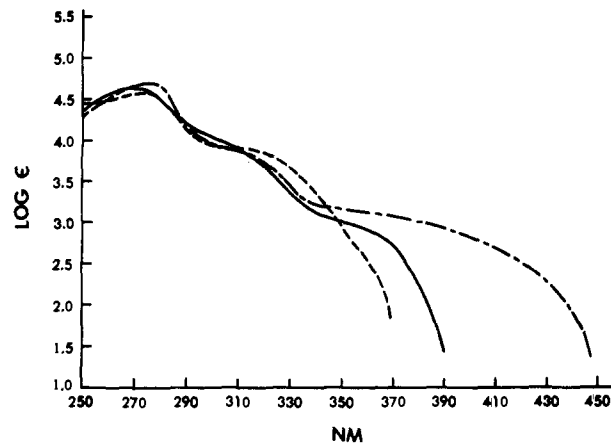


Figure 6. The ultraviolet spectra of the leuconitriles of (- - -) *p*-CH₃CO and (- . - .) *p*-NO₂ Malachite Green and (—) Basic Blue 7.

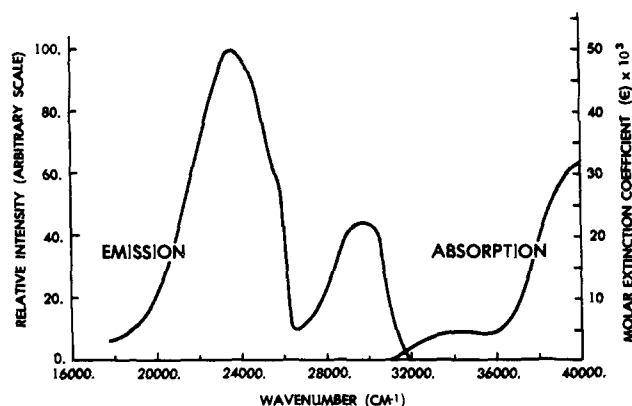


Figure 7. Absorption and emission spectra of the leuconitrile of Doebner's Violet (**1a**) in ethanol.

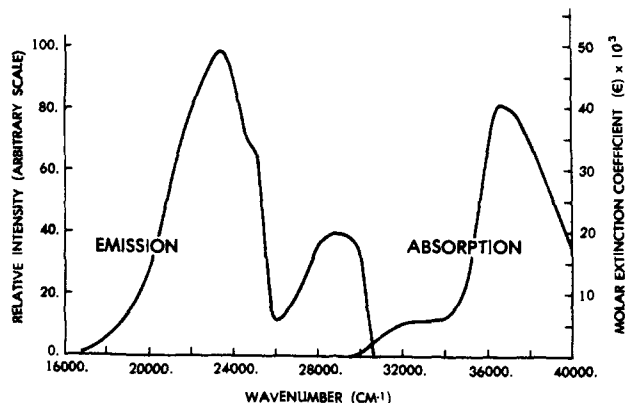


Figure 8. Absorption and emission spectra of the leuconitrile of Malachite Green (**2a**) in ethanol.

which are listed the emission characteristics for the leuconitriles, for similar substituted aromatic compounds of simpler structure, and also for the triphenylmethane analogs of Malachite Green and Doebner's Violet.

Thus, the room temperature emission for most of the leuconitriles and the model compounds is due to the phenylamine moiety and is found between 340 and 360 nm. However, those leuconitriles containing the naphthylamine, the nitrophenyl, and the acetophenyl chromophores have lower singlet and triplet excited state energies than do the anilines. Consequently, the emission of BB7 (**14a**) is similar to that of naphthylamine. The leuconitriles with the nitro or carbonyl substituents do not emit at room temperature, as is typical of their simpler analogs. The efficiencies of luminescence (ϕ_c) measured at room temperature are lower than

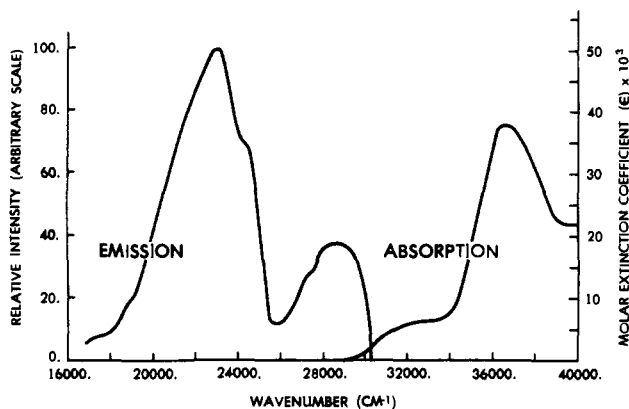


Figure 9. Absorption and emission spectra of the leuconitrile of *m*-methoxy Malachite Green (11a) in ethanol.

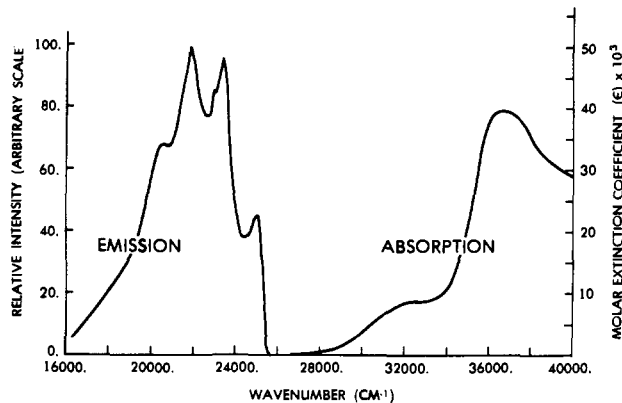


Figure 12. Absorption and emission spectra of the leuconitrile of *p*-acetyl Malachite Green (13a) in ethanol.

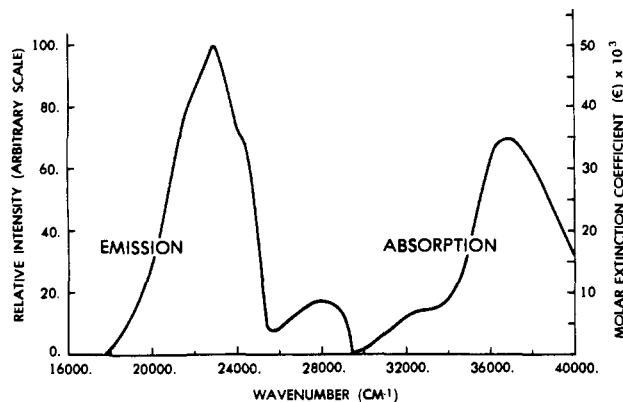


Figure 10. Absorption and emission spectra of the leuconitrile of *p*-CF₃ Malachite Green (7a) in ethanol.

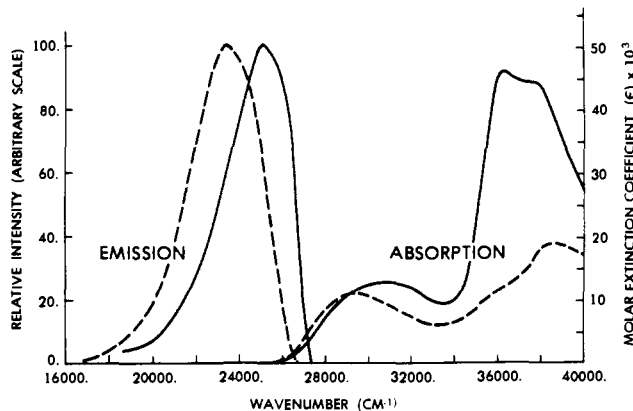


Figure 13. Absorption and emission spectra of the leuconitrile of Basic Blue 7 (12a) in ethanol. Emission at RT (---) and at 77 K (—); absorption in neutral (—) and in acidified (---) solution.

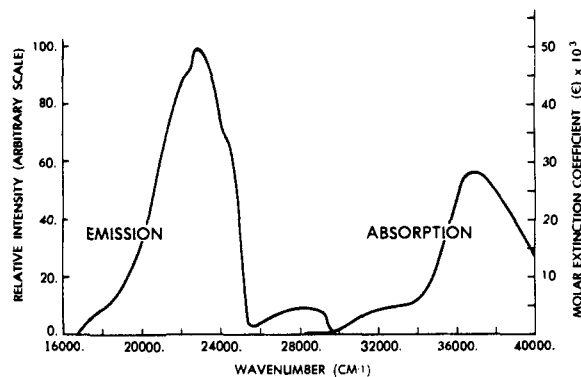


Figure 11. Absorption and emission spectra of the leuconitrile of *p*-B Malachite Green (8a) in ethanol.

the values found for the model compounds, except in the case of the leuconitrile of Basic Blue 7 (12a). The fact that φ_c was considerably reduced in most cases indicated the existence of other routes for the dissipation of the absorbed energy, especially the photoionization reaction.

At room temperature, the photochemical effect of ultraviolet light on the triarylmethane leuconitriles caused decreases in the intensity of fluorescence and, in some cases, caused an enhanced emission at longer wavelengths. The latter emission may reasonably be attributed to a photochemical product, most likely the dye cation which converts back to leuconitrile at a very slow rate^{13,14} without an excess of cyanide ion present. When a small amount of potassium cyanide was present in the solutions used for emission studies, the intensity of the spectra did not significantly change during the time interval of a measurement, and reproducible results could be obtained.

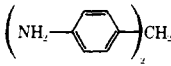
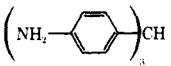
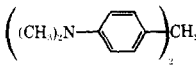
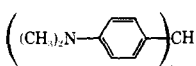
The emission spectra at 77 K in deoxygenated solutions demonstrate that the phosphorescence emission is due to the chromophore with the lowest triplet excited state energy. Data on the measured phosphorescence spectra, such as spectral distribution, observed phosphorescence decay time (τ_p), and intersystem crossing ratio (the intensity of phosphorescence relative to the intensity of fluorescence, χ) are collected in Table II.

For those compounds which do not have a strong auxochrome on the third ring, the phosphorescence emission is characteristic of the π, π^* triplet state of the aminophenyl moiety; this can be seen by comparing (Table II) data reported for the anilines and the Malachite Green derivatives²⁷ and the results found here for the model compounds (i.e., the methylene dianilines and the leucobase).

In all these compounds, as can be seen in Figures 7–11, the spectral shape and distribution ($E_1 = 74$ kcal) and the observed phosphorescence decay time ($\tau_p = 2$ sec) are characteristic of the lowest triplet (3L_a) of the toluidine moiety. The more sensitive intersystem crossing ratio (χ) also shows excellent consistency for these compounds. The small variations in χ seen with compounds substituted by halogen-containing groups appear to illustrate the molecular heavy atom effect on emission. Substitution on the third ring of the leuconitriles with a chlorine atom or the trifluoromethyl group doubles the observed ratio, while the presence of a bromine atom quadruples the ratio, with a concurrent decrease in τ_p .

Those three compounds with a longer wavelength chromophore as the third aromatic group must again be considered separately. The leuconitrile of Basic Blue 7 (12a) has a large emission efficiency ($\varphi_c = 0.62$) but does not phosphoresce even at liquid nitrogen temperature ($\chi = 0$). The ob-

Table II

Compd	Solvent	T, K	Fluorescence		Phosphorescence		
			$h\nu_f$	φ_e	χ	$h\nu_p$	τ_p , sec
Aniline	EtOH	RT	296, ^e 338 ^c	0.3–0.6 ^c			
	Cyclohexane	RT	327 ^a	0.8 ^a		373 ^{c,e}	4.7 ^f
	EPA	77	340 ^d			373, ^b 387, 400	
<i>N,N</i> -Dimethylaniline	EtOH	RT	344, ^d 348 ^a			416 (max) ^d	
	Cyclohexane	RT	333 ^a	0.11			
<i>N,N</i> -Dimethyl- <i>p</i> -toluidine	3-Methylpentane	77					2.6 ^g
	EPA	77		0.7, ^h	<i>h</i>	473 ^b	0.20 ^h
Nitrobenzene	EtOH	RT	291 ^a				
Anisole	Cyclohexane	RT	289, ^a 278 ^e	0.24 ^e		354 ^e	3.0 ^e
	Polar	RT	325, 339, ^a 317 ^e	0.25, ^a 0.21 ^e		480 ^e	
1-Methylnaphthalene	EtOH	RT	429 ^a				
1-Naphthylamine	Cyclohexane	RT	375	0.46 ^a			
	EPA	77				497.5, ^b 526 ^e	1.5 ^e
	3-Methylpentane	77					2.03 ^g
Malachite Green Leucocarbinol 	MCH	RT	332, 342				
		77	348		0.38	390, 414, 444	1.90
	MCH	RT	330				
		77	346		0.57	395, 406, 440	2.02
	MCH	RT	346				
		77	338		4.9	388, 394, 408 419, 432, 446	2.29
	MCH	RT	344				
		77	332, 340		5.7	370, 388, 402 428, 446	2.35
DVLN	(1) MCH and EtOH	RT	334	0.058 and 0.011			
	EtOH	RT		None			
	EtOH	77	338		4.2	388, 392, 427	1.45
MGLN	(2) MCH	RT	346	0.04–0.13			
		77	339.5		4.2	383, 398, 421, 435	1.80
	EtOH	RT	346	0.038		402	
Crystal Violet	(3) Benzene	RT	347				
		77	344		3.7	430, 455, 490, 532	0.15
		77	352	0.011	6.1	394, 412, 434, 460	2.02
<i>p</i> -PhOMGLN	(4) EtOH	RT	332, 347, 372	0.011		489	
<i>p</i> -CH ₃ OMGLN	(5) EtOH	RT	356	0.013		490	
		77	352		5.1	388, 414, 436	2.59
<i>m</i> -CF ₃ MGLN	(6) EtOH	RT	342	0.006		411	
		77	358		11	392, 412, 422	1.90
<i>p</i> -CF ₃ MGLN	(7) EtOH	RT	353	0.014		510	
		77	350		12	388, 412, 434, 460	2.02
<i>p</i> -BrMGLN	(8) EtOH	RT		0.00			
		77	352		22	392, 410, 438, 452	1.63
<i>o</i> -ClMGLN	(9) MCH	RT	330	0.001			
	EtOH	RT	320	0.015		405	
<i>p</i> -CH ₃ MGLN	(10) EtOH	RT	356	0.014		386, 408, 430, 444	1.77
		77	354		6.2	500 390, 400, 410, 438	2.18
<i>m</i> -CH ₃ OMGLN	(11) EtOH	RT	356	0.014		485	
		77	344		5.6	388, 410, 434	2.85
BB7LN	(12) EtOH	RT	427.5	0.64			
		77	363, 398			None	
	EtOH + H ⁺	RT	430	0.43			
<i>p</i> -CH ₃ COMGLN	(13) EtOH	RT	367, 401		0	None	
		77	331	0.01		414	
		77	None			400	0.121
						426	0.138
					456	0.187	
					388, 400, 426		
					456, 484		
<i>p</i> -NO ₂ MGLN	(14) EtOH	RT		0			
		77	570		0.6	387, 428, 450, 457	0.258

^a Reference 27. ^b Reference 18. ^c D. Phillips, *J. Photochem.*, 1, 97 (1972–1973). ^d R. S. Davison and M. Santhanam, *J. Chem. Soc. B*, 1151 (1971). ^e Reference 28. ^f J. W. Budge and R. T. Williams, *Nature (London)*, 196, 59 (1962). ^g Reference 26. ^h J. A. Baltrop and N. J. Bunce, *J. Chem. Soc. C*, 1467 (1968).

served emission (Figure 13) can therefore be attributed to the fluorescence of $n-\pi^*$ excited singlet state of the 1-naphthylamine chromophore, which occurs at the same wavelengths.

At the other extreme, the *p*-acetyl-substituted Malachite

Green Leuconitrile **13a** exhibits only phosphorescence ($\chi > 10^3$). The emission here (Figure 12) is characteristic of the n,π^* triplet state, with an observed lifetime typical of substituted acetophenones ($\tau_p \approx 0.15$ sec)²⁹ and vibrational spacings (1550 cm^{-1}) expected in this type of triplet emis-

sion. However, for an n,π^* state, the spectrum is relatively unstructured and, in addition, the observed phosphorescence decay time varies with the wavelength (Table II). Despite the fact that the phosphorescence decay curve for this compound is exponential (i.e., has one apparent decay component), these variations, considered in light of the overlap of the phosphorescence band from the two chromophores (i.e., aniline with $E_1 = 74.1$ kcal), suggest a mixed phosphorescence with the minor component attributable to the $^3L_{\pi}$ state of the substituted aniline *N,N*-dimethyl-*p*-toluidine.

The *p*-nitro-Malachite Green Leuconitrile **14a** did not emit at room temperature. At 77 K, this compound produced a weak phosphorescence emission similar to the peaks due to the aminobenzene moiety of the other compounds in its spectral distribution, but with a shorter observed lifetime of 0.26 sec. In addition, a fluorescence peak was observed with λ_{\max} 570 nm. At the present time, the source of these emissions has not been clearly demonstrated, and the conclusions (vide infra) concerning their origins are drawn from analogy with the properties of nitrobenzene and the leuconitriles of the other triarylmethanes. Further work is contemplated in this area.

Quantum Yields of Photoionization. The quantum yields of photoionization, or photocoloration, for the series of triarylmethanes (φ_c) has been measured in aerated 95% ethanol solutions using the Malachite Green Leuconitrile actinometer.² The irradiations were carried out in a slight excess of acid at low light intensities (10^{16} photons sec^{-1}) to give in all cases less than 5% conversion to the dye form **b**. All but two of the photoionizing compounds have absorption curves very similar in shape to that of the actinometric solution which was used. With the majority of the compounds, solutions were prepared whose absorption curves could be matched with that of the reference solution by the use of appropriate concentrations. With the leuconitrile of BB7 (**12a**), both the reference solution and the reactant solution were made opaque by the use of high concentrations of leuconitrile. In these cases, the amount of light absorbed by these "matched" solutions was exactly measured by the actinometric solution of Malachite Green Leuconitrile.

The Doebner's Violet, however, has a spectrum shaped differently than the reference. Its quantum yield was calculated from the Malachite Green actinometer data by use of a correction factor to compensate for the absorption by the actinometer solution of 334.1-nm light which could not be entirely removed by the filter system.

The results of the measurement of these quantum yields of photoionization are shown in Table III. It can be seen that the change in substituent groups causes φ_c to vary between 1 and 0. Since no correlation with any of the constants related to the free energy relationships can be found, this variation does not appear to be dependent on any established substituent effect.

Discussion

Although the photoionization of the leuconitriles to form the dye carbocation has been a much studied and much used reaction,^{8,13} no photochemical mechanism has yet been proposed.¹⁵ It would appear from our data that, for this general class of compounds, the excited state which leads to the formation of dye cation by photoionization in 95% ethanol solutions is the lowest lying singlet.

The absorption of light by any of the triarylmethane leuconitriles results, in effect, in the promotion of the molecule to its lowest energy excited singlet state. The excitation of any insulated chromophore which has a higher energy excited singlet within a leuconitrile leads to a highly efficient intramolecular singlet-singlet energy transfer which places the excitation energy on the chromophore with the lowest

Table III

Compd	χ	φ_c^c	Photons sec^{-1} (sec)
DVLN	(1) 4.2	0.83 (0.04)	7.41×10^{16} (270)
MGLN	(2) 4.7	0.91 ^a	
Crystal Violet	(3) 3.7	1.02 ^b	2.58×10^{16} (270)
<i>p</i> -PhO-MGLN	(4) 6.1	0.95 (0.02)	3.74×10^{16} (270)
<i>p</i> -CH ₃ OMGLN	(5) 5.1	0.85 (0.02)	6.81×10^{16} (270)
<i>m</i> -CF ₃ MGLN	(6) 11	0.68 (0.01)	3.74×10^{16} (270)
<i>p</i> -CF ₃ MGLN	(7) 12	0.74 (0.02)	6.51×10^{16} (255)
<i>p</i> -BrMGLN	(8) 22	0.67 (0.02)	3.43×10^{17} (360)
<i>o</i> -ClMGLN	(9) 11	0.57 (0.02)	3.01×10^{16} (360)
<i>p</i> -CH ₃ MGLN	(10) 6.2	0.48 (0.02)	6.81×10^{16} (270)
<i>m</i> -CH ₃ OMGLN	(11) 5.6	0.37 (0.01)	6.81×10^{16} (270)
BB7LN	(12) 0	0.21 (0.01)	3.01×10^{16} (360)
<i>p</i> -CH ₃ COMGLN	(13) ∞	<0.01	4.07×10^{16} (270)
<i>p</i> -NO ₂ MGLN	(14) ∞	<0.01	3.25×10^{16} (360)

^a Actinometer as in ref 2. ^b One determination. ^c Three or more determinations. Standard deviation in parentheses.

energy singlet state.¹⁶ In most cases, this singlet is the toluidine moiety;¹⁵ in other leuconitriles, the singlet is the naphthylamine, the nitrophenyl, or the acetophenone moiety. The efficiency of the intramolecular internal conversion can be seen in that in all cases the emission, both phosphorescence and fluorescence, is characteristic of the chromophore which has the lowest energy excited state. None of the compounds in this series contains two groups which might have reversals in the lowest energy moiety between the excited singlet and triplet levels to cause ambiguities. That is, all the compounds have one chromophore which has both the lowest energy triplet and singlet excited state.

The *p*-nitro derivative of Malachite Green Leuconitrile **14a**, like many common nitro aromatics, does not fluoresce.¹⁷ The spectra measured in ethanol at liquid nitrogen temperature is attributed to the photochemical products of this compound. The emission spectra has two peaks. The higher energy, longer lived peak is similar in shape, location, and lifetime to the *p*-acetyl compound. The second, very short-lived, weak emission falls at about 570 nm. It is shown that the nitrophenyl group is very similar in its photochemistry to the carbonyl compounds.¹⁸ Also, the triplet excited state energy of nitrobenzene has been found to be 60 kcal (478 nm),¹⁹ and the intersystem crossing efficiency has been found by Testa²⁰ to be greater than 0.6. Further, Testa found that the excited n,π^* triplet state undergoes a very rapid (10^9 sec^{-1}) and efficient radiationless decay. Thus, the phosphorescence emitted by **14a** would be expected to be short lived and very weak in intensity and would be found at about 485 nm. Possibly this is the source of the longer wavelength emission of this nitro compound.

The possibility that the photoionization reaction occurs from the triplet excited state can be discounted for several reasons. As has been mentioned by previous workers,²² oxygen is an excellent intermolecular quencher for triplet molecules; yet the high quantum yields (yields approaching unity) have been measured by us and other workers for a number of these compounds in aerated solutions. In addition, the triarylmethane dyes that are produced as the photoproduct are known to phosphoresce in the near-infrared region of the spectrum ($E_1 = 30$ –50 kcal).²² If the reactive excited state is a triplet, these dyes should also act as quenchers to cause a reduction in the high quantum yields of coloration.

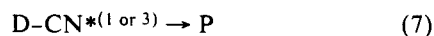
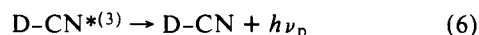
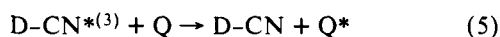
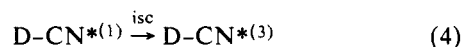
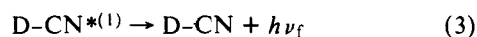
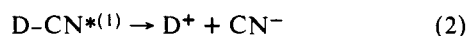
In fact, an increase in the efficiency of triplet excited state formation, as indicated by increasing intersystem crossing ratios (χ), causes a significant decrease in the efficiency of the photoionization, as evidenced in the case of the halogenated leuconitriles. In the extreme case, with leuconitriles which have a n,π^* singlet excited state, the photochemical heterolytic cleavage is totally absent. The nitro-

and acetyl-substituted leuconitriles have this n, π^* excited singlet state, as evidenced by their lack of fluorescence emission. So due to the inherent properties of this type of singlet (the longer lifetimes and greater spin-orbital interaction), the predominant route for energy loss from this excited state in these leuconitriles is intersystem crossing to give essentially 100% conversion to the excited triplet and thus effectively quench the photocoloration reaction.

Thirdly, the photoactive compounds typically have long-lived π, π^* triplet excited states, but the rate of the coloration has been measured in the past to be greater than 10^5 sec^{-1} ,²³ and recently greater than ca. 10^8 sec^{-1} .²⁴ Thus, the species which precedes the heterolytic cleavage has reacted long before the triplets decay.

Finally the lifetimes of the triplet excited states are essentially the same ($\tau_p = 2 \text{ sec}$) for the photocoloring leuconitriles and the model compounds which exhibit no photochemistry. The photoionization process, therefore, does not cause a more rapid depopulation of the triplet excited state and gives further support to a singlet mechanism.

It appears from our data, then, that the following sequence of reactions affords a satisfactory explanation of the photochemistry of the triarylmethane leuconitriles in 95% aqueous ethanol.



The initial promotion of the photoactive triarylmethaneleuconitrile produces an excited n, π^* singlet state (k_1). The chemistry of the active excited state, which may possibly be a n, π^* or a π, π^* excited singlet produced by internal conversion, is characteristic of the methylene insulated chromophore that has the lowest singlet energy. The singlet undergoes an efficient photoionization, which is extremely rapid ($k_2 = 10^9 \text{ sec}^{-1}$)²⁴ and, thus, effectively prevents deactivation by the other competitive routes such as fluorescence ($k_3 = 3 \times 10^8 \text{ sec}^{-1}$)²⁴ or intersystem crossing ($k_4 = 10^7 \text{ sec}^{-1}$). One result of this competition for the excitation energy is reduction in ϕ_e found for the leuconitrile compounds in comparison with their model compounds.

With the modification of structure or the addition of certain substituent groups, the photophysical properties of molecules which normally undergo facile photoionization are changed so that other processes can effectively compete with the reaction to form dye cation. With the leuconitrile of Basic Blue 7 (**12a**), the relatively longer lived naphthylamine excited state singlet (20 nsec as compared with 3 nsec for aniline) undergoes efficient fluorescence to reduce the efficiency of the photochemical reaction. Examples of a second competitive route for the excited state singlet energy, intersystem crossing, are found with the halogenated leuconitriles, which undergo more efficient triplet formation due to the heavy atom effect ($k_4 = k_2$), and with the acetyl and nitro substituted leuconitriles, which have lowest n, π^* excited singlet states that inherently undergo an extremely facile change in multiplicity ($k_4 > k_2$).

In addition to eq 1-6 which show predominant modes of energy dissipation, the excited molecules can be deactivated by radiationless decay to the ground state, or by other pho-

tochemical reactions of the singlet or triplet excited states (eq 7). Examples of the possible excited-state reactions are photoxidative cleavage to separate the *N*-alkyl groups²¹ and, in the case of the molecules with low lying n, π^* excited triplet states, photoreduction and bond cleavage typical of these classes. In comparison with the predominant modes of energy dissipation, these routes for deactivation are of importance only in the compounds which do not photocolor. Since for most of the photoactive leuconitriles of triarylmethanes the primary photoprocesses, such as photoionization and emission, account for most, or all, of the light absorbed, the photodegradative processes which have been reported²⁵ to rapidly "fatigue" the triarylmethane leuconitriles most probably occur through photooxidation of the dye cation. In support of this observation, it may be noted that the triarylmethane dyes themselves are notably light sensitive and are rapidly converted to colorless species,²⁶ whereas even the minor photodegradative processes found for the leuconitriles of the dyes produce compounds with the triarylmethane chromophore intact.

In conclusion, it appears that the photoheterolytic cleavage of the triarylmethane leuconitriles takes place from an excited singlet state, and that an increased intersystem crossing efficiency or increased singlet emission accounts for the reduction in the quantum yield of ionization. For these leuconitriles, the major pathway for energy deactivation is through photocoloration or emission, and other degradative pathways are not significant in their photochemistry.

Experimental Section

General. NMR spectra were measured on either a Varian A-60 or HA-100 spectrometer in CDCl_3 with an internal tetramethylsilane reference. IR spectra were determined in potassium bromide on a Perkin-Elmer Model 521 spectrometer. Mass spectra (70 eV) were obtained on a Perkin-Elmer Model 270 or a Consolidated Model 21-110 spectrometer. UV and visible spectra were taken on a Cary 17I spectrometer; extinction coefficients were determined from the slopes of linear regressions of optical density vs. concentration. Emission spectra were measured on a Baird Atomic SF-1 fluorescence spectrometer with phosphoroscope attachment. Melting points were taken in an uncorrected Thomas-Hoover melting point apparatus. Elemental microanalyses were performed by Midwest Microlab, Ltd., Ind.

Chemicals. The following reagent grade dyes were used in the preparation of the leuconitriles: Crystal Violet, Malachite Green (J. T. Baker Chemical Co.), and Rhoduline Blue (**9b**) (GAF Corp.). Doebner's Violet was prepared from its known triphenylmethane by a chloranil oxidation.³⁰

Benzene and methylcyclohexane, spectral grade, were distilled before use. Distillation of the ethanol (95%) was found to be unnecessary and, in general, this solvent was used without further purification.

Preparation of Triphenylmethane. Those triphenylmethanes prepared in this study were synthesized using standard procedures by condensation of the appropriately substituted benzaldehyde with *N,N*-dimethylaniline.⁶ The isolation of the product was carried out by neutralization of the reaction solution, followed by vacuum evaporation in a steam bath to remove solvent and unreacted starting materials. The residue was repeatedly extracted with chloroform and the chloroform extract thoroughly washed with water, dried, and reduced in volume. Then 95% ethanol (2 \times the solution volume) was added and the volume reduced until cooling produced crystals of the desired triphenylmethane. The product was purified by recrystallization from ethanol.

Preparation of Leucocarinols. A. The carbinol bases of the *p*-bromo- (**8**), *p*-nitro- (**14**), and *m*-trifluoromethylphenyl-*p'*,*p''*-bis(*N,N*-dimethylaminophenyl)methanols (**6**) were prepared by the oxidation of the corresponding triphenylmethane with excess chloranil in 95% ethanol.⁶

B. The *p*-methoxyphenyl-*p'*,*p''*-bis(*N,N*-dimethylaminophen-

Table IV. Physical Properties of the Leuconitriles

Compd	Mp, °C	Ir (cm ⁻¹) ^a	M ⁺	NMR (ppm from Me ₄ Si) ^b	Analysis		
					C	H	N
1	226–227	3480, 3490, 2240, 830, 776, 705	299	7.26 (s, 5), 6.65 (q, 8), 5.22 (s, 4) ^c	Calcd: 80.24 Found: 79.84	5.72 5.87	14.04 13.75
2	176–177	2920, 2230, 812, 760, 700	355	7.28 (s, 5), 6.86 (q, 8), 2.93 (s, 6)			
3	293 dec	2890, 2805, 2240, 1230, 815	398	6.85 (q, 12), 2.92 (s, 18)			
4	154–155	2885, 2800, 2231, 1245, 816, 752, 694		7.14 (q, 4), 7.12 (m, 5), 6.88 (q, 8), 2.91 (s, 12)	Calcd: 80.50 Found: 80.87	6.53 6.60	9.39 9.55
5	230–232	2900, 2795, 2230, 1255, 1180, 820, 840		7.00 (q, 4), 6.86 (q, 8), 3.76 (s, 3), 2.92 (s, 12)	Calcd: 77.89 Found: 77.98	7.06 6.98	10.90 10.95
6	164–165	2870, 2805, 2227, 1136, 950, 820, 810, 708, 680		7.47 (d, 4), 6.82 (q, 8), 2.92 (s, 12)	Calcd: 70.90 Found: 71.11	5.71 5.64	9.92 10.01
7	201–202	2995, 2890, 2800, 2222, 1125, 830, 810		7.50 (q, 4), 6.86 (q, 8), 2.92 (s, 12)	Calcd: 70.90 Found: 70.75	5.71 5.65	9.92 9.71
8	233.5–235.5	2890, 2803, 2229, 1109, 811		7.32 (q, 4), 6.88 (q, 8), 2.92 (s, 12)	Calcd: 66.36 Found: 66.23	5.57 5.59	9.68 9.76
9	200.5	2880, 2800, 2230, 815, 760, 767	390	7.33 (m, 4), 6.84 (q, 8), 2.91 (s, 12)	Calcd: 73.92 Found: 73.81	6.20 6.34	10.78 11.07
10	211–212	2880, 2800, 2230, 810		7.12 (s, 4), 6.84 (q, 8), 2.94 (s, 12), 2.33 (s, 3)	Calcd: 81.26 Found: 81.28	7.34 7.22	11.37 11.36
11	167	2890, 2810, 2236, 1250, 815, 795, 778, 697		7.00 (m, 4), 6.85 (q, 8), 3.73 (s, 3), 2.93 (s, 12)	Calcd: 77.89 Found: 78.05	7.06 7.40	10.90 10.81
12	235 dec	3424, 2965, 2924, 2881, 2220, 810, 796, 746		8.1–6.3 (m, 6, naphthyl), 6.81 (q, 8), 4.30 (b, 1), 3.32 (q, 10, <i>J</i> = 3.5 Hz), 1.36 (t, 3, <i>J</i> = 3.5 Hz), 1.15 (t, 12, <i>J</i> = 3.5 Hz)	Calcd: 80.91 Found: 80.58	7.99 8.14	11.10 10.85
13	210.5–211.5	2896, 2810, 2230, 1686, 815		7.68 (q, 4), 6.63 (q, 8), 2.93 (s, 12), 2.57 (s, 3)	Calcd: 78.56 Found: 78.62	6.85 7.00	10.57 10.64
14	190.5–191.5	2896, 2810, 2230, 1520, 1350, 814		7.83 (q, 4), 6.85 (q, 8), 2.93 (s, 12)	Calcd: 71.98 Found: 71.99	6.04 6.13	13.99 14.25

^aIn KBr. ^bb = broad, s = singlet, d = doublet, t = triplet, q = quartet (due to AB systems in the para-substituted phenyl rings). ^cDisappears with deuterium exchange.

yl)methanol (**5**) was prepared by the addition of the appropriate arylsodium salt to Michler's ketone.⁸

C. The remaining substituted triphenylmethanols (**4**, **6**, **7**, **10**, **11**, and **13**) were synthesized by the reaction of the appropriate aryllithium salt with Michler's ketone.

Preparation of the Triarylmethane Leuconitriles. The dye cation was produced in 25 ml of dimethyl sulfoxide either by solvation of the dye chloride (1 g) with a 1 × excess of acid, or by treatment of the dye leucocarbonyl (1 g) with a 2 × excess of acid. The resulting deeply colored solution was heated on a steam bath and then decolorized with 0.70 g (0.108 mol) of potassium cyanide in a fume hood. This mixture was filtered, the filter pack washed with 10 ml of hot 95% ethanol, and the filtrate heated to a boil. Water (ca. 10 ml) was slowly added with stirring to fog the hot filtrate. The fogged mixture was then digested on a hot plate and cooled to give crystals which could be purified by repeated recrystallization from a chloroform–ethanol solution to give good yields of the leuconitrile.

Physical constants for the compounds are shown in Table IV.

Emission Studies. Emission spectra were measured on a Baird-Atomic SF-1 spectrofluorimeter and were recorded on a Houston Instruments X-Y recorder. The spectra were corrected for the relative response characteristics of the instrument.³¹ The quantum yields of fluorescence were calculated by comparing the integrated area under the corrected fluorescence spectra and a reference sample of quinine sulfate in 0.1 *N* sulfuric acid prepared to give approximately same absorbance at the exciting wavelength. A value of 0.55 was used as the quantum yield of fluorescence for quinine sulfate.³²

The emission spectra were measured using solutions 5 × 10⁻⁵ *M* in leuconitrile, a concentration at which self-quenching is not a significant process. The room temperature absorption and fluorescence spectra were measured in 1-cm quartz cells. At liquid nitrogen temperature (77 K), the emission spectra were measured in Supersil sample tubes within the quartz dewar of the phosphoroscope of the Baird Atomic SF-1 spectrofluorimeter. The samples were degassed by at least four freeze–pump–thaw cycles at 10⁻³ mm pressure and sealed under argon. By use of the rotating shut-

ter, the phosphorescence was separated from the total emission. Comparison of the total corrected emission and the corrected emission due to phosphorescence permitted calculation of the intersystem crossing ratio.

Phosphorescent lifetime measurements were made using the spectrofluorimeter whose output at a pure phosphorescence wavelength was fed to a Tektronix 454 oscilloscope and recorded on Polaroid film. The oscilloscope was triggered when the light source of the spectrofluorimeter was turned off. Lifetimes were obtained by digitization of the data on Hewlett-Packard calculator, which also was used to calculate the rate of the simple exponential decay by standard regression techniques. In all cases, the correlation coefficient for the decay curve for up to 3 half-lives was greater than 0.99. The reported lifetimes (Table III) are the mean of at least three determinations.

Quantum Yields of Photoionization. Irradiations were performed in parallel on a "merry-go-round" apparatus (Rayonet MGR-500) with a Hanovia 100-W high-pressure mercury lamp (SOL 608A-36) contained in a water cooled, Pyrex (Corning 7740) immersion well. A 2-cm filter solution of nickel sulfate and cobaltous sulfate³³ with a Corning 7740 glass sleeve was used to isolate the 3130–3341 Å lines. In some runs, the intensity of the lamp was further attenuated by a neutral density screen to allow longer irradiation times. The "merry-go-round" ensures that the same intensity of radiation impinges on each sample of a set of simultaneously irradiated samples.

All quantum yields for the formation of dye cations were measured relative to the Malachite Green actinometer.^{1,2} Solutions (25 ml) containing known concentrations of leuconitrile and 1 ml of 0.3 *M* hydrochloric acid were prepared in 95% ethanol in volumetric flasks. Then 5.5-ml portions of these solutions were placed in 16 × 150 mm lime glass culture tubes or quartz tubes (Rayonet RQV-7). These solutions were ca. 5 × 10⁻⁴ *M* in leuconitrile for most of the compounds. With Doebner's Violet (**1**), Crystal Violet (**3**), and the *p*-acetyl Malachite Green (**13**) Leuconitriles, the concentration was ca. 3 × 10⁻³ *M* in leuconitrile. Due to the similarity of the absorption characteristics of most of the leuconitriles with that of the leuconitrile of Malachite Green, it was possible to pre-

pare the solutions of reactant leuconitrile to match the absorption of the actinometer solution or to prepare solutions (ca. $3 \times 10^{-3} M$) that were opaque ($OD > 2$) over the wavelengths at which the light source was emitting. All the solutions in each run were opaque ($<0.1\% T$) at 313 nm where the light source emitted 74.9% of its light. In this manner, the solutions in each run absorbed the same amount of light.

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Dodecachlorotetracyclo[7.2.1.0^{2,8}.0^{5,12}]dodeca-3,6,10-triene, a Fully Chlorinated Valence Isomer of [12]Annulene

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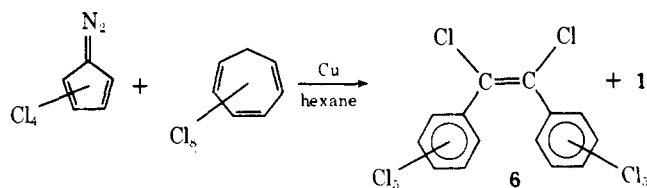
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Abstract: The title compound (**1**), representing a new tetracyclic ring system, has been synthesized from tetrachlorodiazocyclopentadiene and octachlorocycloheptatriene. The structure of **1** was established by single crystal X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$, with $a = 14.655$ (5) Å, $b = 16.874$ (5) Å, $c = 7.637$ (1) Å, $\alpha = 100.43$ (2)°, $\beta = 102.19$ (2)°, $\gamma = 89.89$ (2)°, $V = 1814.0$ (8) Å³, and $Z = 4$. Data were collected on an autodiffractometer and refined with anisotropic least-squares to a final unweighted R value of 3.2%. When **1** is heated with copper, it is converted to perchloroacenaphthylene.

Complete substitution with chlorine is known to confer stability on otherwise rather unstable hydrocarbons.¹ In an attempt to synthesize a precursor to perchloropentaheptafulvalene, we have inadvertently synthesized dodecachlorotetracyclo[7.2.1.0^{2,8}.0^{5,12}]dodeca-3,6,10-triene (**1**), the first example of a new tetracyclic ring system.² Compound **1** is a stable, fully chlorinated valence isomer of [12]annulene.³

The reaction of tetrachlorodiazocyclopentadiene⁴ with octachlorocycloheptatriene⁵ in the presence of finely divided copper afforded two C₁₂Cl₁₂ compounds in about a 2:5 ratio for a total yield of 70-75%. The rather insoluble minor component was identified as perchloro-*cis*-stilbene (**6**) by comparison of its infrared spectrum with that of an authentic sample.⁶

The major component **1** was a white solid soluble in organic solvents, showing two olefinic absorptions in the infrared at 1625 and 1585 cm⁻¹ (CHCl₃ solution). The spectrum in chloroform showed little change in position or in-



tensity of the olefinic absorptions between -50 and +50°C, suggesting that a temperature-dependent equilibrium of valence isomers was absent and that only one isomer was involved. The ultraviolet spectrum showed only a single absorption at 226 nm ($\log \epsilon$ 3.76), thereby excluding conjugated structures such as **2** or **3**.

