# 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.<sup>1,2</sup> 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,<sup>3</sup> independent of light intensity<sup>4</sup> and temperature.<sup>5</sup> 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 leucontriles 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 ( $\varphi_c$ ) 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,<sup>2</sup> compared with the earlier reported value at 1.00.<sup>1</sup> 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 aryllithium<sup>7</sup> or sodium<sup>8a</sup> 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.<sup>6</sup> 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



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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 $(11.3)$ , <sup>d</sup> 590 $(11.)$ <sup>c</sup>
p-Phenoxy-MG	(4)	272 (4.73), 304 (0.628)	$616(10.3), 455(3.08)^a$
p-Methoxy-MG	(5)	270 (3.88), 303 (0.514)	$610.5 (9.89), 464 (2.90)^a$
m-Trifluoromethyl-MG	(6)	272 (3.67), 308 (0.585)	634 (9.66), 423.8 (1.57) <sup>e</sup>
p-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)	$628.5 (10.1), 433 (2.15)^a$
			$628.5 (10.2), 433 (2.28)^{e}$
o-Chloro-MG	(9)	272 (3.80), 307 (0.543)	$640 (12.6), 410 (1.84)^d$
p-Methyl-MG	(10)	272 (3.64), 304 (0.509)	618 (10.6), 438 (2.74) <sup>a</sup>
m-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)	586 $(14.7)^d$
		259 (1.92), 341 (1.08)	
p-Acetyl-MG	(13)	273 (3.93), 308 (0.847)	$629 (9.31), 432 (2.16)^a$
p-Nitro-MG	(14)	271.5 (4.97), 309 (0.731)	646 (7.88), 428 $(1.61)^a$
-		351 (0.159)	





Figure 1. A plot of Hammett  $\sigma$  against  $\nu_{max}$  for the substituted Malachite Green dyes from this work (+) and from other work<sup>7</sup> (O). The substitution as numbered in the figure are: (1) p-N(CH<sub>3</sub>)<sub>2</sub>; (2) p-PhO-, (3) p-CH<sub>3</sub>O; (4) p-CH<sub>3</sub>; (5) m-CH<sub>3</sub>; (6) p-Ph; (7) H; (8) m-Ph; (9) m-CH<sub>3</sub>O; (10) p-Br; (11) m-CO<sub>2</sub>CH<sub>3</sub>; (12) m-CF<sub>3</sub>; (13) p-CO<sub>2</sub>CH<sub>3</sub>; (14) p-CH<sub>3</sub>CO; (15) p-CF<sub>3</sub>; (16) m-CN; (17) m-SO<sub>2</sub>CH<sub>3</sub>; (18) p-CN; (19) m-NO<sub>2</sub>; (20) p-SO<sub>2</sub>CH<sub>3</sub>; (21) p-NO<sub>2</sub>.

leucocarbinols to their leuconitriles was carried out in dimethyl sulfoxide containing excess potassium cyanide.<sup>9</sup>

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 leucocarbinol 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-CF<sub>3</sub>, 6) and the pure triphenylmethane could be quantitatively converted to the dye cation,<sup>10</sup> 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 linear 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.<sup>2</sup> 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-CH<sub>3</sub> 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 Ritchie<sup>6</sup> in methanol and by Hallas et al.<sup>7,12</sup> 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.<sup>7</sup>

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 chromophores<sup>28</sup> (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  $(---) m-CF_3$  and  $(----) p-CF_3$  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-CH<sub>3</sub>O; (--) p-PhO; and (--) m-CH<sub>3</sub>O 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-CH<sub>3</sub>CO and (- - -) p-NO<sub>2</sub> Malachite Green and (-) Basic Blue 7.



Figure 7. Absorption and emission spectra of the leuconitrile of Deebner'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 ( $\varphi_c$ ) measured at room temperature are lower than

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24000

20000

16000.



28000

32000

36000

(E) × 10<sup>3</sup>

MOLAR EXTINCTION COEFFICIENT

30

20

10

40000



Figure 10. Absorption and emission spectra of the leuconitrile of p-CF<sub>3</sub> Malachite Green (7a) in ethanol.



Figure 11. Absorption and emission spectra of the leuconitrile of p-Br 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  $\varphi_c$  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<sup>13,14</sup> 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.



Figure 12. Absorption and emission spectra of the leuconitrile of p-acctyl Malachite Green (13a) 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.

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  $(\tau_p)$ , and intersystem crossing ratio (the intensity of phosphorescence relative to the intensity of fluorescence,  $\chi$ ) 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  $\pi$ ,  $\pi^*$  triplet state of the aminophenyl moiety; this can be seen by comparing (Table II) data reported for the anilines and the Malachite Green derivatives<sup>27</sup> 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 ( $E_t = 74$  kcal) and the observed phosphorescence decay time ( $\tau_p = 2$  sec) are characteristic of the lowest triplet ( ${}^{3}L_{a}$ ) of the toluidine moiety. The more sensitive intersystem crossing ratio ( $\chi$ ) also shows excellent consistency for these compounds. The small variations in  $\chi$  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  $\tau_p$ .

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 ( $\varphi_e = 0.62$ ) but does not phosphoresce even at liquid nitrogen temperature ( $\chi = 0$ ). The ob-

				Fluorescence		Phosphorescence		
Compd		Solvent	<i>T</i> , K	hvf	Ψe	x	hνp	$\tau_{p}$ , sec
Aniline		EtOH Cyclohexane EPA	RT RT 77	296, <sup>e</sup> 338 <sup>c</sup> 327 <sup>a</sup> 340 <sup>d</sup>	0.3-0.6 <sup>c</sup> 0.8 <sup>a</sup>		373 <sup>c,e</sup> 373, <sup>b</sup> 387, 400	4.7 <i>f</i>
N, N-Dimethylaniline		EtOH Cyclohexane	RT RT	344, <sup>d</sup> 348a 333a	0.11		416 (max) <sup>d</sup>	
N, N-Dimethyl-p-toluidine Nitrobenzene Anisole		3-Methylpentane EPA EtOH	77 77 RT	2914	0 <i>f</i> , <i>h</i>	h	473 <sup>b</sup>	2.6 <sup>g</sup> 0.20 <sup>h</sup>
1-Methylnaphthalene		Cyclohexane Polar FtOH	RT RT RT	289, <sup>a</sup> 278 <sup>e</sup> 325, 339, <sup>a</sup> 317 <sup>e</sup> 429 <sup>a</sup>	0.24 <sup>e</sup> 0.25, <sup>a</sup> 0.21 <sup>e</sup>		354e 480 <sup>e</sup>	3.0 <sup>e</sup>
Malachite Green Leucocarbinol		Cyclohexane EPA 3-Methylpentane	RT 77 77	375	0.46 <sup>a</sup>		497.5, <sup>b</sup> 526 <sup>e</sup>	1.5 <sup>e</sup> 2.03 <sup>g</sup>
		МСН	RT 77	332, 342 348		0.38	390, 414, 444	1.90
		МСН	RT 77	330 346		0.57	395, 406, 440	2.02
$(CH_3)_2 N \rightarrow CH_2$		МСН	RT 77	346 338		4.9	388, 394, 408	2.29
((CH <sub>3</sub> ) <sub>2</sub> N-CH		МСН	RT 77	344 332, 340		5.7	419, 432, 448 370, 388, 402	2.35
DVLN	(1)	MCH and EtOH EtOH	RT RT	334	0.058 and 0.011 None		428, 440	
MGLN	(2)	EtOH MCH	77 RT	338 346	0.04-0.13	4.2	388, 392, 427	1.45
		EtOH	77 RT	339.5 346	0.038	4.2	383, 398, 421, 435 402	1.80
Crystal Violet	(3)	Benzene	77 RT	340 347 344		5.6 3.7	382, 404, 426	1.79
p-PhOMGLN	(4)	EtOH	RT 77	332, 347, 372 352	0.011	6.1	489 394, 412, 434, 460	2.02
<i>p</i> -CH <sub>3</sub> OMGLN	(5)	EtOH	RT 77	356 352	0.013	5.1	490 388, 414, 436	2.59
<i>m</i> -CF₃MGLN	(6)	EtOH	RT 77	342 358	0.006	11	411 392, 412, 422	1.90
p-CF <sub>3</sub> MGLN	(7)	EtOH	RT 77	353 350	0.014	12	510 388, 412, 434, 460	2.02
p-BIMGLN	(8)	EtOH	77 77	352	0.00	22	392, 410, 438, 452	1.63
0-CIMOLIN	()	EtOH	RT 77	320 348	0.015	11	405 386 408 430 444	177
<i>p-</i> CH₃MGLN	(10)	EtOH	RT 77	356 354	0.014	6.2	500 390, 400, 410, 438	2.18
m-CH <sub>3</sub> OMGLN	(11)	EtOH	RT 77	356 344	0.014	5.6	485 388, 410, 434	2.85
BB7LN	(12)	EtOH EtOH + H <sup>+</sup>	RT 77 RT	427.5 363, 398 430	0.64 0.43		None	
<i>p-</i> CH₃COMGLN	(13)	EtOH	77 RT 77	367, 401 331 None	0.01	0	None 414 400 426 456 388, 400, 426	0.121 0.138 0.187
p-NO <sub>2</sub> MGLN	(14)	EtOH	RT 77	570	0	0.6	456, 484 387, 428, 450, 457	0.258

<sup>a</sup> Reference 27. <sup>b</sup> Reference 18. <sup>c</sup> D. Phillips, J. Photochem., 1, 97 (1972–1973). <sup>d</sup> R. S. Davison and M. Santhanam, J. Chem. Soc. B, 1151 (1971). <sup>e</sup> Reference 28. <sup>f</sup> J. W. Budges and R. T. Williams, Nature (London), 196, 59 (1962). <sup>g</sup> Reference 26. <sup>h</sup> 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-naph-thylamine chromophore, which occurs at the same wavelengths.

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

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

sion. However, for an  $n,\pi^*$  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  $E_t = 74.1$  kcal), suggest a mixed phosphorescence with the minor component attributable to the  ${}^{3}L_{a}$ 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  $\lambda_{max}$  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 ( $\varphi_c$ ) has been measured in aerated 95% ethanol solutions using the Malachite Green Leuconitrile actionometer.<sup>2</sup> The irradiations were carried out in a slight excess of acid at low light intensities  $(10^{16} \text{ photons sec}^{-1})$  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  $\varphi_c$  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,<sup>8,13</sup> no photochemical mechanism has yet been proposed.<sup>15</sup> 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
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Compd		x	$\varphi_c^c$	Photons sec <sup>-1</sup>	(sec)
DVLN	(1)	4.2	0.83 (0.04)	7.41 × 10 <sup>16</sup>	(270)
MGLN	(2)	4.7	0.91 <sup>a</sup>		
Crystal Violet	(3)	3.7	$1.02^{b}$	$2.58 \times 10^{16}$	(270)
p-PhO-MGLN	(4)	6.1	0.95 (0.02)	$3.74 \times 10^{16}$	(270)
p-CH_OMGLN	(5)	5.1	0.85 (0.02)	$6.81 \times 10^{16}$	(270)
m-CF_MGLN	(6)	11	0.68 (0.01)	$3.74 \times 10^{16}$	(270)
p-CF MGLN	(7)	12	0.74 (0.02)	$6.51 \times 10^{16}$	(255)
p-BrMGLN	(8)	22	0.67 (0.02)	$3.43 \times 10^{17}$	(360)
o-CIMGLN	(9)	11	0.57 (0.02)	$3.01 \times 10^{16}$	(360)
p-CH_MGLN	(10)	6.2	0.48 (0.02)	$6.81 \times 10^{16}$	(270)
m-CH,OMGLN	(11)	5.6	0.37 (0.01)	$6.81 \times 10^{16}$	(270)
BB7LN	(12)	0	0.21(0.01)	$3.01 \times 10^{16}$	(360)
p-CH_COMGLN	(13)	80	< 0.01	$4.07 \times 10^{16}$	(270)
p-NO <sub>2</sub> MGLN	(14)	œ	< 0.01	$3.25 \times 10^{16}$	(360)

<sup>a</sup> Actinometer as in ref 2. <sup>b</sup> One determination. <sup>c</sup> Three or more determinations. Standard deviation in parentheses.

energy singlet state.<sup>16</sup> In most cases, this singlet is the toluidine moiety;<sup>15</sup> 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.<sup>17</sup> 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.<sup>18</sup> Also, the triplet excited state energy of nitrobenzene has been found to be 60 kcal (478 nm),<sup>19</sup> and the intersystem crossing efficiency has been found by Testa<sup>20</sup> to be greater than 0.6. Further, Testa found that the excited  $n,\pi^*$  triplet state undergoes a very rapid  $(10^9 \text{ sec}^{-1})$  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,<sup>22</sup> 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).<sup>22</sup> 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  $(\chi)$ , 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  $n,\pi^*$  singlet excited state, the photochemical heterolytic cleavage is totally absent. The nitroand acetyl-substituted leuconitriles have this  $n,\pi^*$  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 longlived  $\pi,\pi^*$  triplet excited states, but the rate of the coloration has been measured in the past to be greater than  $10^5$  sec<sup>-1</sup>,<sup>23</sup> and recently greater than ca.  $10^8 \text{ sec}^{-1}$ .<sup>24</sup> 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.

$$D-CN + h\nu \to D-CN^{*(1)}$$
(1)

$$D-CN^{*(1)} \rightarrow D^+ + CN^-$$
(2)

$$D-CN^{*(1)} \rightarrow D-CN + h\nu_{\rm f} \tag{3}$$

$$D-CN^{*(1)} \xrightarrow{isc} D-CN^{*(3)}$$
(4)

$$D-CN^{*(3)} + Q \rightarrow D-CN + Q^{*}$$
(5)

$$D-CN^{*(3)} \rightarrow D-CN + h\nu_p \tag{6}$$

$$D-CN^{*(1 \text{ or } 3)} \rightarrow P \tag{7}$$

The initial promotion of the photoactive triarylmethaneleuconitrile produces an excited  $n,\pi^*$  singlet state  $(k_1)$ . The chemistry of the active excited state, which may possibly be a  $n,\pi^*$  or a  $\pi,\pi^*$  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  $\varphi_e$  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  $n,\pi^*$  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 photochemical 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 groups<sup>21</sup> and, in the case of the molecules with low lying  $n, \pi^*$  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 reported<sup>25</sup> 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,<sup>26</sup> 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. If 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.<sup>30</sup>

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.<sup>6</sup> 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 × 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 Leucocarbinols.** 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.<sup>6</sup>

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

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					Analysis		
Compd	Mp, °C	Ir $(cm^{-1})a$	М+	NMR (ppm from Me <sub>4</sub> Si) <sup>b</sup>	C	Н	N
1	226-227	3480, 3490, 2240, 830, 776, 705	299	7.26 (s, 5), 6.65 (q, 8), 5.22 (s, 4) <sup><math>c</math></sup>	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	<b>9.92</b> 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, J = 3.5 Hz), 1.36 (t, 3, J = 3.5 Hz), 1.15 (t, 12, J = 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

a In KBr. b b = broad, s = singlet, d = doublet, t = triplet, q = quartet (due to AB systems in the para-substituted phenyl rings). c Disappears with deuterium exchange.

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

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  $\times$  excess of acid, or by treatment of the dye leucocarbinol (1 g) with a 2  $\times$  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.<sup>31</sup> 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.<sup>32</sup>

The emission spectra were measured using solutions  $5 \times 10^{-5} M$ 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 shutter, 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 sulfate<sup>33</sup> 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.<sup>1,2</sup> 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  $\times$  150 mm lime glass culture tubes or quartz tubes (Rayonet RQV-7). These solutions were ca.  $5 \times 10^{-4} M$  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.  $3 \times 10^{-3} M$  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 prepare 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<sup>2,8</sup>.0<sup>5,12</sup>]dodeca-3,6,10-triene, a Fully Chlorinated Valence Isomer of [12]Annulene

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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) Å<sup>3</sup>, 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.<sup>1</sup> In an attempt to synthesize a precursor to perchloropentaheptafulvalene, we have inadvertently synthesized dodecachlorotetracyclo[7.2.1.0<sup>2,8</sup>.0<sup>5,12</sup>]dodeca-3,6,10-triene (1), the first example of a new tetracyclic ring system.<sup>2</sup> Compound 1 is a stable, fully chlorinated valence isomer of [12]annulene.<sup>3</sup>

The reaction of tetrachlorodiazocyclopentadiene<sup>4</sup> with octachlorocycloheptatriene<sup>5</sup> in the presence of finely divided copper afforded two  $C_{12}Cl_{12}$  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<sup>-1</sup> (CHCl<sub>3</sub> 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.

