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Fluorine-containing Dyes

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The methods of synthesis, properties, and applications of fluorine-containing dyes of all classes are examined. The influence of fluorine atoms and fluorinated substituents on the spectroscopic properties of dyes is discussed. It is shown that the introduction of fluorine-containing substituents makes it possible to obtain dyes which are resistant to oxidation, light, and other physical influences.
The bibliography includes 271 references.

CONTENTS

I. Introduction 993
II. Polymethine dyes 993
III. Diphenylmethane and triphenylmethane dyes 999
IV. Nitrodiphenylamines dyes 1000
V. Azo-dyes 1001
VI. Indigoid and thioindigoid dyes 1003
VII. Benzoquinone, napthoquinone, and anthraquinone dyes 1003
VIII. Phthalocyanine dyes with fluorine-containing substituents 1005

I. INTRODUCTION

The vigorous development of the chemistry of organofluorine compounds and the development of convenient methods for their synthesis[1-7] have made it possible to introduce fluorine atoms and fluorine-containing substituents into the molecules of various organic substances and hence to modify their properties within wide limits. Representatives of all classes of organic dyes with fluorine-containing substituents have now been synthesised. The influence of these substituents on the colour and other properties of the dyes has been investigated and dyes with properties of practical values have been discovered.

This review deals mainly with dyes which make it possible to elucidate the influence of fluorine-containing substituents on their colour and properties. Consideration of the available data will help in the development of a theory of the colour of organic dyes, in the expansion of experimental research in this field, and in the practical utilisation of fluorine-containing dyes.

The review covers the literature up to 1981 inclusive.

II. POLYMETHINE DYES

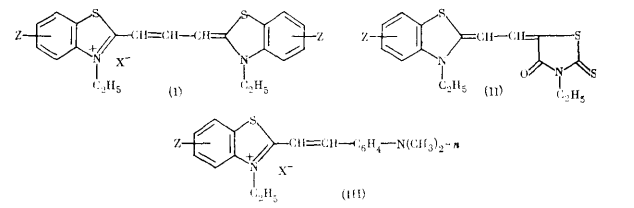
Fluorine-containing cyanine dyes were first synthesised by Kiprianov and Yagupol'skii in 1950.[8] Since then numerous communications dealing with the study of the influence of fluorine atoms and fluorine-containing substituents on the absorption spectra of dyes and their properties have been published. Some fluorine-containing-dyes have found important practical applications as cinefilm photosensitisers.

1. Dyes with Fluorine-containing Substituents in Heterocyclic Nuclei

The influence of fluorine atoms and fluorine-containing substituents in heterocyclic nuclei on the absorption spectra has been studied in detail in relation to benzothiazole derivatives—thiacarbocyanines (I), merocyanines (II), and styryl dyes (III) (Table 1).

Fluorine atoms and fluorine-containing substituents have been introduced into heterocyclic nuclei by methods dealt with in monographs and reviews[1-7]. The dyes (I)–(V) (Tables 1 and 2) were synthesised from the quaternary salts of substituted heterocyclic bases by the usual methods of the chemistry of cyanine dyes.

Table 1. The absorption maxima of dyes (I)–(III) in ethanol.



Z	Dye (I)		Dye (II)		Dye (III)	
	λ, nm	Δλ	λ, nm	Δλ	λ, nm	Δλ
H	558	—	524 [9]	—	530 [8]	—
5-F	562 [9]	4	—	—	—	—
6-F	558 [8]	0	—	—	543 [8]	4
5-CF_3	557 [9]	−1	—	—	540 [9]	10
6-CF_3	561 [10]	3	—	—	548 [10]	18
5,6-$(CF_3)_2$	557 [11]	−1	—	—	—	—
6-CH=$CHCF_3$	582 [12]	24	530 [12]	6	550 [12]	20
6-CF=$CFCF_3$	579 [12]	21	525 [12]	1	556 [12]	26
5-OCF_3	561 [13]	3	—	—	545 [13]	15
6-OCF_3	560 [13]	2	—	—	540 [13]	10
5-SCF_3	560 [14, 15]	2	—	—	543 [13]	13
6-SCF_3	568 [15]	10	—	—	540 [14]	10
5-SO_2CF_3	556 [16]	−2	505 [10]	−19	555 [16]	25
6-SO_2CF_3	575 [10]	17	513 [10]	−11	566 [10]	36
6-$SeCF_3$	570 [17]	12	522 [17]	−2	549 [17]	19
5-$NHCOCF_3$	573 [18]	15	526 [18]	2	—	—
6-$NHCOCF_3$	580 [18]	22	532 [18]	8	—	—
5-$NHSO_2CF_3$	562 [18]	4	—	—	—	—
6-$NHSO_2CF_3$	565 [18]	7	—	—	—	—

Note. Here and in the other Tables the numbers in square brackets denote references (Ed.of Translation).

Monomethine di- and tri-carbothiacyanine dyes with the 6-F,[8] 5-CF_3,[9] 5-SCF_3,[15] and 6-SCF_3 [15] substituents, pentacarbothiacarbocyanines with the 5-CF_3, 6-CF_3, and 5-SO_2CF_3 substituents[19], thiacarbocyanines containing methyl and ethyl groups in the β-position in the chain and the 5-F or 6-F,[8,9]

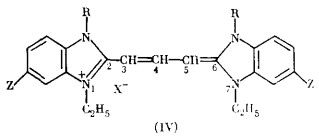
5-CF_3,[9] 5 or 6-OCF_3,[13] 5- or 6-SCF_3,[15] 5- or 6-$NHCOCF_3$,[18] and 6-$SeCF_3$ [17] substituents in the nuclei, and dyes with a condensed 2-trifluoromethyloxazole ring in the 4,5-positions[20] have also been described. Certain asymmetric dyes[8,9,14,15,21,22] as well as thiacarbocyanines with two substituents in the nuclei [5-OCF_3 and 6-X (X = Cl, I, SCH_3, NH_2, or $NHCOCH_3$) [23] and 5,6-OCF_2O [24]] are known.

Fluorine atoms in benzothiazole nuclei have little influence on the absorption spectra of dyes but reduce their basicity[25] and lower the electron-donating capacity[26] (the Brooker basicity[27]) of the heterocyclic residues. The electron-donating capacity of the benzothiazole residues is reduced to an even greater extent under the influence of the electron-accepting substituents CF_3, OCF_3, SCF_3, SO_2CF_3, $NHCOCF_3$, and $NHSO_2CF_3$, which have positive σ_n constants[28]. As a result of this, the electronic asymmetry and the deviation in styryl dyes are reduced, while in merocyanines they are enhanced[26]. Fluorine-containing substituents in styryl dyes and merocyanines give rise respectively to greater and smaller bathochromic or hypsochromic effects than in the symmetrical carbocyanines.

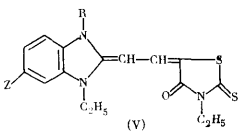
For the dyes (I) substituted in the 6,6'-positions, a correlation has been found between their basicity (pK_a) and the σ_n constants of the substituents[25,29].

Table 2 presents the spectroscopic data for the benzimidazole dyes (IV) and (V).

Table 2. The absorption maxima of dyes (IV) and (V) in ethanol.



(IV)



(V)

R	Z	Dye (IV)		Dye (V)	
		λ, nm	Δλ	λ, nm	Δλ
C_2H_5	H	498 [30]	—	514 [30]	—
C_2H_5	F	502 [30, 31]	4	515 [31]	1
C_2H_5	CF_3	501 [32]	3	515 [30]	1
C_2H_5	$C(CF_3)_3$	504 [33]	6	514 [33]	0
C_2H_5	OCF_3	502 [31]	4	518 [31]	4
C_2H_5	SCF_3	511 [17, 31]	13	520 [30, 31]	6
C_2H_5	$SeCF_3$	510 [17]	12	520 [17]	6
C_2H_5	$SOCF_3$	516 [31, 34]	18	520 [29, 35]	6
C_2H_5	SO_2CF_3	522 [30, 32]	24	524 [30, 31]	10
C_2H_5	SO_2CHF_2	515 [36]	17	519 [36]	5
C_2H_5	$SO_2C_3F_7$	525 [35]	27	525 [37]	11
C_2H_5	$SO_2CF(CF_3)_2$	526 [37]	28	525 [37]	11
C_2H_5	$SO_2C(CF_3)_3$	528 [37]	30	525 [37]	11
C_2H_5	$N(CF_3)_2$	502 [18]	4	514 [18]	0
C_6H_5	H	508 [30, 38]	—	518 [38]	—
C_6H_5	F	512 [31]	4	— —	—
C_6H_5	CF_3	511 [32]	3	511 [32]	—8
C_6H_5	SCF_3	517 [35]	9	520 [35]	1
C_6H_5	$SOCF_3$	520 [35]	12	520 [35]	1
C_6H_5	SO_2CF_3	525 [32]	17	—	—
CF_2CHF_2	H	511 [39, 40]	—	—	—

Dyes of types (IV) and (V) containing the $SO_2CF_2CHF_2$, SO_2CF_2CHClF, $SO_2CF_2CHFCF_3$,[41] $SO_2CH_2CO_2CF_3$,[34] CH=CH–CF_3,[12] CF=CF–CF,[12,30] and N=N–CF_3 [18] substituents in the nuclei and the CF_3CHClF, CF_2CHFCF_3,[39,40] $C_6H_4SO_2.CF_3$-*p*, $C_6H_4CF_3$-*m* [42] substituents at the nitrogen atoms, dyes with two substituents in the 5,6-positions (F,F;[31] CF_3, $COOCH_3$;[38] CF_2OCF_2;[31] OCF_3, Cl;[30] SO_2CF_3, Cl;[30] SO_2CF_3, OCH_3;[30] CF_3, CN [44,45]) and the 5,7-positions (SO_2CF_3, Cl;[43] CF_3, CF_3 [43]), styryl dyes with the CF=CClF or CF=$CFCF_3$ substituents at the nitrogen atom of the benzimidazole ring[40,46], imidadicarbocyanines and imidatricarbocyanines with the SO_2CF_3 groups in the nuclei[35,47], imidacarbocyanines with two chlorine atoms and the CF_3 and SO_2CF_3 groups in the nucleus and the $(CH_2)_nCF_3$ (n = 1–3) group at the nitrogen atom[39,40,48], certain asymmetric dyes with the benzimidazole nucleus containing the CF_3 [22,49] and SO_2CF_3 [50] substituents, imidadicarbocyanine with the SO_2CF_3 substituent in the nucleus and a chlorine atom in the γ-position in the chain[51], and dyes of types (IV) and (V) in which all the hydrogen atoms in the benzene ring have been substituted by fluorine atoms[52] have also been described.

Fluorine-containing substituents are electron acceptors and, after the introduction into the benzene rings of symmetrical imidacarbocyanines (IV), give rise to a bathochromic effect [from 3–4 nm for the fluorine atoms and CF_3 groups to 25–30 nm for the most electron-accepting SO_2CF_3 and $SO_2C.(CF_3)_3$ groups]. The spectroscopic effects of the substituents are then as a rule greater than in the analogous dyes of the benzothiazole series.

The bathochromic effect of electron-accepting substituents in the series of benzimidazole dyes can be explained not only by an increase in the length of the chromophoric system but also apparently by the fact that the conjugation of the substituent with one of the nitrogen atoms of the benzimidazole ring increases the hypsochromic influence of this atom as an electron-donating substituent in the polymethine chain. According to the Förster–Knott–Dewar rule[53,54] (the FKD rule), electron-donating substituents in the even positions of the polymethine chromophore [see the numbering of the atoms in formula (IV)] have a hypsochromic effect on the colour of the dye while electron-accepting substituents have a bathochromic effect. The blue shift of the colour of imidacarbocyanines (IV) compared with the thiacarbocyanines (I) can be explained by the hypsochromic influence of the nitrogen atoms. The introduction of phenyl or polyfluoroalkyl groups (R = C_6H_5, CF_2CHF, etc.) at the nitrogen atoms of the dyes (IV) diminishes the electron-donating hypsochromic influence of the nitrogen atoms and induces a red shift of the colour than for R = C_2H_5.

Fluorine-containing substituents in benzimidazole nuclei as a rule reduce the basicity of the corresponding dyes[25,29] and a correlation is observed between the pK_a and the σ_n constants of the substituents in the nuclei[29].

For dyes containing two substituents in the nucleus, the spectroscopic effects and the pK_a are approximately additive[56,57], but, when steric hindrance displaces one of the substituents from the plane of the benzene ring, the influence of the latter on pK_a and λ_{max} diminishes[57,58].

Linear correlations between the absorption frequencies of the carbonyl groups and the σ_n constants of the substituents in the nuclei have been found for the merocyanine dyes (III) and (V).[59]

The introduction of electron-accepting substituents into the imidacarbocyanine molecule improves its sensitising properties[60]. Among imidacarbocyanines with fluorine-containing substituents (for example, SO_2CF_3), effective sensitisers have been discovered and these have found applications in the cine-photo industry[61].

Table 3 presents the absorption maxima of carbocyanines, merocyanines, and styryl dyes containing pyridine, 4-methylthiazole, quinoline, and 3,3-dimethylindolenine rings. Apart from carbocyanines, perfluoroalkyl-substituted di- and tricarbocyanines and derivatives of pyridine[62], quinoline[64], and indolenine[68] have been described.

Table 3 shows that the bathochromic influence of perfluoroalkyl groups on the absorption spectra of symmetrical carbocyanines is particularly pronounced in dyes where these substituents have been introduced directly into the heterocyclic nucleus. The substituents in condensed benzene rings usually also exhibit a bathochromic effect but it is weaker and in the case of indolenine derivatives they actually have a hypsochromic effect.

Table 3. The absorption maxima of dyes derived from pyridine (P),[62,63] 4-methylthiazole (T),[63] quinaldine (Q),[64–66] lepidine (L),[64,65,67] and 3,3-dimethylindolenine (I).[68]

Heterocyclic nucleus	Substituent		Carbocyanines		Merocyanines		Styryl dyes	
	in nuclei	at nitrogen atoms	λ, nm	Δλ	λ, nm	Δλ	λ, nm	Δλ
P	2-C_3F_7	CH_3	643	43	584	19	—	—
	2-C_3F_7	C_2H_5	645	42	—	—	547	67
	3-C_3F_7	C_2H_5	610	7	567	17	533	53
	2-$(CF_2)_2$Ph	CH_3					526	
T	5-C_3F_7, 4-CH_3	C_2H_5	563	13	524	−15		
Q	4-CF_3	CH_3	637	32	575	7	571	49
	6-F	C_2H_5	612	7	572	4	536	9
	6-CF_3	C_2H_5	608	3	570	2	558	31
	6-OCF_3	C_2H_5	610	5	—	—	548	21
	6-SCF_3	C_2H_5	617	12	568	0	560	33
	6-SO_2CF_3	C_2H_5	623	18	—	—	586	59
L	2-CF_3	CH_3	731	25	588	28	632	86
	6-F	C_2H_5	718	7	625	11	564	18
	6-CF_3	C_2H_5	717	6	621	7	580	34
	6-OCF_3	C_2H_5	720	9			576	30
	6-SCF_3	C_2H_5	730	19	618	4	586	40
	6-SO_2CF_3	C_2H_5	745	34	618	4	626	80
I	4CF_3	CH_3	540	−8	—	—	—	—
	5-CF_3	CH_3	542	−6	—	—	—	—
	6-CF_3	CH_3	539	−9	—	—	—	—
	5-SCF_3	CH_3	552	+4	—	—	570	25
	5-SO_2CF_3	CH_3	556	+8	—	—	581	36
4,5-Benzo-I	H	$CH_2CF_2CF_2H$	596	+48*	—	—	—	—
	6-CF_3	CH_3	580	−14	—	—	572	14
	6-SCF_3	CH_3	579	−15	—	—	573	15
	6-SO_2CF_3	CH_3	572	−22	—	—	576	18

*Δλ is quoted relative to the dye with the NCH_3 group.

The bathochromic effect of substituents increases when their electron-accepting properties are enhanced. The most electron-accepting group SO_2CF_3 in the 6,6′-positions of the lepidine and quinaldine dyes displaces the absorption bands towards longer wavelengths by 34 and 18 nm respectively.

Comparison of the spectroscopic effects of substituents in dyes with different heterocyclic nuclei (Table 4) shows that these effects are minimal in indolenine derivatives, increase on passing to benzothiazole, benzimidazole, and 2-quinoline derivatives, and are maximum in dyes derived from 4-quinoline.

Table 4. The spectroscopic effects (Δλ) of the fluorine-containing substituents Z in the *p*-position relative to the nitrogen atom.

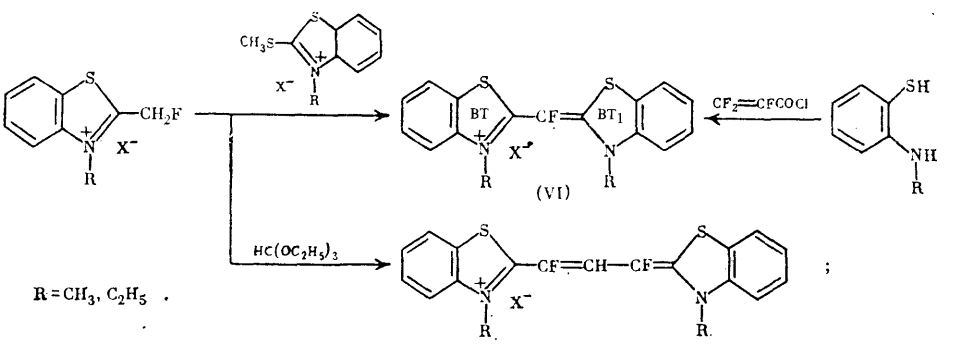
Z	I		BT			BI			Q			L		
	S	C	S	C	M	S	C	M	S	C	M	S	C	M
F	—	—	4	0	—	—	4	1	9	7	4	18	7	11
CF_3	—	−6	18	3	—	—	3	1	31	3	2	34	6	7
OCF_3	—	—	10	2	—	—	4	4	21	5	—	30	9	—
SCF_3	25	4	10	10	—	—	13	6	33	12	0	38	10	4
SO_2CF_3	26	8	36	17	−11	53	18	10	59	18	—	80	34	4

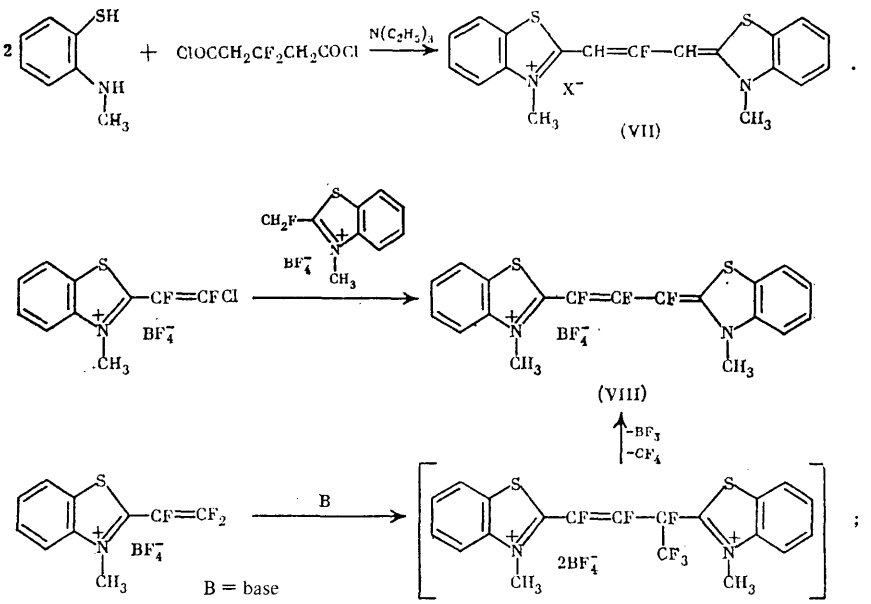
Notation. The following abbreviations for heterocyclic nuclei are used in Tables 4–7 in the names and formulae of the dyes: BT = benzothiazole, BO = benzoxazole, BI = benzimidazole, BS = benzoselenazole, I = indolenine, Q = quinaldine, L = lepidine, R = ethyl- or methyl-rhodanine; the same abbreviations combined with the numeral 1 represent heterocyclic residues in their electron-donating form [see, for example, the formula of dye (VI) in the text]; S = styryl dye; C = carbocyanine; M = merocyanine (derivative of *N*-ethylrhodanine).

Merocyanine dyes, derived from rhodanine, usually exhibit positive solvatochromism, i.e. in polar solvents (alcohols) they have a colour corresponding to a lower frequency than in non-polar (benzene) or less polar (chloroform) solvents[62–67]. However, merocyanines with a benzimidazole nucleus, which exhibit negative solvatochromism, are exceptions[30,31].

2. Dyes with Fluorine-containing Substituents in the Polymethine Chain

The influence of substituents in the polymethine chain on the colour of cyanine dyes has been studied in particular detail in relation to derivatives of benzothiazole. Dyes with a fluorine atom in the α-position in the chain have been synthesised from quaternary 2-fluoromethylbenzothiazolium salts[69] by reactions usually employed to obtain cyanine dyes[69–72]. The dye (VI) can also be synthesised by the reaction of trifluoroacryloyl chloride with *N*-ethyl-*o*-aminothiophenol[73]:





β-Fluorothiacarbocyanine (VII) has been synthesised by the condensation of the dichloride of β,β-difluoroglutaric acid with *N*-methyl-o-aminothiophenol: [74]

The synthesis of α,β-difluoro-substituted dyes has been achieved with the aid of 2-trifluorovinyl or (better) β-chloro-difluorovinyl-benzothiazole and the corresponding quaternary salts [75,76,79]. A dye with a fully fluorinated polymethine chain, namely α,β,γ-trifluorothiacarbocyanine (VIII), has been obtained from the same compounds [76,77,79]:

Other dyes containing fluorine atoms in the polymethine chain have been obtained by analogous procedures (Table 5).

The fluorine atoms in the polymethine chain influence the absorption spectra of the dyes to a much greater extent than those in the heterocyclic nuclei. The influence of the fluorine atom on the spectrum depends on its position in the chain: the introduction of fluorine atoms in the α- and α,γ-positions shifts the absorption band towards longer wavelengths, while the introduction of a fluorine atom in the β-position causes a hypsochromic shift. In conformity with the FKD rule, the electron-donating substituent exerts such an influence [84,85]. Consequently a fluorine atom in the polymethane chain behaves as an electron-donating substituent, which can be explained by the fact that the conjugation of the substituents in the chain exerts a stronger influence on the absorption spectra of the dyes than the inductive effect [84–86].

The introduction of a fluorine atom in the α-position in the heterocyclic residue enhances its electron-donating properties, which entails an increase of the deviation [from coplanarity?] in styryl dyes and a decrease of Δλ (compared with the effect in the symmetrical carbocyanine), while in merocyanine dyes the deviation diminishes and the bathochromic effect of the fluorine atom increases.

The thiacarbocyanine with a fully fluorinated polymethine chain absorbs light at longer wavelengths than the unsubstituted dye and its absorption intensity is higher, which indicates the possibility, in principle, of the existence of a new type of polymethine dyes with fully fluorinated chains.

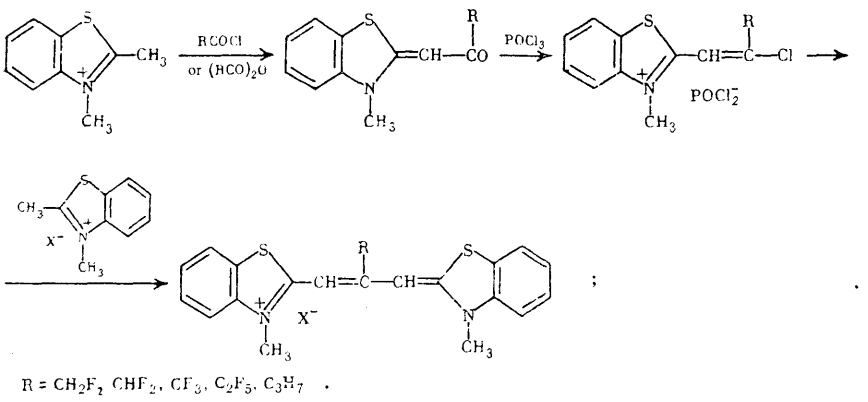
Fluoroalkyl substituents have been introduced only in the β-position of the polymethine chains of cyanine dyes.

Table 5. The absorption maxima of cyanine dyes containing fluorine atoms in the chain.

Formula of dye	λ, nm	Δλ
BT–CF=BT$_1$	453 [69, 73]	30
BT*–CF=CH–CH=BT$_1$	567 [72]	9
BT–CF=CH–CH=BT$_1$	575 [71, 78]	17
BT*–CH=CF–CH=BT$_1^{\dagger}$	522 [74]	—36
BT*–CF=CH–CF=BT$_1^{\dagger}$	592 [70]	34
BT–CF=CH–CF=BT$_1$	605 [69]	47
BT*–CF=CF–CH=BT$_1^{\dagger}$	545 [72, 79]	—13
BT–CF=CF–CH=BT$_1$	547 [71]	—11
BT*–CF=CF–CF=BT$_1^{\dagger}$	578 [76, 79]	20
BT–CF=CH–CH=CH–CF=BT$_1$	703 [69]	53
BT–CH=CH–CF=CH–CH=BT$_1$	666 [80]	16
BT*–CF=CH–C$_6$H$_4$N(CH$_3$)2-*p*	525 [70]	—3
BT–CF=CH–C$_6$H$_4$N(CH$_3$)2-*p*	532 [69]	2
BT–CF=CF–C$_6$H$_4$N(C$_2$H$_5$)2-*p*	530 [71]	0
BT$_1^{\dagger}$=CF–CH=R	547 [70]	23
BT*–CF=CH–CH=CH–C$_6$H$_4$N(CH$_3$)2-*p*	570 [81]	—2
BO*–CF=CH–CH=BO$_1^{\dagger}$	500 [82]	18
BO*–CF=CH–CF=BO$_1^{\dagger}$	517 [82]	35
BO–CF=CH=CF=BO$_1$	518 [82]	35
BO–CF=CH–C$_6$H$_4$N(CH$_3$)2-*p*	492 [82]	—4
BO$_1$=CF–CH=R	513 [82]	21
Q*–CF=CH–CH=Q$_1$	640	35
Q–CH=CH–CF=CH–CH=Q$_1$	717 [80, 83]	7
H–CH=CH–CF=CH–CH=I$_1$	654 [80, 83]	18
BS–CH=CH–CF=CH–CH=BS$_1$	675 [80]	15

*Methyl groups are attached to the nitrogen atoms of the heterocycles; in the remaining cases the nitrogen atoms are combined with ethyl groups.

The thiacarbocyanine and selenacarbocyanine with the CH_2F group in the β-position have been obtained by the condensation of the corresponding quaternary salts with the iminoester of monofluoroacetic acid [71]. Acylmethylene derivatives and the β-chloroalkenyl-substituted quaternary salts of nitrogen-containing heterocycles have been used to synthesise dyes with other fluoroalkyl groups in the β-position, for example [74]:



R = CH_2F, CHF_2, CF_3, C_2F_5, C_3H_7 .

Dyes containing simultaneously fluorine atoms and trifluoromethyl groups in the chain have been synthesised analogously[87] (Table 6).

Table 6. The absorption maxima of cyanine dyes with fluoroalkyl groups in the polymethine chain.

Formula of dye	λ, nm (ethanol)	Δλ
BT* – CH = C(CH_3) – CH = BT†	540 [88]	—18
BT* – CH = C(CH_2F) – CH = BT†	548 [69]	—10
BT* – CH = C(CHF_2) – CH = BT†	568 [74]	10
BT* – CH = C(CF_3) – CH = BT†	581 [74]	23
BT* – CH = C(C_2F_5) – CH = BT†	590 [74]	32
BT* – CH = C(C_3F_7) – CH = BT†	593 [74]	35
BO* – CH = C(CF_3) – CH = BO†	525 [82]	43
Q – CH = C(CH_3) – CH = Q_1	649 [89]	43
BT_1 = CH – C(CH_3) = R	532 [90]	11
BT_1 = CH – C(CH_2F) = R*	538 [74]	17
BT_1 = CH – C(CHF_2) = R*	549 [74]	28
BT_1 = CH – C(CF_3) = R*	555 [74]	34
BT_1 = CH – C(CF_3) = R*	486 [74]	—25
BT* – CF = C(CF_3) – CH = BT†	627 [87]	69
BO* – CF = C(CF_3) – CH = BO†	556 [82]	74
BT* – C(OCH_3) = C(CF_3) – CH = BT†	624 [87]	66
BT† = CF – C(CF_3) = R*	597 [87]	76
BT* – CF = C(CF_3) – C(OH) = BT†	672 ** [91]	114
BT* – C(OCH_3) = C(CF_3) – C(OH) = BT_1^*	644 ** [91]	86
BT* – CF = C(CN) – CH = BT†	630 ** [92]	74
BT* – C(CN) = CF – CH = BT†	495 ** [92]	—61
BT* – C(CF_3) = CH – $C_6H_4N(CH_3)_2$-p	495 [93]	—53
BT – CH = C(CF_3) – $C_6H_4N(CH_3)_2$-p	530 [93]	2

*See the footnote to Table 5.
**In nitromethane; dyes with the cyano-group are quoted for comparison.

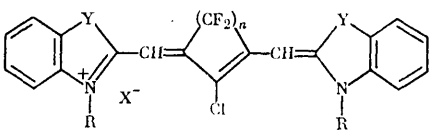
Electron-accepting substituents in the β-position of the polymethine chain of cyanine dyes should exert a bathochromic influence according to the FKD rule. Indeed, the electron-accepting trifluoromethyl groups cause a bathochromic shift of the absorption bands.

Table 6 shows that successive substitution of the hydrogen atoms in the methyl group by fluorine atoms entails a gradual bathochromic shift of the absorption maxima of thiacarbocyanines and merocyanines. In the series of thiacarbocyanines the CH_3 and CH_2F substitutents exhibit hypsochromic effects, while CHF_2, CF_3, C_2F_5, and C_3F_7 exhibit gradually increasing bathochromic effects. A correlation between the absorption frequency and the σ_i and σ_c constants of the substituents has been found for thiacarbocyanines containing substitutents in the β-position[84].

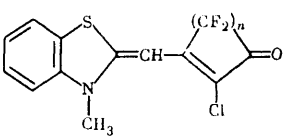
The fluoroalkyl groups in merocyanine dyes derived from benzothiazole exhibit a bathochromic effect, which reflects their electronic and steric influences. The steric hindrance generated by these substituents causes rotation of the predominantly double bond, which entails a bathochromic shift of the absorption bands[74]. In the analogous benzimidazole dye, in which a delocalised ionic structure predominates, the steric hindrance caused by the trifluoromethyl group is responsible for rotation about the predominantly single bond and therefore gives rise to a hypsochromic effect[74].

A spectroscopic effect of the interaction of the substituents is characteristic of cyanine dyes containing electron-donating substituents (fluorine atoms and methoxy-groups) in the α-position of the chain and electron-accepting substituents (trifluoromethyl or cyano-groups) in the β-position: the shift of the absorption band under the influence of two substituents of opposed electronic types exceeds the sum of the shifts induced by the individual substituents in the corresponding monosubstituted dyes[87,91,92]. The bathochromic influence of two electron-donating substituents (F, OH and OCH_3, OH) in the α,γ-positions and of one trifluoromethyl group in the β-position is particularly pronounced (in excess of 100 nm) (Table 6).

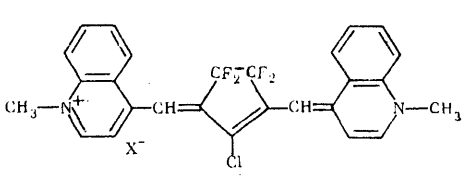
Cyanine dyes containing fluorinated rings in the polymethine chain have been described recently[94,95]:



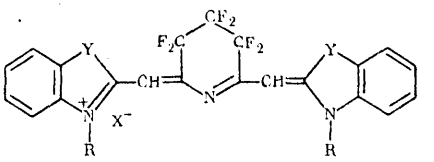
R	Y	n	λ, nm	$\Delta\lambda^*$
CH_3	S	2	660	10
C_2H_5	CH=CH	2	700	-10
C_2H_5	CH=CH	3	758	48



n	λ, nm
2	471
3	500



λ = 773 nm, $\Delta\lambda^*$ = -40 nm



R	Y	λ, nm	$\Delta\lambda^*$
CH_3	CMe_2	572	
CH_3	S	573	9
C_2H_5	CH=CH	621	25

*relative to the dye unsubstituted in the chain.

The fluorinated bridges in the polymethine chains of these dyes can be regarded as electron-accepting perfluoroalkyl substituents, which usually exert a bathochromic influence in conformity with the FKD rule. A hypsochromic influence is observed only in the case of sterically hindered quinoline dyes.

3. Aromatic Azomethines and Azacyanines

The influence of fluorine atoms, trifluoromethyl groups, and other fluorine-containing substituents in the chains of azomethines and azacyanines has been investigated (Table 7). The azomethines (IX) and (X) have been synthesised in accordance with the scheme[96]

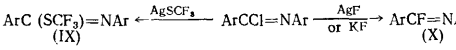
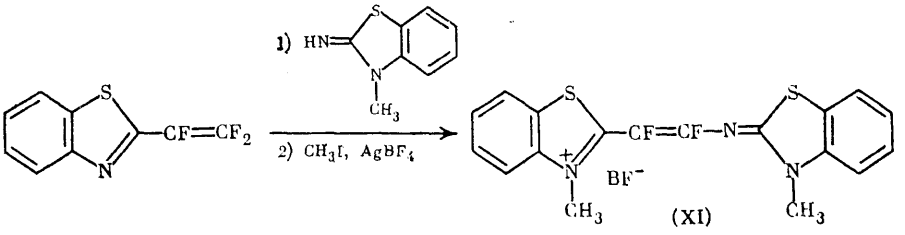


Table 7. The absorption maxima of azomethines and azacyanines with fluorine-containing substituents in the chain.

Formula	λ_{max}, nm (hexane)	$\Delta\lambda$
p-$(CH_3)_2NC_6H_4$-CH = CH-$C_6H_4SO_2CHF_2$-p	400 [100]	60
p-$(CH_3)_2NC_6H_4CH = NC_6H_4SO_2CHF_2$-$p$	385 [100]	30
p-$F_2CHSO_2C_6H_4CH = NC_6H_4N(CH_3)_2$-$p$	430 [100]	55
p-$F_2CHSO_2C_6H_4CH = NC_6H_5$	332 [100]	20
p-$(CH_3)_2NC_6H_4CH = NC_6H_4SO_2CF_3$-$p$	395 [100]	40
p-$(CH_3)_2NC_6H_4CH$ = CH-CH = $NC_6H_4SO_2CHF_2$-p	410 [100]	
$C_6H_5CF = NC_6H_5$	285 [96, 101]	—27
$C_6H_5C(CF_3) = NC_6H_5$	322 [96, 101]	10
$C_6H_5C(SCF_3) = NC_6H_5$	323 [96, 101]	11
p-$O_2NC_6H_4C(CF_3) = NC_6H_4N(CH_3)_2$-$p$	412 [102]	—38
p-$(CH_3)_2NC_6H_4C(CF_3) = NC_6H_4NO_2$-$p$	365 [102]	—40
p-$O_2NC_6H_4CF = NC_6H_4OCH_3$-$p$	361 [102]	—14
p-$CH_3OC_6H_4CF = NC_6H_4NO_2$-$p$	310 [102]	—37
BT-CH = CF-N = BT_1	451 * [98]	—16
BT-CF = CF-N = BT_1	477 * [97, 99]	10
BT-CF = C(CN)-N = BT_1	514 * [98]	47
BT-CH = (CF_3)-N = BT_1	453 [99]	—14
BT-CH = $C(C_2F_5)$-N = BT_1	439 [99]	—28
BT-CH = $C(C_3F_7)$-N = BT_1	437 [99]	—30
BT-CF = $C(CF_3)$-N = BT_1	460 [99]	—7

*In nitromethane.



Y = F, Cl ;

$R = CF_3, C_2F_5, C_3F_7$.

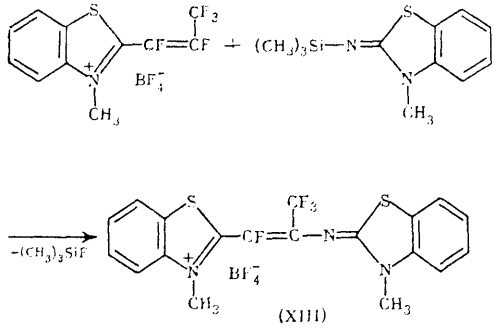
Azomethines with a CF_3 group have been synthesised by the Wittig–Staudinger reaction[96]:

$$ArCOCF_3 + (C_6H_5)_3P{=}NAr \rightarrow ArC(CF_3){=}NAr \ .$$

The azacyanine (XI) with two fluorine atoms in the chain has been obtained from 2-trifluorovinylbenzothiazole[97]: see page 998.

The dyes (XII) with perfluoroalkyl groups in the chain have been synthesised with the aid of the corresponding quaternary benzothiazolium salts[98,99]: see page 998.

The dye (XIII) has been obtained in accordance with the scheme[99]



More complex azomethines with fluorine atoms and trifluoromethine groups in the aromatic nuclei[103] as well as triazacyanines with CF_3 groups in the heterocyclic nuclei[104] have been described. Certain azomethine dyes with CF_3 groups in the nuclei are used in the dyeing of polyester fibres[105,106]. The SO_2CHF_2 and SO_2CF_3 groups in aromatic nuclei have a marked bathochromic effect on the colour of azomethines. The introduction of a fluorine atom in the azomethine groups entails a hypsochromic shift of the absorption bands. The absorption intensity then increases, since the non-planar azomethine molecule usually approaches coplanarity more closely under these conditions[101]. This is probably caused by the fact that the fluorine atom is involved in conjugation with the azomethine linkage. The introduction of a CF_3 group at the methine carbon atom results in a bathochromic effect and reduces the light absorption intensity, since this group gives rise to steric hindrance and enhances the non-coplanarity of the molecule[102].

The sequence in which the ability of the groups to transmit conjugation (to effect the displacement of electrons from left to right) diminishes has been established by comparing the absorption maxima of azomethines containing various substituents in the chain[102]:

$$N{=}CH > N{=}C(CF_3) > CH{=}N > C(CF_3){=}N \text{ and } N{=}CF > N{=}CH > CH{=}N > CF{=}N \ .$$

The fluorine atoms in the chains of azacyanines influence the colour like electron-donating substituents, in conformity with the FKD rule, but their spectroscopic effects are weaker than in thiacarbocyanines[97–99]. The influence of perfluoroalkyl groups in the β-position in azathiacyanines depends mainly on the steric hindrance generated by them, which induces rotation of the predominantly single C–N bonds and hence a hypsochromic shift of the absorption bands[99].

III. DIPHENYLMETHANE AND TRIPHENYLMETHANE DYES

1. Diphenylmethane Dyes

Diphenylmethane dyes containing a fluorine atom or fluoroalkyl groups at the methine carbon atom (compounds XIV, a–d) have been synthesised[86].

A dye with a fluorine atom has been obtained by treating Michler's ketone with difluorophosgene:

$$p\text{-}(CH_3)_2NC_6H_4\underset{\underset{O}{\|}}{C}C_6H_4N(CH_3)_2\text{-}p \xrightarrow{COF_2} (CH_3)_2N{-}\langle\rangle{-}CF{=}\langle\rangle{=}\overset{+}{N}(CH_3)_2 \ .$$
(XIVa) X^-

The dyes (XIV, b–d) with R = CHF_2, CF_3, and C_3F_7 have been obtained from the corresponding carbinols (XV):

$$p\text{-}(CH_3)_2NC_6H_4\underset{\underset{O}{\|}}{C}R \xrightarrow{BrMgC_6H_4N(CH_3)_2\text{-}n} p\text{-}(CH_3)_2NC_6H_4\underset{OH}{\overset{|}{C}}R \times$$

$$\times\ C_6H_4N(CH_3)_2\text{-}p \xrightarrow{SOCl_2} (CH_3)_2N{-}\langle\rangle{-}CR{=}\langle\rangle{=}\overset{+}{N}(CH_3)_2$$
(XV) (XIV, b–d) Cl^-

R	H	F	Cl	CH_2F	CF_3	C_3F_7	CN
λ_{max}, nm	607	588	626	665	693	703	716
Δλ, nm	0	−19	19	58	86	96	109

In accordance with the FKD rule, electron-donating substituents have a hypsochromic effect on the colour compared with the unsubstituted dye, while electron-accepting groups have a bathochromic effect. A fluorine atom at the methine carbon atom influences the absorption spectra like an electron-donating substituent, analogously to its influence in the chains of polymethine dyes. Like the cyano-group, fluoroalkyl groups give rise to a strong bathochromic shift of the absorption maximum. A correlation equation relating the absorption frequencies of the dyes to the electronic nature of the substituents (their σ_i and σ_c constants) has been found[86]. The conjugation effects of the substituents R have a preferential influence on the colour. Bulky substituents, for example the CF_3 group, lead to the breakdown of the coplanarity of the dye molecule, reducing the absorption intensity.

The bis(*p*-dimethylaminophenyl)trimethine dye with one or two fluorine atoms in the chain has been synthesised[107]:

$$(CH_3)_2N{-}\langle\rangle{-}\overset{6}{C}{=}\overset{7}{C}{-}\overset{8}{C}{=}\langle\rangle{=}\overset{+}{N}(CH_3)_2 \ X^-$$
(R, R^1, R^2 = H, H, H; F, H, H; F, F, H)

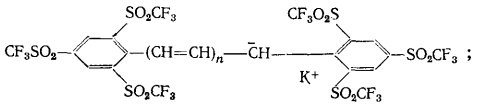
	R	R^1	R^2	$\lambda(CH_3NO_2)$, nm	Δλ
	H	H	H	700	—
(XVI)	F	H	H	693	−7
(XVII)	F	F	H	746	+26

The dye (XVII) has been synthesised in accordance with the scheme

$$p\text{-}(CH_3)_2NC_6H_4CF{=}CFCl \xrightarrow[2.\ n\text{-}(CH_3)_2NC_6H_4CHO]{1.\ BuLi} \text{(XVII)} \ .$$

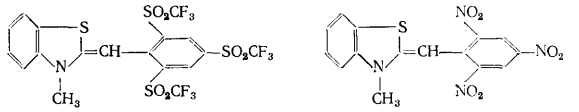
A fluorine atom in the chains of vinylene homologues of diphenylmethane dyes influences the colour like an electron-donating substituent, in conformity with the FKD rule: its effect on the colour is hypsochromic in the even positions within the chain and bathochromic in the odd positions. Both diphenylmethane and polymethine dyes of a new type with a

conjugated anion have been synthesised[108]:



λ_{max}=590 (n=0), 640 (n=1) nm (ethanol).

The analogous anionic dye with nitro-groups absorbs at longer wavelengths (at 622 nm for n = 0), since the SO_2CF_3 group, which is difficult to polarise, is a weaker auxochrome than the nitro-group[108]. This is also evident in relation to the following dyes[109]:

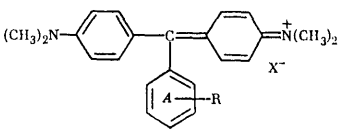


λ_{max} = 504 nm (benzene) λ_{max} = 522 nm (benzene)

2. Triphenylmethane Dyes

Triphenylmethane dyes (analogues of Malachite Green) containing a fluorine atom or a CF_3 group, have been obtained by the Grignard reaction[110,111]. The introduction of the CF_3 group increase the light stability[111]. Crystal Violet with a trifluoromethyl group in the m-position in one of the rings has been synthesised analogously[110].

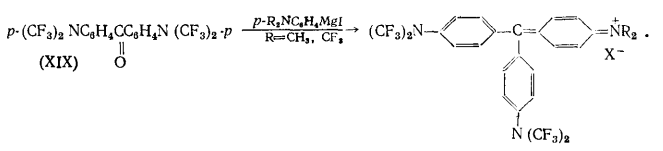
Derivatives of Malachite Green containing one or two trifluoromethylgroups in the A ring [compound (XVIII)] absorb at a lower frequency, like the dyes with an NO_2 group, than the unsubstituted dye[111–113]:



(XVIII)

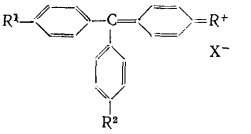
R	4-CH_3	H	3-CF_3	4-CF_3	4-NO_2	3,5-$(CF_3)_2$	F_5
λ_{max}, nm	616	621	634	637	645	647	658
$\Delta\lambda$	—5	0	13	16	24	26	37

Triphenylmethane dyes containing two trifluoromethyl groups at the nitrogen atom have been synthesised[115]. The analogue of Crystal Violet with one $N(CF_3)_2$ group has been obtained from p-chloro-N,N-bis(trifluoromethyl)aniline and Michler's ketone by treatment with metallic sodium. A fluorine-containing analogue of Michler's ketone (XIX) has been used to obtain dyes with two and three $N(CF_3)_2$ groups:



The replacement of one $N(CH_3)_2$ group in the Crystal Violet by $N(CF_3)_2$ leads to a bathochromic shift of the long-wavelength absorption band by 42 nm. Further substitution of the $N(CH_3)_2$ groups by $N(CF_3)_2$ increases significantly the absorption frequency of the dyes, since the bis(trifluoromethyl)amino-group is a very weak auxochrome[115]. Triphenylmethane dyes containing 2,2,2-trifluoroethyl groups at the nitrogen atom in one or two rings have been proposed for the dyeing of polyacrylonitrile fibre[116].

Triphenylmethane dyes containing one and three $C_2H_5NCH_2.(CF_2CF_2)_nH$ groups, where n = 1, 2, have been synthesised[117]. The absorption maxima of such dyes with n = 1 and 2 hardly differ. The accumulation of the $C_2H_5NCH_2(CF_2CF_2)_nH$ groups in the dye causes a hypsochromic shift of the absorption maximum, although dyes with one such group absorb at a lower frequency, as in the case of $N(CF_3)_2$, than Crystal Violet. The $C_2H_5NCH_2(CF_2CF_2)_nH$ groups are fairly powerful auxochromes, which has been demonstrated also in relation to styryl dyes[117]:

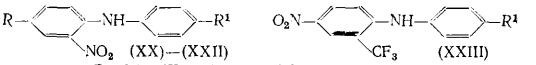


R	R^1	R^2	λ_{max}, nm
$(CH_3)_2N$	$(CH_3)_2N$	$C_2H_5NCH_2CF_2CF_2H$	540, 594
$(CH_3)_2N$	$C_2H_5NCH_2CF_2CF_2H$	$C_2H_5NCH_2CF_2CF_2H$	540, 580
$C_2H_5NCH_2CF_2CF_2H$	$C_2H_5NCH_2CF_2CF_2H$	$C_2H_5NCH_2CF_2CF_2H$	578

IV. NITRODIPHENYLAMINE DYES

Nitrodiphenylamine dyes containing fluorinated groups have found applications as yellow disperse dyes for artificial and synthetic fibres. Dyes of this type have been obtained by the condensation of substituted chlorobenzenes containing the CF_3,[118–120] CF_3CO,[121] or CF_3SO_2 [119,122] groups with arylamines.

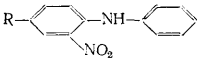
The dyes (XX)–(XXIII) produce yellow coloure on acetate silk and Lavsan with a high stability in relation to light soap, and sublimation[121,124,125]:



(XX)–(XXII) (XXIII)

R=CF_3 (XX), SO_2CF_3 (XXI), $COCF_3$ (XXII);
R^1=H, CH_3O, C_2H_5O, Cl, CH_3, $NHCOCH_3$.

The fastness to light of trifluoroacetophenone (XXII) derivatives reaches 7 units, which is lower by 1–2 units than for the corresponding acetophenone derivatives; the stabilities in relation to soap, friction, and sublimation are different. The nitrodiphenylamine dye (XX, R = H) has a higher light stability than its isomer with the NO_2 group in the p-position[126]. The introduction of a second nitro-group into the dye (XX, R = H) in the 6-position lowers the fastness to light[127]. Electron-donating substituents R in 2-R-4-NO_2- and 4-R-2-NO_2-diphenylamines produce a bathochromic shift of the long-wavelength band, while electron-accepting substituents give rise to a hypsochromic shift of the absorption maximum[120,128,129]. Such influence of the substituents is consistent with the FKD rule:



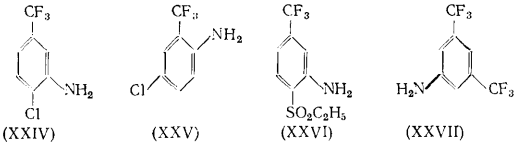
R	CH_3O	H	CF_3CO	CF_3	CF_3SO_2	NO_2
λ_{max}, nm (alcohol)	465	425	417 (benzene)	410	397	353
$\Delta\lambda$	40	0	—8	—15	—28	—72

The substituents R^1 in the dyes (XX) and (XXIII) have an analogous influence, but it is weaker than that of the substituent R.

Nitrodiphenylamine dyes exhibit positive solvatochromism, for example, for the dye (XX, R = H), λ_{max} is 432 nm in water, 410 nm in alcohol, and 401 nm in hexane.

V. AZO-DYES

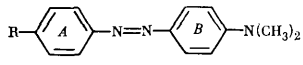
Azo-dyes with fluorine-containing substituents constitute a large group of disperse, cold, cationic, and active dyes. They are used to dye natural, artificial, and synthetic fibres and frequently exhibit a high stability in relation to light, oxidation, and other physical and chemical influences. Fluorine-containing substituents have been introduced into both diazo- and azo-components. The methods for their introduction have been satisfactorily developed[6,7,132]. The azoamines (XXIV)–(XXVII) with a trifluoromethyl group are used for the cold dyeing of cotton[130,131]. They are manufactured on an industrial scale.



(XXIV) (XXV) (XXVI) (XXVII)

These amines give rise to brilliant fast orange and red colours. The dyes based on the azoamines Brilliant Orange K (XXIV) and Brilliant Yellow G (XXV) are particularly brilliant and light-fast.

Table 8. The absorption maxima of dimethylaminoazo-dyes and their salts[133–137]

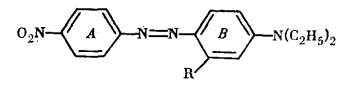


R	λ_{max}, nm		$\Delta\lambda$*	R	λ_{max}, nm		$\Delta\lambda$
	alcohol	alcohol + HCl			alcohol	alcohol + HCl	
CH_3O	497	555	148	CF_3	427	505	78
CH_3S	420	555	135	$(CF_3)_3CS$	444	512	68
CH_3	467	533	126	CHF_2SO	445	511	66
H	407	518	111	CF_3SeO	448	510	62
F	407	518	111	CF_3SO	447	507	60
Cl	417	522	105	$(CF_3SO_2)_2N$	449	507	58
CF_3O	419	512	93	CHF_2SO_2	463	503	40
CHF_2S	429	520	91	FSO_2	463	498	35
CF_3Se	430	517	87	NO_2	475	508	33
CF_3S	432	514	82	CF_3SO_2	476	500	24
CF_3SO_2O	424	508	84	$(CF_3)_3CSO_2$	485	500	15

*$\Delta\lambda = \lambda_{max}$(alcohol + HCl) − λ_{max}(alcohol).

Table 8 lists the absorption maxima of dimethylaminoazobenzenes (DAAB), containing fluorinated groups in the diazo-component of the dye. The absorption maxima of DAAB with electron-donating substituents give rise to a bathochromic shift of the absorption maximum, which is greater the more pronounced the electron-accepting properties. A fluorine atom does not influence the absorption spectrum. The CHF_2SO_2 and FSO_2 groups have effects similar to that of the NO_2 group, while the CF_3SO_2 and $(CF_3)_3CSO_2$ groups have a more marked influence and are the most powerful electron acceptors. When the molecules of azo-dyes are excited by light, electrons are displaced from the *B* ring to the azo-group and the *A* ring. Electron-accepting groups in the *A* ring and electron-donating groups in the *B* ring therefore as a rule cause a bathochromic shift in the colour of azo-dyes. The excitation of the molecules of salts of azo-dyes is accompanied by an electron shift in the opposite direction.

The absorption maxima of azo-dyes in an acid medium undergo a bathochromic shift after the introduction of electron-donating substituents into the *A* ring and electron-accepting substituents into the *B* ring (Table 8).[133,138,139] The influence of substituents in the *B* ring is illustrated below:



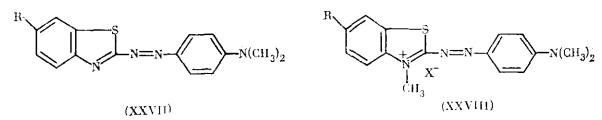
	R	CH_3O	CH_3	H	F	NO_2	CF_3	CN
λ_{max}, nm	alcohol	501	497	486	469	470	467	472
	alcohol + HCl	486	513	515	505	514	530	550
	$\Delta\lambda$	−15	16	29	36	44	63	78

(The difference between the absorption maxima of the DAAB derivatives and their salts is an indication of the halochroism of azo-dyes. It is linearly related to the Hammett σ constants of the substitutents:

$$\Delta\lambda = 125-101\sigma_p \ (r = 0.997); \quad \Delta\lambda = 115-70\sigma_m \ (r = 0.986).$$

Analogous equations have been obtained for *N*,*N*-di-(hydroxyethyl)aminoazo-dyes[133] and the bases of diazastyryl dyes (XXVII).[140]

The influence of substituents in the 6-position of the benzothiazole ring on the colour of the bases (XXVII) and the diazastyryl dyes (XXVIII)[140] is analogous to their influence in DAAB and their salts:

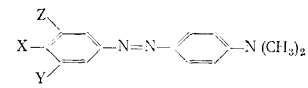


(XXVII) (XXVIII)

	R	CH_3O	CH_3	H	CF_3O	CF_3	CF_3S	CF_3SO	NO_2	CF_3SO_2
	alcohol	511	510	509	518	526	529	536	548	546
λ_{max}, nm	alcohol + HCl	610	600	508	596	598	588	584	584	562
	$\Delta\lambda$	99	90	89	78	62	59	51	36	16

The curves and the absorption maxima for the diazastyryl derivatives (XXVIII) and the hydrochlorides of the bases (XXVII) do not differ. This shows that the proton adds to the nitrogen atom in the benzothiazole ring and not the azo-group. Despite the difference between the structures of the diazastyryl dyes and DAAB, the influence of their substituents is of the same type.

The introduction of electron-donating substituents into DAAB leads to high values of $\Delta\lambda$ (Table 8). These dyes possess indicator properties. Lower values of $\Delta\lambda$ correspond to electron-accepting substituents. Such dyes are less halochromic and more suitable for the dyeing of fabrics and they are resistant to the gases in smoke. The introduction of highly electron-accepting fluorine-containing groups into the DAAB molecule makes it possible to observe the influence of negative halochroism—a hypsochromic shift of the absorption maximum in an acid medium[138]:



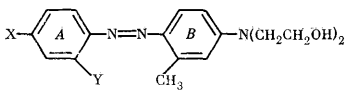
X	Y	Z	λ_{max}, nm		$\Delta\lambda$
			alcohol	alcohol + HCl	
NO_2	CF_3	—	487	503	16
CF_3	CF_3	CF_3	493	493	0
CH_3SO_2	CF_3SO_2	—	497	494	−3
CF_3SO_2	NO_2	—	522	490	−32

The negative halochroism can be explained by the fact that, in the case of strong electron-accepting substituents, the boundary resonance structures of the dye base approach energetic equivalence. Such dyes absorb at low frequencies.

After the introduction of electron-accepting substituents into the dye salts, there is a sharp increase of the contribution of the structure (which is dominant in any case) having a positive charge on the nitrogen atom of the dialkylamino-group, which causes a hypsochromic shift in the colour of the dye compared with the colour in a neutral medium.

A valuable quality of many fluorine-containing azo-dyes is high fastness to light in which the position and character of the fluorinated groups play a major role (Table 9).[141] When the electron-accepting properties of the substituents in the *o*- and *p*-positions in monosubstituted dyes (Nos.1–13) are enhanced, a bathochromic shift is observed. *p*-Substituted dyes (Nos.10 and 12) absorb at longer wavelengths than the *o*-isomers (Nos.11 and 13). Monosubstituted dyes with electron-donating and weak electron-accepting substituents (Nos 1, 2, and 4–9) are less light-fast than the unsubstituted dye (No.3). Electron acceptors (the nitro- and trifluoroethanesulphonyl groups) increase somewhat the light-fastness. No differences are observed between the light-fastnesses of monosubstituted dyes with the same substituent in the *o*- and *p*-positions.

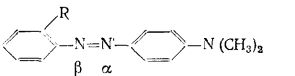
Table 9. The absorption maxima and fastness to light of fluorine-containing azo-dyes[141]



(XXIX)

No.	X	Y	λ_{max}, nm		Fastness to light, units
			alcohol	alcohol + HCl	
1	CH_3	H	416	538	3
2	H	CH_3	418	522	3
3	H	H	415	524	5
4	CF_3O	H	424	515	3—4
5	H	CF_3O	430	505	3—4
6	CF_3	H	434	509	3
7	H	CF_3	434	492	3—4
8	CF_3S	H	440	515	2—3
9	H	CF_3S	438	508	3
10	NO_2	H	492	520	5—6
11	H	NO_2	450	518	5
12	CF_3SO_2	H	484	503	5—6
13	H	CF_3SO_2	470	493	5—6
14	CF_3	NO_2	485	504	4—5
15	NO_2	CF_3	522	490	6—7
16	CF_3S	NO_2	490	510	4—5
17	NO_2	NO_2	533	504	5
18	CF_3SO_2	NO_2	538	492	5
19	NO_2	CF_3SO_2	564	484	6—7

Among the isomeric disubstituted dyes Nos.14 and 15 and Nos.18 and 19, the dyes Nos.15 and 19 containing the CF_3 and CF_3SO_2 groups in the *o*-position, absorb at the lowest frequencies and show the greatest fastness to light. For the substituent in the *p*-position, the length of the chromophore chain has the greatest influence on the colour. The trifluoromethanesulphonyl group, which is a stronger electron acceptor than the nitro-group like all sulphur-containing substituents, has a tetrahedral structure. Conjugation does not therefore reach the oxygen atoms, being restricted to the sulphur atom by virtue of the involvement of its *d* orbitals and the conjugation chain is shorter than for the *p*-NO_2 group[147]. The conjugation of the *o*-NO_2 group is greatly influenced by steric factors. The breakdown of coplanarity for the CF_3SO_2 group does not affect significantly its conjugation with the dye chromophore. The fastness to light of the disubstituted dyes depends on the positions of the substituents. Dyes Nos.15 and 19 are more light-fast than dyes Nos. 16–18. This can be apparently explained by the fact that the bulky electron-accepting CF_3 and CF_3SO_2 groups in the *o*-position relative to the azo-group protect the latter against photochemical oxidation to a greater extent than the nitro-group. This is confirmed by the comparison of the absorption intensities of the salts of substituted DAAB.[145] Even a proton, which is small, adds to only an insignificant extent to the β-nitrogen atom of the azo-group in the presence of the CF_3 group in the *o*-position.



λ_{max}, nm (10^{-4} *E* given in brackets)

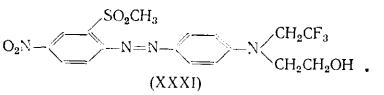
R	alcohol	alcohol + HCl
CH_3	410 (2.70)	520 (1.00)
H	407 (2.80)	518 (4.60)
CF_3	425 (2.98)	479 (0.008)
NO_2	440 (2.68)	500 (1.11)

In order to obtain light-fast dyes, it is necessary that two electron-accepting substituents be present in the *A* ring. A bulky fluorine-containing group in the *o*-position has a favourable effect. In those dyes where a trifluoromethyl group is already present in the *o*-position relative to the azo-group, the introduction of a bromine atom or a CF_3 group in the second *o*-position does not lead to a further increase of the fastness to light of the colour[146].

Among the dyes of type (XXIX) (Table 9), those where X = NO and Y = CF_3, C_2F_5, CF_2SO_2, or CHF_2SO_2 exhibit the highest light-fastness for different azo-components. Such dyes are of practical interest[146–164]. Stable colours on polyamide and polyester fibres have been obtained by dyeing the latter with disperse azo-dyes containing the fluorosulphonyl group[165–167]. The azoamines (XXIV)–(XXVII) [168–180] as well as their trifluoromethanesulphonyl analogues[181,182] are used to prepare pigments of cold, disperse, cationic, and azid azo-dyes. Disperse and cationic azo-dyes based on hereocyclic diazo-components, obtained from amino-derivatives of thiazole, thiadiazole, benzothiazole and pyrazole containing the CF_3 and $(CF_3)_2COH$ groups, are of practical interest for the colouring of artificial and synthetic fibres[183–190]. Certain disperse azo-dyes containing the CF_3 [191–196] and $COCH_3$ [197] groups have a low stability in relation to sublimation. Because of this "deficiency" they have found applications as dyes for thermal transfer printing on polyester and polyamide fibres. Dyes with the CHF_3, SO_2F, SO_2CHF_2, and SO_2CF_3 substituents in the benzoisothiazole ring, used for transfer printing on polyacrylonitrile and polyester fibres, are also mentioned in a patent[194].

The arylamines $C_6H_5NRCH_2CH_2OH$ (XXX),[198] where R = $C_3F_7CH_2$, CF_3CH_2, CHF_2CH_2, $CH_3CF_2CH_2$, $CF_3CH_2CH_2$, $CHF_2CH_2CH_2$, $CH_3CF_2CH_3CH_2$, CH_2FCH_2, $CH_3CF_2CF_2CH_2CH_2$, or $CH_3CF_2CH_2CH_2CH_2$ are used as the azo-component. They have been obtained by the reaction of aniline with fluorine-containing alkyl bromides followed by treatment with epoxyethane[199,200]. The study of the properties of azo-dyes with azo-components of type (XXX) has shown that, with increase of the distance between the nitrogen atom and the carbon atom linked to the fluorine atom and with decrease of the number of fluorine atoms in the alkyl group, the colour of the dyes shifts bathochromically. The fastness to light increases with increase of the number of fluorine atoms in the *N*-alkyl group and as they come closer to the nitrogen atom[201]. The dye (XXXI) on acetate silk[201] and the dyes with the $N(CH_2)_nC_2F_5$ (n = 1, 2) groups in the azo-component on

polyester fibre[202–206] show an excellent fastness to light.



(XXXI)

Many new fluorine-containing azo-components $C_6H_5NRCH_2.(CF_2CF_2)_nH$ (XXXII, R = H, CH_3, C_2H_5, C_2H_4OH, or C_2H_4CN; n = 1, 2) have been synthesised by alkylating arylamines with the polyfluoroalkanesulphonates of fluorinated telomeric alcohols $H(CF_3CF_2)_nCH_2OH$ (FTA).[207,208]

The substituents R in disperse azo-dyes obtained from the azo-components (XXXII) can be arranged in the following sequence in terms of the bathochromic shift of the colour: $C_2H_5 \geq C_2H_4OH > CH_3 > C_2H_4CN$.[209] An increase in the number of difluoromethylene groups n leads to a hypsochromic shift of the absorption maximum by 6–7 nm. All the dyes exhibit a high fastness to light and some of them readily sublime and are suitable for thermal transfer printing.

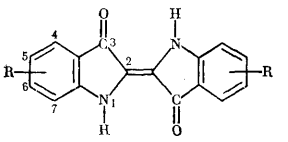
Dyes containing the CF_3 groups in the *o*-positions of the benzene ring of the azo-component are more light-fast than the corresponding dyes with the CH_3 group[140,210,217].

The absorption spectra and fastness to light of disperse azo-dyes derived from *N*-(2,2,2-trifluoroethyl)tetrahydroquinoline have been investigated[216].

The active dyes in which fluorine-containing groups, for example, a fluorine-substituted triazine or polyfluorocyclobutyl group[218–221], form a strong linkage with the fibre, are widely used, although certain fluorine atoms are then substituted and are no longer present in the dye on the fibre. If trifluoromethyl groups are present in the molecules of the azo-dyes forming part of the active dye[222–228], then such dyes give rise to light-fast colours.

VI. INDIGOID AND THIOINDIGOID DYES

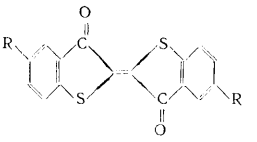
Isatins and indigoid dyes containing fluorine atoms and trifluoromethyl groups have been described[126,229–234]. Electron-donating substituents in the 5,5′-positions in indigo cause a bathochromic shift in the colour, while electron-accepting substituents cause a hypsochromic shift. The substituents in the 6,6′-positions act in the opposite manner.



R	λ_{max}, nm (tetrachloroethane) 5,5′	6,6′	4,4′	7,7′
CH_3O	645	570	—	—
H	605	605	605	605
F	615	570	—	560
CF_3	—	—	605	580
NO_2	580	635	—	—

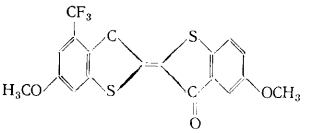
The fluorine atoms in the 5,5′- and 6,6′-positions influence the colour like electron-donating substituents. The inductive effect of the substituents in the 7,7′-positions has a marked influence. Fluorine atoms give rise to a greater hypsochromic shift of the absorption maximum of the dye than the CF_3 group. Comparison of the stabilities of the colours of 5,5′- and 7,7′-difluoroindigos with that of the colour of 5,5′-dibromoindigo showed that the fluoro-derivatives are more light-fast[234].

The replacement of the ethyl group in the vat dye diethoxyviolanthrone by the trifluoroethyl group causes a hypsochromic shift in the colour of the dye—the latter changes from green to blue[126]. Derivatives of thioindigo containing fluorine atoms and fluorinated groups have been obtained by oxidising the corresponding thionaphthenes[235–239]:



R	F	H	CF_3O	CF_3S	CF_3	NO_2
λ_{max}, nm (benzene)	559	545	549	548	535	513
$\Delta\lambda$	14	0	4	3	−10	−32

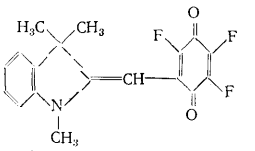
Electron-accepting substituents in the 5,5′-positions of thioindigo hinder the shift of electrons from the sulphur atom to the carbonyl group. This leads to a hypsochromic shift of the absorption maximum of the dye. $\Delta\lambda$ diminishes in the following sequence of substituents in the 5,5′-positions: C_2H_5O > I > F, Cl, Br > CH_3 > CF_3O > CF_3S > H > CF_3 > CH_3SO_2 > NO_2. 5,5′-Bis(trifluoromethyl)thioindigo derivatives exhibit a weak affinity for fibre[239]. Asymmetric dyes of the type



impart a bright red and fast colour to cotton, which makes them suitable for dyeing and printing[236].

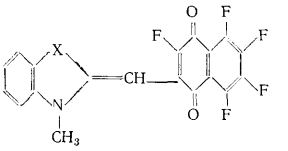
VII. BENZOQUINONE, NAPHTHOQUINONE, AND ANTHRAQUINONE DYES

The merocyanine dyes (XXXII) and (XXXIII) have been obtained by the reaction of methylene-substituted bases of nitrogen-containing heterocycles with the corresponding perfluoroquinones[240]:



(XXXII)

λ_{max}, nm	$\Delta\lambda$
692	+38

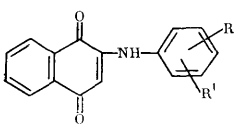


(XXXIII)

X	λ_{max}, nm	$\Delta\lambda$
$C(CH_3)_2$	635	+35
S	668	+53
CH=CH	685	+15

The introduction of fluorine atoms into the quinonoid nuclei of dyes leads to a considerable bathochromic shift. Like the corresponding compounds without fluorine, the dye (XXXII) with a perfluorobenzoquinone ring absorbs at longer wavelengths than the dye (XXXIII) with a perfluoronaphthoquinone residue. As the electron-donating properties of the heterocyclic residues are enhanced, the colour of the dye changes bathochromically.

Napthoquinone dyes (2-phenylamino-1,4-naphthoquinones) containing fluorinated groups in the benzene ring have been synthesised[241].

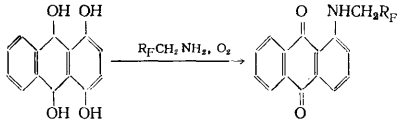


R, R′	λ_{max}, nm	R, R′	λ_{max}, nm
H, H	462	H, 3-CF_3	449
H, 4-F	460	H, 3-NO_2	443
H, 4-CF_3O	456	2-Cl, 5-CF_3	441
H, 4-CF_3S	454	2-NO_2, 5-CF_3	438
H, 4-CF_3SO_2	440	2-Cl, 5-CF_3SO_2	426

Fluorine-containing substituents shift the absorption maximum of the dye towards shorter wavelengths, since they withdraw electrons from the amino-group and prevent their transfer to the oxygen atom. Naphthoquinone dyes with fluorine-containing substituents are faster in relation to all kinds of treatment on Lavsan than dyes of the same series with non-fluorinated groups.

2-Trifluoromethylanthraquinone has been used as an intermediate in the synthesis of vat dyes[242]. 1-Isocyanato-5-trifluoromethylanthraquinone has been recently patented for the same purpose[243].

Dyes of the aminohydroxyanthraquinone series containing fluoroalkyl substituents at the nitrogen atom of the amino-group, have been obtained by treating leucoquinizarin with fluoroalkylamines and subsequent oxidation[244]:

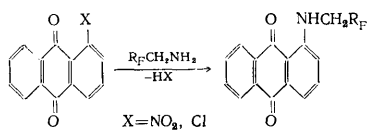


Fluorine-containing alkyl substituents in the alkylamino-group induce a hypsochromic shift and increase the fastness to light of the dyes in the sequence $CH_3CF_2CH_2CH_2CH_2$, $CHF_2CH_2CH_2 < CH_3CF_2CH_2 < CHF_2CH_2$, CF_3CH_2, $CH_3(CF_3)CH$ (Table 10).

Table 10. The absorption maxima of anthraquinone derivatives containing polyfluoroalkyl groups[246].

No.	Ring substituents	λ_{max}, nm	
		methylene chloride	alcohol
1	1-NH$_2$	465	483
2	1-NHCH$_2$CF$_2$CF$_2$H	470	480
3	2-NH$_2$	410	452
4	2-NHCH$_2$CF$_2$CF$_2$H	420	450
5	1,4-(NH$_2$)$_2$	545, 582	552, 593
6	2-NHCH$_2$(CF$_2$CF$_2$)$_2$H	—	442
7	1,4-(NHCH$_3$)$_2$	620	593, 641
8	1,4-(NHCH$_2$CF$_2$CF$_2$H)$_2$	555, 594	568, 608
9	1-OH	405	408
10	1-OCH$_2$CF$_2$CF$_2$H	336	367
11	1-OCH$_2$(CF$_2$CF$_2$)$_2$H	343	351
12	2-OH	365	380
13	2-OCH$_2$CF$_2$CF$_2$H	328	330
14	1-NH$_2$-4-OH	528, 554	534, 570
15	1-NHCH$_2$CF$_2$CF$_2$H-4-OH	534, 570	537, 571
16	1-NH$_2$-4-Cl	472	484
17	1-NH$_2$-4-OCH$_2$CF$_2$CF$_2$H	476	496
18	1-NH$_2$-4-OCH$_2$(CF$_2$CF$_2$)$_2$H	476	496

α-Polyfluoroalkylaminoanthraquinone dyes have also been synthesised by the reaction of fluoroalkylamines with α-nitro-anthraquinone[245] or α-chloroanthraquinone[246]:



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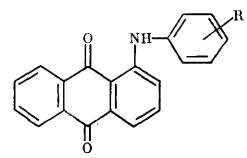
1,4-Bis(1′,1′,3′-trihydrotetrafluoropropyl)anthraquinone has been obtained by substituting two hydroxy-groups in leucoquinizarin by polyfluoroalkylamino-groups. The same product as well as β-polyfluoroalkylaminoanthraquinone has been synthesised by alkylating aminoanthraquinones by FTA sulphones[246,247]. When α- and β-chloroanthraquinones were treated with sodium alkoxides derived from FTA, polyfluoroalkoxyanthraquinones were obtained[246].

The substitution of the hydrogen atom of the hydroxy-group by a polyfluoroalkyl group influences the absorption maximum to a greater extent than the substitution of a hydrogen atom in the amino-group; the colour undergoes a hypsochromic shift to the extent of 50 nm. The β-polyfluoroalkylamino- and β-polyfluoroalkoxy-anthraquinones have colours in a shorter wavelength range than the corresponding α-derivatives.

The substitution of two hydrogen atoms in 1,4-diaminoanthraquinone (one in each amino-group) induces a bathochromic shift of the absorption band of the residue by 15 nm. However, dye No.8 (Table 10) has a colour corresponding to a much shorter wavelength than 1,4-bis(methylamino)-anthraquinone (No.7).

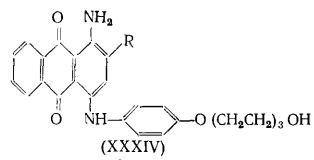
1-Amino-4-polyfluoroalkoxyanthraquinones (Nos.17 and 18) have only one absorption maximum in the visible region, in contrast to 1-amino-4-hydroxy- and 1,4-diamino-anthraquinones, because the polyfluoroalkoxy-groups are not involved in conjugation with the carbonyl group and in the formation of the hydrogen bond.

Arylaminoanthraquinone dyes containing fluorinated substituents in the benzene ring are suitable as disperse dyes for synthetic fibres. Electron-donating substituents in the benzene ring, like those introduced directly into the anthraquinone nucleus, induce a bathochromic shift of the absorption maximum of the dye, while electron-accepting substituents give rise to a hypsochromic shift[249].



R	λ_{max}, nm (alcohol)		
	p-	*m*-	*o*-
CH_3O	515	506	521
H	508	508	508
CF_3	496	492	486
NO_2	482	486	481

Dyes containing the CF_3 group impart to polyester fibre a red colour which is fast to light[248–251]. Comparison of the stabilities of the colours on acetate silk showed that the dye (XXXIV), containing the CF_3 group, has the highest fastness to light[244]:



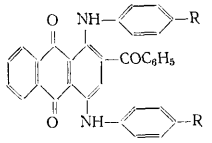
(XXXIV)

R=CF_3, $CONH_2$, CN, CH_3S, CH_3SO_2 .

The CF_3O group has been introduced into arylaminoanthraquinones in addition to the CF_3 group[252,253]. Colours more resistant to wet treatments and light have been obtained on polyester fibre than in the case of fluorine-free dyes. A series of 4-arylamino-1-hydroxyanthraquinones with substituents in the benzene ring [CF_3,[254,255] CHF_2,[256] OCF_2CHFX (X = H, F, or Cl),[257] CF_3O,[253] $C(CF_3)_2OH$ [258]] as well as pentafluorobenzamidoanthraquinone[259] have been patented.

1,4-Diarylaminoanthraquinones are obtained by arylating 1,4-diaminoanthraquinone. The substitution of the *p*-position in the benzene ring by the fluorine-containing groups CF_3CO and CF_3SO_2 leads to a hypsochromic shift of the long-wavelength absorption maximum as a consequence of the electron-accepting influence of such groups: $CF_3SO_2 > NO_2 >$

$CF_3CO > H > CH_3$:[260,261]



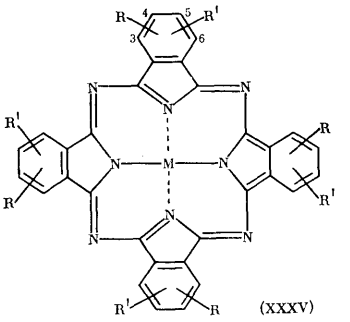
R	λ_{max}, nm (trichlorobenzene) ($\Delta\lambda$)	
CH_3	442 (10)	677 (11)
H	432	666
CF_3CO	440 (8)	617 (—49)
NO_2	448 (16)	612 (—54)
CF_3SO_2	419 (—13)	595 (—71)

These dyes impart to polyester fibre a bright green colour with high parameters of resistance to all physical and chemical influences. Patents describe 1,4- and 1,5-diarylaminoanthraquinone dyes containing the CF_3,[262–264] CF_3O, CF_3CO, CF_3SO_2,[260,261,265,266] $OCHF_2$, and OCF_2CHF_2 [267] groups in the benzene ring. They are used to impart fast blue and green colours to cellulose esters, polyesters, and polyamides.

VIII. PHTHALOCYANINE DYES WITH FLUORINE-CONTAINING SUBSTITUENTS

The introduction of fluorine atoms and fluorine-containing substituents into phthalocyanine dyes not only influences their absorption spectra but also increases their fastness to light, solubility, and resistance to the action of oxidants.

Table 11 lists the absorption maxima of metal-free phthalocyanines[268–270], copper-containing phthalocyanines (XXXV), and naphthalocyanines[270]:



(XXXV)

Table 11. The absorption maxima of fluorine-containing phthalocyanines (Pc) and naphthalocyanines (Nc).[268–270]

No.	Compound	λ_{max}, nm (in C_6H_5Cl)	No.	Compound	λ_{max}, nm (in C_6H_5Cl)
1	PcH_2	92, 665, 638, 601 [271]	14	$(CF_3S)_4$-3-PcH_2	701, 670, 639
2	PcCu	678, 648, 611 [271]	15	$(CF_3S)_4$-3-PcCu	682, 625
3	Γ_4-3-PcCu	680, 646, 611 [271]	16	$(CF_3S)_4$-4-PcH_2	699, 663, 645, 633, 603
4	F_4-4-PcCu	666, 632, 597 [271]	17	$(CF_3S)_4$-4-PcCu	679, 610
5	$(CF_3)_4$-3-PcH_2	681, 646, 620, 584	18	$(CF_3S)_8$-4,5-PcH_2	708, 675, 652, 612
6	$(CF_3)_4$-3-PcCu	660, 631, 595	19	$(CF_3S)_8$-4,5-PcCu	687, 616
7	$(CF_3)_4$-4-PcCu	669, 637, 601	20	$(CF_3SO_2)_4$-4-PcH_2	700, 672, 636, 610
8	$(CF_3)_8$-4,5-PcCu	669, 639, 601	21	$(CF_3SO_2)_4$-4-PcCu	682, 610
9	$(CF_3)_8$-3,6-PcH_2	702, 674	22	NcCu	776, 695
10	$(CF_3)_8$-3,6-PcCu	680, 616	23	$(CF_3)_4$-6-NcCu	770, 688
11	$(CF_3)_{12}$-3,4,5-PcCu	669, 639, 602	24	$[(CF_3)_3C]_4$-6-NcCu	772, 684
12	$[(CF_3)_3C]_4$-4-PcH_2	692, 655, 593	25	$(CF_3)_8$-6,7-NcCu	766, 714, 678
13	$[(CF_3)_3C]_4$-4-PcCu	672, 602			

*PcH_2 = phthalocyanine without a metal; PcCu = copper-phthalocyanine; NcCu = copper-naphthalocyanine.

The fluorine atoms in the 4-position in the phthalocyanines have virtually no influence on the absorption maxima and those in the 3-position induce a small bathochromic shift. A hypsochromic shift of the absorption bands is characteristic of tetrakis(trifluoromethyl)phthalocyanines (dyes Nos.5–7). The introduction of two or three trifluoromethyl groups in the 4- and 5-positions (dye No.8) or 3-, 4-, and 5-positions (dye No.11) does not induce a shift of the absorption maximum compared with the 4-substituted dye (No.7). The perfluoro-t-butyl group (dyes Nos.12 and 13) hardly affects the position of the long-wavelength absorption maximum. The trifluoromethylthio- and trifluoromethanesulphonyl-groups in dyes Nos.14–21 exhibit small bathochromic effects.

A bathochromic shift of the absorption band by approximately 100 nm is observed in the absorption spectra of naphthalocyanines (Nos.23–25) compared with the perfluoroalkylphthalocyanines.

The introduction of trifluoromethyl and perfluoro-t-butyl groups into phthalocyanine molecules greatly increases their solubility in organic solvents, reduces their basicity, and increases their resistance to oxidation[269].

It is seen from the above that investigations have led to the discovery of certain rules governing the influence of fluorine atoms and fluorine-containing substituents on the colour and properties of all classes of organic dyes. These data can be used for the specific synthesis of dyes with practically valuable properties.

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