Dyes and Pigments 2 (1981) 153–159

N-(1,1-DIHYDRO)POLYFLUOROALKYL SUBSTITUTED TRIPHENYLMETHANE DYES

M. I. DRONKINA, L. A. KHOMENKO, L. Z. GANDEL'SMAN and L. M. YAGUPOL'SKII

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, 252660 Kiev-94, Murmanskaya 5, USSR

SUMMARY

A number of new triarylmethane and styryl dyes with 1,1-*dihydropolyfluoroalkyl groups at the nitrogen atoms have been prepared. We have studied the influence of polyfluoroalkyl groups on the colour of these triarylmethane and styryl dyes. The accumulation of* N-*polyfluoroalkyl radicals in the molecule of triarylmethane dyes exerts a hypsochromic shift of absorption maxima. The styryl dyes absorb at shorter wavelengths than the styryl dyes with dimethylamino groups. These demonstrate the lessening of the basicity of the nitrogen atom, bonded with the* 1,1-*dihydropolyfluoroalkyl radicals. Nevertheless,* $RNCH_2(CF_2CF_2)_nH$ *groups show themselves in the triphenylmethane and styryl dyes as sufficiently strong auxochromes.*

1. INTRODUCTION

Triarylmethane dyes with fluorine-containing substituents attached to the nitrogen atom have not been widely studied. Only some analogues of Crystal Violet with one, two or three bis(trifluoromethyl)amino groups have been synthesized earlier.[1] The latter is a very weak auxochrome and the introduction of one, two or three such groups exerts a substantial hypsochromic shift of the absorption maximum of the triphenylmethane dye. Analogues of Malachite Green with 1,1-dihydropolyfluoroethyl groups attached to the nitrogen atom, used for the dyeing of polyacrilonitrile fibres, are described in a patent.[2] However neither the absorption wavelengths nor the light fastness of the dyes are listed. Dickey[3,4] was the first to obtain the azo and anthraquinone dyes with

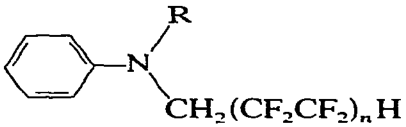
Dyes and Pigments 0143-7208/81/0002-0153/$02.50—© Applied Science Publishers Ltd, England, 1981
Printed in Northern Ireland

fluoroalkylamino groups and to show that the attachment of 1,1-dihydro-2,2-difluoroethyl and 2,2,2-trifluoroethyl groups to the nitrogen atoms leads to the formation of the light fast dyes.

In the circumstances it was considered of interest to obtain triphenylmethane dyes with N-(1,1-dihydro)polyfluoroalkyl groups.

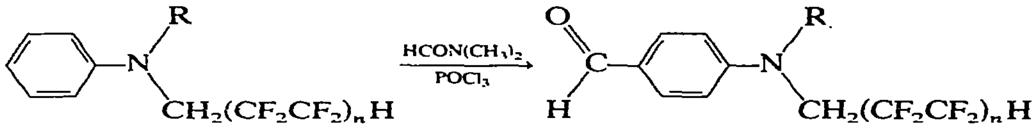
2. RESULTS AND DISCUSSION

Arylamines, described in our earlier paper,[5] were used as starting materials for the preparation of N-(1,1-dihydro)polyfluoroalkyl substituted triphenylmethane dyes:



$R = CH_3$, $n = 1$(**I**), $n = 2$(**II**); $R = C_2H_5$, $n = 1$(**III**), $n = 2$(**IV**).

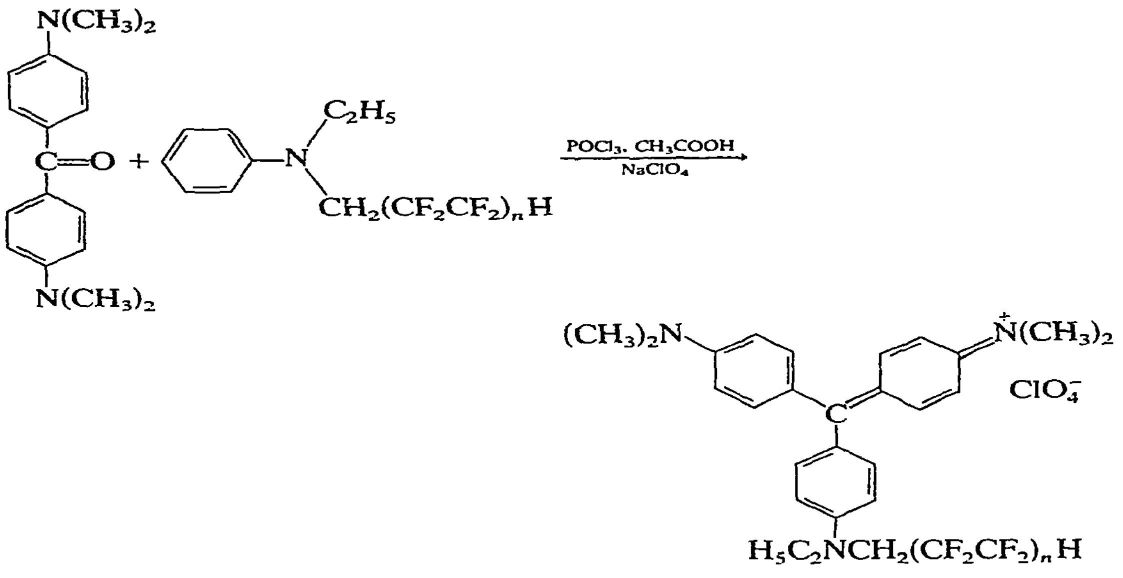
These amines were converted by the Vilsmeiers reaction to the corresponding aldehydes



$R = CH_3$, $n = 1$(**V**), $n = 2$(**VI**): $R = C_2H_5$, $n = 1$(**VII**), $n = 2$(**VIII**)

Dyes **IX** and **X**, containing N-(1,1-dihydro)polyfluoroalkyl groups in only one nucleus, were prepared by condensation of arylamines **III** and **IV** with Michlers ketone.

The condensation of benzaldehyde, *p*-dimethylaminobenzaldehyde or aldehydes **VII**, **VIII** with arylamines **III**, **IV** in the presence of concentrated sulphuric acid, followed by the oxidation of leuco dyes with lead dioxide, led to the dyes with N-polyfluoroalkyl groups in two or three benzene rings. The spectral characteristics, yields, physical properties and results of the microanal-



$n = 1$(**IX**); $n = 2$(**X**)

yses of the synthesized dyes **IX–XV** are summarized in Table 1. The λ_{max} values of some other triphenylmethane dyes are given for comparison.

The substitution of one of the dimethylaminogroups in Crystal Violet for the $C_2H_5NCH_2(CF_2CF_2)_nH$ group exerts a slight (up to 5 nm) bathochromic shift of λ_{max} of the dyes **IX** and **X**. The accumulation of N-polyfluoroalkyl radicals in the molecule of a dye exerts a hypsochromic shift of λ_{max} up to 13 nm in the case of three substituted nuclei (dyes **XIV** and **XV**). The absorption maxima of the triphenylmethane dyes with $n = 1$ and $n = 2$ are practically the same. The dye **XIII** absorbs at shorter wavelengths than Malachite Green.

The fact that the second, less intensive absorption band (λ_{max} 540 nm) appears in the spectra of the analogues of Crystal Violet (**IX–XII**), shows that there is an additional chain of conjugation in these dyes. Its chromogen includes dimethylamino and $H(CF_2CF_2)_nCH_2NC_2H_5$ groups.

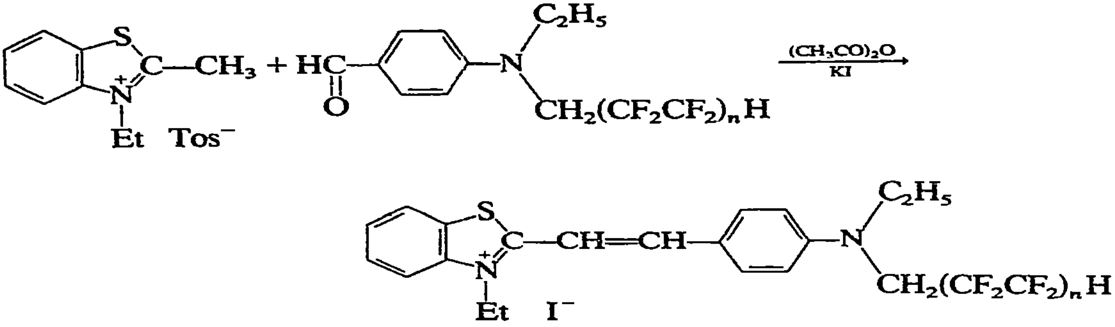
Electrons of the nitrogen atom of N-(1,1-dihydro)polyfluoroalkyl substituted triarylmethane dyes participate in the conjugation with the cation charge to a lesser degree than electrons of the nitrogen atoms of the dimethylamino group. This supposition is confirmed by the spectral characteristic of the styryl dyes. The latter were obtained by condensation of aldehydes **VII** and **VIII** with N-

TABLE 1

TRIPHENYLMETHANE DYES $p\text{-}RC_6H_4\overset{+}{C}(C_6H_4R^1\text{-}p)C_6H_4R^2\text{-}p\ ClO_4^-$

NN	*R*	*R*¹	*R*²	λ_{max} (*nm*)	ε 10⁻⁴	*Yield* (%)	*m.p.* (°C)	*Found* (%)	*Formula*	*Calculated* (%)
	$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_3)_2$	590	11·7					
IX	$N(CH_3)_2$	$N(CH_3)_2$	$N\begin{matrix}C_2H_5\\CH_2CF_2CF_2H\end{matrix}$	540 594	4·25 6·38	82	72–73	F 13·51 13·31	$C_{28}H_{32}ClF_4N_3O_4$	F 12·96
X	$N(CH_3)_2$	$N(CH_3)_2$	$N\begin{matrix}C_2H_5\\CH_2(CF_2CF_2)_2H\end{matrix}$	540 595	5·62 8·12	78	78–79	F 21·84 21·78	$C_{30}H_{32}ClF_8N_3O_4$	F 22·10
XI	$N(CH_3)_2$	$N\begin{matrix}C_2H_5\\CH_2CF_2CF_2H\end{matrix}$	$N\begin{matrix}C_2H_5\\CH_2CF_2CF_2H\end{matrix}$	540 588	2·25 3·25	85	68	F 20·63 20·80	$C_{62}H_{72}Cl_4F_{16}N_6O_2Zn$	F 21·05
XII	$N(CH_3)_2$	$N\begin{matrix}C_2H_5\\CH_2(CF_2CF_2)_2H\end{matrix}$	$N\begin{matrix}C_2H_5\\CH_2(CF_2CF_2)_2H\end{matrix}$	540 581	1·47 2·28	71	43	F 34·05 34·24	$C_{35}H_{34}ClF_{16}N_3O_4$	F 34·21
	H	$N(C_2H_5)_2$	$N(C_2H_5)_2$	623						
XIII	H	$N\begin{matrix}C_2H_5\\CH_2CF_2CF_2H\end{matrix}$	$N\begin{matrix}C_2H_5\\CH_2CF_2CF_2H\end{matrix}$	420 605	7·25	69	125	C 52·03 52·18 H 4·52 4·67	$C_{68}H_{76}Cl_4F_{24}N_6O_2Zn$	C 51·28 H 4·30
XIV	$N\begin{matrix}C_2H_5\\CH_2CF_2CF_2H\end{matrix}$	$N\begin{matrix}C_2H_5\\CH_2CF_2CF_2H\end{matrix}$	$N\begin{matrix}C_2H_5\\CH_2CF_2CF_2H\end{matrix}$	577	7·25	69	95	F 27·99 27·98	$C_{34}H_{36}ClF_{12}N_3O_4$	F 28·00
XV	$N\begin{matrix}C_2H_5\\CH_2(CF_2CF_2)_2H\end{matrix}$	$N\begin{matrix}C_2H_5\\CH_2(CF_2CF_2)_2H\end{matrix}$	$N\begin{matrix}C_2H_5\\CH_2(CF_2CF_2)_2H\end{matrix}$	576	1·31	63	128	F 40·30 40·50	$C_{40}H_{36}ClF_{24}N_3O_4$	F 40·90

ethyl-2-methylbenzothiazolium tosylate in acetic anhydride:



$n = 1$ (**XVII**) λ_{max} 502 nm (ethanol)

$n = 2$(**XVIII**)λ_{max} 493 nm (ethanol)

The styryl dyes **XVI** and **XVII** absorb at shorter wavelengths than those with a dimethylamino group (λ_{max} 530 nm). This shows the lessening of the basicity of the nitrogen atom, bonded with the 1,1-dihydropolyfluoroalkyl radicals. The contribution of a resonance structure with the positive charge on $RNCH_2(CF_2CF_2)_nH$ group is reduced in this case. On the other hand, the styryl dyes **XVI** and **XVII** are coloured substantially deeper than the dye with the $(CF_3)_2N$ group (λ_{max} 366 nm).[1] Growth of a number of difluoromethylene groups leads to the further lessening of basicity. The absorption maximum of the dye **XIII** is shifted to shorter wavelengths by 9 nm in comparison with the dye **XVI**. Nevertheless, $RNCH_2(CF_2CF_2)_nH$ groups show themselves in the triphenylmethane and styryl dyes as a sufficiently strong auxochrome.

3. EXPERIMENTAL

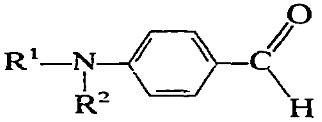
3.1. N,N-*Disubstituted benzaldehydes* (V–VIII)

To dimethylformamide (0·016 mol) phosphorus oxychloride (0·06 mol) is added dropwise with stirring at 0°C and after that amines **I–IV** (0·016 mol) are added in one portion. The reaction mixture is stirred at 100°–110°C for 4 h, cooled, mixed with ice and neutralized with a saturated solution of sodium acetate up to pH 6–8 at 10°–20°C. Benzaldehydes **V–VIII** are extracted with ether, the ethereal solution is dried with sodium sulphate, the solvent is evaporated and the residue is distilled or recrystallized.

Some physical properties, yields and the results of the microanalyses of aldehydes **V–VIII** are summarized in Table 2.

TABLE 2

p-N,N-DISUBSTITUTED BENZALDEHYDES



NN	*R*¹	*R*²	*Yield* (%)	*b.p°C* (*torr*) *m.p.°C* (*hexane*)	*Found* (%)	*Formula*	*Calculated* (%)
I	CH_3	$CH_2CF_2CF_2H$	85	67–68	F 30·49: 30·50	$C_{11}H_{11}F_4NO$	F 31·13
II	CH_3	$CH_2(CF_2CF_2)_2H$	91	78 (0·2)	F 43·03: 43·18	$C_{13}H_{11}F_8NO$	F 43·51
III	C_2H_5	$CH_2CF_2CF_2H$	84	81–82	C 54·33: 54·50 H 4·77; 4·97 F 28·97: 28·56 N 5·50; 5·56	$C_{12}H_{13}F_4NO$	C 54·80 H 4·95 F 28·89 N 5·30
IV	C_2H_5	$CH_2(CF_2CF_2)_2H$	85	82 (0·2) hydrazone 218° (ethanol)	F 41·01: 41·02 F 27·82: 27·99 N 13·50: 13·68	$C_{14}H_{13}F_8NO$ $C_{20}H_{17}F_8N_5O_4$	F 41·84 F 28·00 N 12·89

3.2. *Dyes* IX *and* X

A mixture of Michlers ketone (0·001 mol), aniline (**III** or **IV**) (0·001 mol) and phosphorus oxychloride (5 ml) is heated at 100°C for 5 h. The excess phosphorus oxychloride and unreacted aniline is removed under reduced pressure. The residue is dissolved in water and filtered. The filtrate is acidified with hydrochloric acid and mixed with a concentrated solution of sodium perchlorate. The resulting precipitate is filtered, washed with water, dried, washed with benzene and dried under reduced pressure at 100°C.

3.3. *Dyes* (XI–XV)

A mixture of aniline (**III** or **IV**) (0·002 mol), corresponding aldehyde (0·001 mol) and catalytic amount of concentrated sulphuric acid is heated at 110°C for 4 h. Water (5 ml) is added to the resulting coloured syrupy liquid and the mixture neutralized with ammonia water to pH 6–8. Unreacted reagents are distilled with steam. The leuco base is dissolved in a mixture of acetic and 15% hydrochloric acid (1 : 1) and is oxidized by a theoretical amount of freshly prepared PbO_2. The lead is precipitated with a concentrated solution of sodium sulphate. Then a concentrated solution of sodium perchlorate is added to the filtered solution of the dye. The precipitated crystals of the dye are vacuum filtered, washed with water, dried and washed with benzene–ether mixture (1 : 1) until crystals with a metallic glitter are obtained.

3.4. *Styryl dyes* (**XVI**, **XVII**)

A solution of p-N,N-disubstituted benzaldehyde (**III** or **IV**) (0·001 mol) and 2-methyl-3-ethylbenzothiazolium tosylate (0·001 mol) in acetic anhydride is heated at 110°C for 2·5 h. Acetic anhydride is removed by rotary evaporation *in vacuo*. The residue is dissolved in ethanol and then a saturated solution of potassium iodide is added.

Yield of 2-{2-[4-(N-ethyl-N-1,1,3-trihydroperfluoropropyl)phenyl]ethyl}-3-ethylbenzothiazolium iodide (**XVI**) 77%, m.p. 206–208°C (ethanol). Analysis found (%): F, 13·26; 13·56. Calculated for $C_{22}H_{23}F_4IN_2S$: F, 13·82.

Yield of 2-{2-[4-(N-ethyl-N-1,1,5-trihydroperfluoropentyl)phenyl]ethyl}-3-ethylbenzothiazolium iodide (**XVII**) 71%, m.p. 191–193°C (ethanol). Analysis found (%): F, 22·05; 22·10. Calculated for $C_{24}H_{25}F_8IN_2OS$: F, 22·74.

REFERENCES

1. M. I. Dronkina and L. M. Yagupol'skii, *Zh. Org. Khim.*, **9**, 2167 (1973).
2. G. Kremer, J. Pechmeze and R. Sureau, Fr. pat. 2241590 (1973); C.A. **82**, 172610h (1975).
3. Y. Dickey, E. Towne, M. Bloom, G. Taylor, H. Hill, R. Carbitt, M. McCall and W. Moore, *Ind. Eng. Ch.*, **46**, 2213 (1954).
4. Y. Dickey, E. Towne, M. Bloom, G. Taylor, D. Wallace, I. Sagal, M. McCall and D. Hedberg, *Ind. Eng. Ch.*, **48**, 209 (1956).
5. L. Z. Gandel'sman, V. P. Nazaretyan and L. M. Yagupol'skii, *Zh. Org. Khim.*, **14**, 872 (1978).