



Colour Theory of Polyfluoromethine Systems: 1. Single Fluorine Atom in the Polymethine Chain

M. N. Ushomirsky & L. M. Yagupolskii

Institute of Organic Chemistry, Academy Sciences of the Ukrainian SSR,
Kiev 252660, USSR

(Received 18 April 1990; accepted 3 July 1990)

ABSTRACT

This paper is the first of a series in which we propose to develop the electron structure and colour theory of polyfluoromethine systems. Introduction of a single fluorine atom into the polymethine chain is considered with respect to its influence on the asymmetry of dyes, the basicity of the end-groups, and the relationships between spectral shifts and differences in the basicities of the end-groups. A number of rules have been established for the molecular design of polymethine systems, substituent effects and also for conditions resulting in exceptions to the Forster–Dewar–Knott rule.

1 INTRODUCTION

Polymethine dyes (PMD) containing fluorine atoms in the polymethine chain are of interest for both theoretical and practical studies, since the fluorine atom which is introduced into the conjugated system has minimal steric hindrance effects but has significant conjugative and inductive effects. It is the predominance of the conjugative effect over the inductive effect that results in the saturation where the fluorine atom, contrary to its effect in saturated systems, behaves as an electron donor in cyanine dyes.¹

The synthesis of the first member of the polyfluoromethine dye series (PFMD), viz. thiocarbocyanine with a completely fluorinated chain,¹ has made it possible to investigate new effects. However, to study the electronic effects arising in the PFMD using the classical methods of MO LCAO, even in the π -electron approximation, is too difficult, since a very large volume of calculations are necessary in order to determine the relations between the structure and properties of these compounds.

After the introduction of one fluorine atom, as well as of other substituents, into the dye chromophore, simple perturbation theory may be used to discuss colour and electronic properties.² However, in dyes in which all the hydrogen atoms in the polymethine chain are replaced by fluorine, the application of this theory becomes invalid. In this case the Green function method³ is usually employed but this also becomes rather labour-consuming when studying systems having end-groups of a complex structure.

The possibility of a more effective theoretical study of these problems has arisen following the development of the method of additive generating functions for analysing conjugated systems with periodic chains of an arbitrary structure,⁴⁻⁶ which is genetically related to the Green function method. An increase in the fluorovinylene shift with chain elongation in PFMD, as compared with the classical polymethine chain, was predicted by this method.⁴ However, this problem has been discussed⁴ only at a qualitative level.

We have therefore investigated initially the properties of simpler dyes, in which only one fluorine atom is introduced into the even or odd positions of the polymethine chain (PC) and, following the results of these studies, only then to consider dyes with a completely fluorinated chain.

Since a fluorine atom possesses minimal steric effects and the inductive and conjugated effects partially compensate each other, this atom may be used as a 'probe' for the investigation of electron density distribution in a conjugated chain, in much the same way as a small charge is used as a 'probe' to study an electric field without changing it.

The subsequent development of the electronic PFMD structure theory, and the comparison of theoretical data with experimental data, permit the prediction of the properties of new polymethine systems and the development of a general theory for the electronic structure of organic compounds.

2 RESULTS AND DISCUSSION

2.1 Electronic characteristics of a fluorine atom as a substituent in the conjugated system

The introduction of a fluorine atom into the π -conjugated system is accompanied by inductive and resonance effects. The former is described by an increase ($\Delta\alpha_Y$) of the Coulomb integral (α_Y) of the atom Y, to which the fluorine atom is attached. The latter is expressed by the participation in the conjugation of the unshared electron pair of the fluorine atom and is characterised by the Coulomb (α_F) and the bond resonance (β_{YF}) integrals.

TABLE 1

(1)

R_1	R_2	λ_{\max} (nm)	$\Delta\lambda$ (nm)
<i>in EtOH</i> ¹			
H	H	558	—
H	F	522	-36
F	H	567	+9

Studies on the PMD colour theory have shown that the fluorine atom behaves as an electron donor, giving, in accord with the Forster–Dewar–Knott (FDK) rule,⁷⁻⁹ a hypsochromic shift ($\Delta\lambda < 0$) when substituted in the β -position of thiocarbocyanine and a bathochromic shift ($\Delta\lambda > 0$) when in the α -position (Table 1).¹

Based on these experimental results, that the donor resonance effect predominates over the acceptor inductive effect, a conclusion may then be drawn on the relative value of the quantum chemical parameters describing the fluorine atom in the conjugated system.

For these purposes the perturbation theory of molecular orbitals (MO) is used.² In this case the change in the frequency of the electron transition under the inductive effect ($\Delta\nu_i$) of the fluorine atom is described by eqn (1):

$$\Delta\nu_i = (C_{o,k}^2 - C_{e,k}^2) \cdot \Delta\alpha_C \quad (1)$$

where $C_{o,k}^2$ and $C_{e,k}^2$ are the MO coefficients on the k th molecular atom to which the substituent F is introduced, 'o' corresponds to the highest occupied MO (HOMO), 'e' to the lowest unoccupied MO (LUMO) and $\Delta\alpha_C$ is the change of the carbon atom Coulomb integral caused by the inductive effect of the fluorine atom.

According to MO perturbation theory,² the resonance effect of the fluorine atom is described by eqn (2a):

$$\Delta\nu_M = \frac{C_{e,k}^2 \cdot \beta_{CF}^2}{e_e + \alpha_F} - \frac{C_{o,k}^2 \cdot \beta_{CF}^2}{e_o + \alpha_F} \quad (2a)$$

where e_o and e_e are the HOMO and LUMO energies, respectively.*

* In this paper we assume the so-called physical signs of the energy values: the bonding MO energies are negative and the Coulomb integrals α_F and α_C are positive, i.e. the electron non-bonding energy level (e), which is usually the origin of the energy level scale, is equal to $(-\alpha_C)$ and the energy level e_F at which the unshared electron pair in the isolated fluorine atom is located is equal to $(-\alpha_F)$.

Taking into account that for PMD the values of $C_{e,k}^2$ and $C_{o,k}^2$ have order $1/L$,⁵ where L is the effective dye length,¹⁰ eqn (2a) may be reduced to eqn (2b):

$$\Delta\nu_M = (C_{e,k}^2 - C_{o,k}^2)\beta_{CF}^2/(\alpha_F - \alpha_C) \quad (2b)$$

It should be noted that the assumption of an infinitesimal value for $1/L$ means essentially that we can use the approximation

$$|e_e + \alpha_C| \quad \text{and} \quad |e_o + \alpha_C| \ll (\alpha_F - \alpha_C) \quad (3)$$

since the effective length L , which was empirically introduced into the model of a free electron¹¹ and then strictly into the approximation of 'long' dyes,¹⁰ is the effective number of vinylenes groups which provide the same absorption maximum that the corresponding PMD does. As is known, the chain elongation causes a decrease in the values $|e_o + \alpha_C|$ and $|e_e + \alpha_C|$,^{6,10} and the inequality shown in eqn (3) is valid.

The total spectral shift caused by the introduction of the fluorine atom into the conjugated system has the form

$$\Delta\nu = \Delta\nu_1 + \Delta\nu_M = (C_{e,k}^2 - C_{o,k}^2)\left(\frac{\beta_{CF}^2}{\alpha_F - \alpha_C} - \Delta\alpha_C\right) \quad (4)$$

In the β -position of the symmetrical thiocarboyanine **1** ($R_1 = R_2 = H$), $C_{o,k}^2 = 0$, and a hypsochromic shift ($\Delta\nu > 0$) is observed in this case if the inequality

$$\frac{\beta_{CF}^2}{\alpha_F - \alpha_C} - \Delta\alpha_C > 0 \quad (5a)$$

$$\text{i.e.} \quad \beta_{CF} > \sqrt{\Delta\alpha_C(\alpha_F - \alpha_C)} \quad (5b)$$

is obeyed.

Similar reasoning may be used for the α -position of thiocarboyanine **1**. In this case ($C_{e,k}^2 - C_{o,k}^2 < 0$), then in eqn (4) $\Delta\nu < 0$, the bathochromic shift is observed, and we again arrive at the inequality (5).

Thus only following the inequality (5) will there be a qualitative correspondence between the theoretical results and experimental data.

If parameters $\Delta\alpha_C$, α_F , β_{CF} are expressed according to Ref. 12 via the standard values α_C and β_{CC} in terms of

$$\alpha_F = \alpha_C + h_F\beta_{CC} \quad \beta_{CF} = k_{CF}\beta_{CC} \quad \Delta\alpha_C = \Delta h_C\beta_{CC}$$

then the inequality (5) will take the form

$$t_F = \left(\frac{k_{CF}^2}{h_F} - \Delta h_C\right) > 0 \quad (6a)$$

$$\text{or} \quad k_{CF} > \sqrt{\Delta h_C \cdot h_F} \quad (6b)$$

The value of Δh_C may be estimated¹² by the auxiliary inductive parameter $\delta = 0.1$:

$$\Delta h_C = \delta \cdot h_F \quad (7)$$

In the system of Streitweiser's parameters¹² the values h_F and k_{CF} are recognised as

$$h_F = 3.0 \quad k_{CF} = 0.7 \quad (8)$$

When eqn (7) is assumed, the set of parameters given in eqn (8) does not satisfy the inequality given in eqn (6). This is presumably due to the fact that these values are obtained from Pauling electronegativity data for aliphatic organic compounds.¹² It is much more logical to assume a set of parameters obtained from studies of fluorobenzene:¹³

$$h_F = 1.5-2.1 \quad k_{CF} = 0.5-0.7 \quad (9)$$

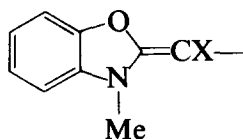
In these ranges most of the values satisfy the inequality of eqn (6). In order to illustrate more clearly the influence of the fluorine atom when it is introduced into PMD, we have chosen the maximum value $t_F = 0.18$ [$h_F = 1.5$; $k_{CF} = 0.7$ (Ref. 10)].

Thus we have defined more precisely the quantum chemical parameters of the fluorine atom from the general conclusions about electronic nature of the fluorine atom as a substituent in a conjugated PMD system.

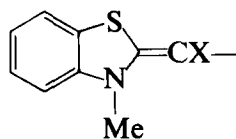
2.2 Introduction of a fluorine atom into the polymethine chain with symmetry breaking

If the spectral shift induced by the introduction of a fluorine atom into the conjugated system according to the classification of Ref. 14 has a first-order value, then its introduction into the PC of a symmetrical PMD, causing the breaking of symmetry, leads to the appearance of second-order effects and, initially, to the Kiprianov-Brooker deviation.^{15,16}

Based on Il'chenko's empirical scale of electron-donating ability (D),¹⁷ it has been shown that the introduction of a fluorine atom into the α -position of the PC enhances the electron-donating ability of the end-group,^{17,18} i.e. an increase in the Kiprianov-Brooker basicity of the hetero-residue:



$X=H$, $D = 1.45$; $X=F$, $D = 1.54$



$X=H$, $D = 1.48$; $X=F$, $D = 1.57$

The values of D ,^{17,19} and of the Platt basicity b ,²⁰ are empirical values

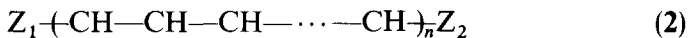
calculated from deviations of corresponding asymmetrical dyes. For *a priori* estimation of the end-group basicity it is possible to use the quantum chemical calculations of electron-donating ability (Φ_0) determined using the 'long PMD' model,^{10,21} and also the method of effective additive parameters⁴⁻⁶ (or additive generator functions). In the latter, the following equation was used:

$$\tan \Phi_0 = -\frac{q_0}{r_0} \quad (10)$$

where q_0 is the value of the secular determinant of the isolated end-group (in this case the $Z=CH\sim$ group)* at the non-bonding level of carbon $2p_z(\pi)$ -electrons and r_0 is the value of a minor of q_0 , obtained by the removal of the atom, with the help of which the end-group was connected to the polymethine chain; in our case it is the secular determinant of the Z-group.

We can additionally use an alternative definition of electron-donating ability,⁶ where Φ_0 is the main value of $\arctan(-q_0/r_0)$, which varies from -90° to $+90^\circ$. This definition is more precise than that given elsewhere,²¹ in which Φ_0 is in the range from 0° to $+90^\circ$.

It has been shown²² that the value of Φ_0 is the quantum chemical equivalent of the basicity of the hetero-residue Z in the polymethine systems **2**, and determines the exchange of the charge between the end-group and the chain in the ground state of the molecule



The end-groups are divided into two types, viz. those having a positive value of Φ_0 ($0^\circ < \Phi_0 < +90^\circ$) and those having a negative value ($-90^\circ < \Phi_0 < 0^\circ$).

Table 2 shows the Φ_0 values for a series of hetero-residues which are most widely utilised in polymethine dyes, **2**.

Based on an analysis of the signs of the parameters, it is possible to derive rules for the molecular design of polymethine dyes, and these have been substantiated in other publications.^{23,24} These rules (I-V) are now described.

Rule I. The two-nuclear PMD (**2**) is a combination of odd external PC ($n = 2k + 1$) with end-groups Z_1 and Z_2 having electron-donating abilities Φ_{01} and Φ_{02} of the same sign (symmetrical cyanines, oxynines, etc.) or a combination of even external PC ($n = 2k$) with the end-groups Z_1 and Z_2 having electron-donating abilities Φ_{01} and Φ_{02} of different signs (mero-cyanines, styryls, etc.).

* Similarly to Refs 4-6, the secular determinant has the form $\det(T + x \cdot E)$ where T is the topological matrix of the end-group, E is the unit matrix and $x = (e + \alpha_c)/\beta_{cc}$.

TABLE 2
End-Group Electron-Donating Ability, Φ

End-group	Φ	End-group	Φ
	-76°		$+14^\circ$
	-45°		$+45^\circ$
	-33°		$+57^\circ$
	-26°		$+64^\circ$
	-24°		$+66^\circ$
	-14°		$+76^\circ$
	-14°		$+76^\circ$

An end-group having a positive value of Φ_{oi} creates a negative charge in the α -position of the PC, and an end-group with a negative value of Φ_{oi} creates a positive charge.²²

Thus the Φ_{oi} -scale from 0° to $+90^\circ$ may be called the basicity scale of end-groups, and the Φ_{oi} -scale from -90° to 0° the acidity scale.²³ The end-group is more basic the closer Φ_{oi} is to $+90^\circ$ and it is more acid when Φ_{oi} is closer to -90° .

The conditional attribution of the neighbouring methine group (or a more longitudinal odd site of PC) results in a change of the end-group type [eqn (11)],⁶ since the methine group directly attached to such an elongated end-

group can now be considered as being in the α -position:

$$\Phi_0(\text{Z}=\text{CH}\sim) = \Phi_0(\text{Z}) - 90^\circ(\text{sign } \Phi_0(\text{Z})) \quad (11)$$

where $\text{sign } \Phi_0(\text{Z}) = +1$, if $\Phi_0(\text{Z}) > 0^\circ$, and $\text{sign } \Phi_0(\text{Z}) = -1$, if $\Phi_0(\text{Z}) < 0^\circ$; $\Phi_0(\text{Z})$ is electron-donating ability Φ_0 of the end-group Z.

On the other hand, one may consider eqn (11) as being a relationship between the acidity and basicity scales for the end-groups. Thus, if it is necessary to estimate the position of the rhodanine nucleus ($\Phi_0 = -26^\circ$, Table 2) in the end-group basicity scale, the value of 90° should be added to $\Phi_0 = -26^\circ$, thus giving $\Phi'_0 = +64^\circ$. By analogy, for the *p*-dimethylamino-styryl nucleus, $\Phi'_0 = +14^\circ$, from $\Phi_0 = -76^\circ$. In contrast, to determine the benzimidazole position ($\Phi_0 = +76^\circ$) on the acidity scale, it is necessary to subtract 90° , i.e. giving $\Phi'_0 = -14^\circ$. Such a position of the end-groups in the acidity and basicity scales is quite logical and corresponds to a series of the Kiprianov-Brooker basicities.^{15,16}

At present the calculation of Φ_0 is one way to estimate *a priori* the basicity of the $\text{Z}=\text{CF}\sim$ heterocycle compared with that of a $\text{Z}=\text{CH}\sim$ heterocycle. We shall deduce the general formula and mark values for $\text{Z}=\text{CF}\sim$ with an index (F) and values for $\text{Z}=\text{CH}\sim$ with an index (H) in eqn (10).

From the Heilbronner formula²⁵ it can be shown that the following equations are observed:

$$q_{0(\text{F})} = q_{0(\text{H})}h_{\text{F}} - k_{\text{CF}}^2 r_{0(\text{H})} + \Delta h_{\text{C}} r_{0(\text{H})} \quad (12)$$

$$r_{0(\text{H})} = r_{0(\text{H})}h_{\text{F}} \quad (13)$$

From eqns (12) and (13), and relationship (10), we have

$$\tan \Phi_0(\text{Z}=\text{CF}\sim) = \tan \Phi_0(\text{Z}=\text{CH}\sim) + t_{\text{F}} \quad (14)$$

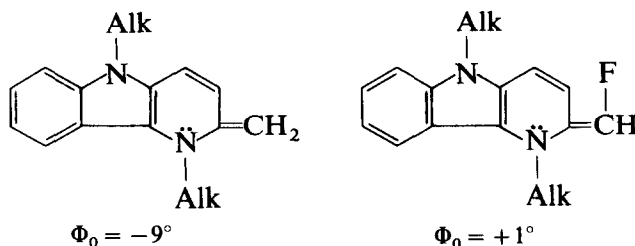
Since the second addendum in eqn (14) is positive [in accord with inequality (6a)] we have the inequality (15):

$$\Phi_0(\text{Z}=\text{CF}\sim) > \Phi_0(\text{Z}=\text{CH}\sim) \quad (15)$$

Thus the introduction of a fluorine atom into the PC results in an increase in the electron-donating ability (basicity) of the end-group at the expense of the electron-donating effect of the fluorine atom. The increase in the value of Φ_0 is defined by the parameter t_{F} [eqn (5a)], which is the sum of the mesomeric and inductive contributions. It should be noted that if $\Phi_0(\text{Z}=\text{CH}\sim)$ is a small negative value with the module less than $\arctan(t_{\text{F}})$, then the sign of $\Phi_0(\text{Z}=\text{CF}\sim)$ is positive. This means that the corresponding symmetrical dye [$\text{Z}=\text{CF}-\text{CH}=\text{CF}-\text{Z}$] will be stable only in the charge form +3 (the charge form of compound [$\text{Z}=\text{CH}-\text{CH}=\text{CH}-\text{Z}$] is +1), i.e. this compound will be stable only when one electron is lost.

So, assuming $t_{\text{F}} = 0.18$ ($\arctan t_{\text{F}} = 10^\circ$), then indolepyridine

$[\Phi_0(\text{Z}=\text{CH}) = -9^\circ]$ will be such a heterocycle which changes the sign of its electron-donating ability Φ_0 on fluorination. In this case the α -fluoromethylene base is already unstable in the uncharged form and it will exist only in the double-ionised form:



The α -position ($\Phi_0 = +1^\circ$) in such a compound will be not nucleophilic but electrophilic.

Assuming the value of t to be a small parameter, one may obtain a relationship with respect to the value of $\Phi_0(\text{Z}=\text{CF}\sim)$, viz.

$$\Phi_0(\text{Z}=\text{CF}\sim) = \Phi_0(\text{Z}=\text{CH}\sim) + t_F \cdot \cos^2 \Phi_0(\text{Z}=\text{CH}\sim) \quad (16)$$

The rule of sensitivity follows from eqn (16).

Rule II. The greater basicity of the end-group Z having a positive sign $\Phi_0(\text{Z})$ (i.e. the closer $\Phi_0(\text{Z})$ is to $+90^\circ$ and $\Phi_0(\text{Z}=\text{CH}\sim)$ to 0°), the more it changes with the introduction of a substituent into the α -position of the PC; if, for the initial nucleus, $\Phi_0(\text{Z})$ is negative, then the change in acidity (basicity) with introduction of the substituent into the α -position of PC is greater, the more acid is the substituent (i.e. less basic) and $\Phi_0(\text{Z})$ is closer to -90° and $\Phi_0(\text{Z}=\text{CH}\sim)$ to 0° .

Thus, in the series of heterocycles having $\Phi_0 > 0^\circ$ in Table 2, benzimidazole [$\Phi_0(\text{Z}) = +76^\circ$] is one of the more sensitive with respect to the end-group basicity on introduction of the fluorine atom into the α -position of the PC, but indolenine [$\Phi_0(\text{Z}) = +45^\circ$] is essentially less sensitive. In contrast, in the heterocycles with $\Phi_0 < 0^\circ$ in Table 2, the weakly basic *p*-dimethylaminostyryl ($\Phi_0 = -76^\circ$) is the most sensitive, and rhodanine, with $\Phi_0(\text{Z}) = -26^\circ$, is considerably less sensitive.

Table 3 presents the calculated values of Φ_0 , both on the basicity scale and the acidity scale, for nuclei $\text{Z}=\text{CH}\sim$ and $\text{Z}=\text{CF}\sim$. Unfortunately, at present, the experimental data which would confirm the above 'sensitivity rule' are not available. The difference in the basicity of benzoxazole ($\Phi_0 = +61^\circ$) and benzothiazole ($\Phi_0 = +57^\circ$) is too small for these rules to be confirmed. However, the sensitivity of cyanine hetero-residues to the introduction of substituents into the position *para* to the nitrogen atom, and the influence of carbocyanines on $\text{p}K_a$, may be considered as indirect

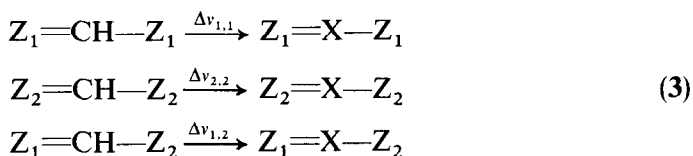
TABLE 3
Electron-Donating Ability of the End-Groups with CH and CF Groups in the α -Position of the Polymethine Chain

Z	$\Phi_0(Z)$	$\Phi_0(Z=CH\sim)$	$\Phi_0(Z=CF\sim)$	$[\Phi_0(Z=CF\sim) - \Phi_0(Z=CH\sim)]$
	-76°	$+14^\circ$	$+23^\circ$	9°
	-26°	$+64^\circ$	$+66^\circ$	2°
	$+45^\circ$	-45°	-39°	6°
	$+61^\circ$	-29°	-21°	8°
	$+57^\circ$	-33°	-25°	8°
	$+66^\circ$	-24°	-15°	9°
	$+76^\circ$	-14°	-4°	10°
	$+76^\circ$	-14°	-4°	10°

confirmation of the rules.²⁶ In these series the heterocycle is more sensitive to substitution the higher its initial basicity.²⁶

2.3 Introduction of a fluorine atom in the *meso*-position of the polymethine chain

Let us consider the possibility of using a fluorine atom as a 'probe' on its introduction into the *meso*-position of both symmetric and asymmetric PMD, i.e. the spectral shifts $\Delta\nu_{i,j}$ in triads:



where the index of $\Delta\nu_{i,j}$ indicates the end-groups Z_i included in the PMD. In the general case, the end-group Z_i may contain the part of PC and if the fluorine atom is used as a 'probe', then $\text{X} = \text{CF}$.

In the equally bound PC model, relationships have been obtained⁵ between the spectral shifts in symmetrical and asymmetrical molecules (3) which show the influence of differences in the electron-donating ability of the end-groups:

$$(-1)^{l_{1,2}} \frac{2 \cos(\Phi_{02} - \Phi_{01})}{\Delta\nu_{1,2}} = \frac{(-1)^{l_{1,1}}}{\Delta\nu_{1,1}} + \frac{(-1)^{l_{2,2}}}{\Delta\nu_{2,2}} \quad (17)$$

where $l_{1,2} = [1 + \text{sign}(\Phi_{01} + \Phi_{02})]/2$, $l_{1,1} = [1 + \text{sign}(\Phi_{01})]/2$ and $l_{2,2} = [1 + \text{sign}(\Phi_{02})]/2$.

Since, according to the design rule I of classical PMD (3), the signs of the electron-donating abilities Φ_{01} and Φ_{02} are the same [that is the integer numbers l have equal evenness and these factors in eqn (17) may be not taken into account], then it follows directly from eqn (17) that the spectral shift in the asymmetrical system due to the difference in basicities ($\Delta\Phi_0 = \Phi_{02} - \Phi_{01}$) will decrease compared with the calculated value, i.e. the mean harmonic (18) of the spectral shifts in the 'parent' dyes:

$$\Delta\nu_{\text{calc}} = 2 \cdot \Delta\nu_{1,1} \cdot \Delta\nu_{2,2} / (\Delta\nu_{1,1} + \Delta\nu_{2,2}) \quad (18)$$

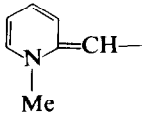
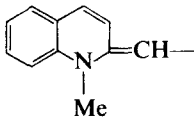
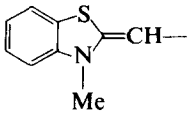
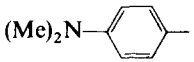
Thus in the 'long PMD approximation' there are a number of qualitative relationships III between spectral shifts in asymmetrical and 'parent' dyes.

Rule III. (i) $\Delta\nu_{1,2} < \Delta\nu_{\text{calc}}$ (19)

(ii) The FDK rule should be observed both for asymmetrical dyes and for symmetrical 'parent' molecules, i.e. the spectral shift in the asymmetrical dye

TABLE 4

Spectral Shifts in the Triad of Dyes (3) and Relationships for Introduction of the Nitrogen Atom in the *meso*-Position of the Chain^a

No.	Z\Z	1	2	3	4
1		620 ^b			
2		$\frac{550^c}{650} = 0.8 \pm 0.2$	680		
3		$\frac{830}{803} = 1.0 \pm 0.2$	$\frac{790}{850} = 0.9 \pm 0.2$	1 140	
4			$\frac{1515}{1081} = 1.4 \pm 0.16$	$\frac{960}{1590} = 0.6 \pm 0.07$	2 630

^a Calculations were carried out using the experimental data in Ref. 30.^b In diagonal cells of the table, the spectral shift (cm⁻¹) is shown for the introduction of the nitrogen atom in the *meso*-position of the symmetrical dyes (3).^c In non-diagonal cells, the ratio ($\Delta\nu_{1,2}/\Delta\nu_{\text{calc}}$) of the spectral shift (cm⁻¹) in the asymmetrical dye to the spectral shift calculated by eqn (18) from the shifts of the 'parent' dyes is shown. The accuracy of these relationships is dependent on the accuracy of the absorption maximum measurements (± 1 nm).

on the introduction of a substituent into the PC should have the same sign as the spectral shifts in the 'parent' dyes.

It is of interest to analyse the validity of the above relationships in a series of PMD. The results for the calculations of the relationship ($\Delta\nu_{1,2}/\Delta\nu_{\text{calc}}$) in a series of aza-substituted PMD,¹⁹ where X = —N=, are presented in Table 4.

These results, and the accuracy of the relationships given in Table 4, show that over a sufficiently wide range of differences in the electron-donating ability (basicity) of the end-groups the relationship (19) is observed. Therefore eqn (17) may be used to predict the spectral shifts in asymmetrical molecules based on the experimental data available for the 'parent' compounds. In all the examples shown in Table 4 the FDK rule was also used.

However, in a number of cases, the relationship (19) was not followed and it appears that, although the spectral shift in asymmetrical dyes follows the FDK rule, the shift is larger than that calculated as the mean harmonic of the spectral shifts of 'parent' molecules. This may be because the nitrogen atom

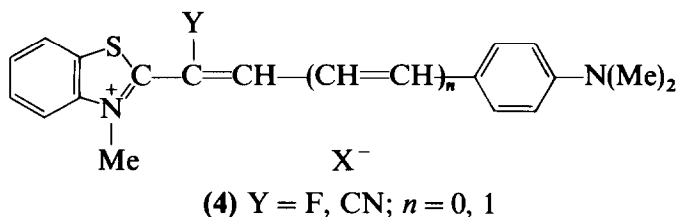
should not be considered as a 'probe', since it contributes greatly to changes in the electron density distribution in dyes. In symmetrical molecules it leads to strong alternation of bonds from the ends to the centre of the chain.²⁷ This lowers the spectral shifts in the 'parent' compounds.

On the other hand, from the values of $\Delta\nu_{i,j}$ ($i, j = 1, 2$) it is possible to calculate the differences in the electron-donating abilities $\Delta\Phi_0$ by using eqn (20):

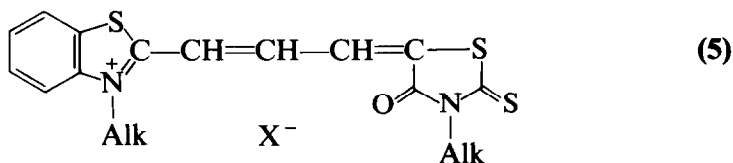
$$\Delta\Phi_0 = \arccos(\Delta\nu_{1,2}/\Delta\nu_{\text{calc}}) \quad (20)$$

This equation, with the introduction of the fluorine atom into the *meso*-position of the chain in the dye triad **3**, may be used to obtain data irrespective of the deviation method or the difference of the end-group basicities.

A second possibility for the non-applicability of eqn (17) is a difference in the direction of the spectral shift in asymmetrical dyes compared with that in the 'parent' symmetrical dyes, i.e. the FDK rule is not obeyed in the asymmetrical dyes. This possibility has not been extensively discussed in the previous literature, with the exception^{19,28} of the observed non-applicability of the FDK rule when F and CN groups are introduced into the α -position of the PMD (**4**):



It follows from eqn (17) that, for the negative relationship ($\Delta\nu_{1,2}/\Delta\nu_{\text{calc}}$), the difference in the electron-donating ability of end-groups for asymmetrical structures **3** should exceed 90° . Since each of the values Φ_0 is within the limits -90° to $+90^\circ$, then the difference $\Delta\Phi_0$ is only greater than 90° , when the values of Φ_{02} and Φ_{01} have different signs, and this implies a deviation from molecular design rule I for classical PMD, because for asymmetrical dyes **3** having an odd chain the electron-donating abilities will have different signs. Thus, if benzothiazole and rhodanine were bound in one molecule by an odd external chain, then the result would not be an ordinary merocyanine but a so-called Hunig²³ or heterylpolyene²⁸ system (**5**):



It has been shown²³ that the Hunig (heterylpolyene) systems can be described by design rule IV, which is an alternative to design rule I for classical PMD.

Rule IV. The two-nuclear Hunig systems (heterylpolyenes) (**2**) are either compounds in which the odd external PC ($n = 2k + 1$) is connected with end-groups having electron-donating abilities Φ_{02} and Φ_{01} of different signs, or in which the even external PC ($n = 2k$) is connected with end-groups having electron-donating abilities Φ_{02} and Φ_{01} of the same sign.

Thus from eqn (17) it is heterylpolyenes that would have property of inversion for the FDK rule as compared with the 'parent' dyes. But since compounds **3** are not heterylpolyenes but asymmetrical classical PMD, then the violation of the FDK rule in them is a non-classical effect that is not taken into account in the linear theory.

The violation of the FDK rule in asymmetrical systems may also be considered with respect to the phenomenological deviation theory.

The absorption wavelength of the asymmetrical dye ($\lambda_{1,2}$) in the substituted and unsubstituted triads may be expressed by eqns (21) and (22), respectively:

$$\lambda_{1,2}(\text{CH}) = (\lambda_{1,1}(\text{CH}) + \lambda_{2,2}(\text{CH}))/2 - d(\text{CH}) \quad (21)$$

$$\lambda_{1,2}(\text{X}) = (\lambda_{1,1}(\text{X}) + \lambda_{2,2}(\text{X}))/2 - d(\text{X}) \quad (22)$$

where symbols (CH) and (X) relate to the unsubstituted and substituted triads (**3**) and d is the deviation of an asymmetrical dye. Subtracting eqn (21) from eqn (22) we obtain the spectral shift [eqn (23)] which is induced by substitution in the asymmetrical dye:

$$\Delta\lambda_{1,2} = \lambda_{1,2}(\text{X}) - \lambda_{1,2}(\text{CH}) = (\Delta\lambda_{1,1} + \Delta\lambda_{2,2})/2 - \Delta d \quad (23)$$

This is equal to a half of the sum of the spectral shifts for symmetrical 'parent' molecules, minus the deviation difference [$\Delta d = d(\text{X}) - d(\text{CH})$] in the substituted and unsubstituted dyes. Since in symmetrical 'parent' dyes the FDK rule is observed, then $\Delta\lambda_{1,1}$ and $\Delta\lambda_{2,2}$ have identical signs. The sign of the value $\Delta\lambda_{1,2}$ is the same as the sign of the value of $(\Delta\lambda_{1,1} + \Delta\lambda_{2,2})/2$ if the FDK rule is observed, and it has the opposite sign when the FDK rule is violated in asymmetrical dyes.

Conditions (rule V) of the FDK rule violation in the asymmetrical PMD are therefore apparent.

Rule V. (i) The FDK rule is violated for asymmetrical PMD in the case when the absolute value of the deviation variation for substitution exceeds the mean spectral shift in the 'parent' systems:

$$|\Delta d| > |(\Delta\lambda_{1,1} + \Delta\lambda_{2,2})/2| \quad (24)$$

(ii) The sign of the deviation variation resultant from the substitution should be equal to the sign of the spectral shift in the 'parent' dyes:

$$\Delta d \cdot (\Delta\lambda_{1,1} + \Delta\lambda_{2,2})/2 > 0 \quad (25)$$

It should be emphasised that the direction of the deviation variation, i.e. its decrease ($\Delta d < 0$) or increase ($\Delta d > 0$), itself plays no role on the introduction of a substituent into the asymmetrical dye. The only factor of importance is the combination of these signs. Violation of the FDK rule will be observed if, according to the FDK rule, the bathochromic shift due to the substituent is also accompanied by an increase in asymmetry, i.e. by an increase in the deviation. Conversely, a hypsochromic shift will, according to the FDK rule, be accompanied by a considerable decrease in the asymmetry of the system, i.e. by a deviation decrease.

The above factors have been qualitatively used^{19,28} to explain the FDK rule violation resulting from the introduction of a fluorine substituent into the α -position of asymmetrical styryls (4). However, they were considered to be unacceptable in the case of the electron-acceptor CN group. It was concluded that only the deviation increase may lead to FDK rule violation, and an assumption of additional conjugation between the CN group and the styryl residue was used to explain this phenomenon. However, from the above considerations, these effects may be accounted for by similar reasoning. Moreover, the one-electron theory takes into account such a conjugation and, as eqn (17) demonstrates, this does not cause violation of the FDK rule.

A more complete theory for these dye systems is therefore required.

3 CONCLUSION

In this paper we have analysed the influence of a single fluorine atom on the properties of polymethine dyes, defined more precisely the values of the quantum chemical parameters for this atom within the framework of the one-electron theory and compared a number of results of the theory with experimental data. Naturally the mechanisms affecting the spectral properties of dyes are not limited by electronic influences only. However, we deliberately limited our investigation to this influence in order to study its regularities and possible effects. With the development of a theoretical model, we were able to predict a number of new effects during monosubstitution of polymethine dyes, and to evaluate to what extent the observable effects were accounted for by available theory. The sensitivity rule makes it possible to demonstrate the degree of variation of the end-group basicity with introduction of the fluorine atom into the α -position of

the PC. The use of a fluorine atom as a 'probe' allows the study of the electron structure of polymethine systems, irrespective of other methods of investigating colour theory.

REFERENCES

1. Yagupolskii, L. M., Il'chenko, A. Ya. & Kul'chitskii, M. M., *Dokl. Akad. Nauk SSSR* (in Russian), **209** (1973) 138.
2. Dewar, M. J. S., *The Molecular Orbital Theory of Organic Chemistry*. McGraw-Hill, New York, 1969.
3. Koster, G. F. & Slater, J. C., *Phys. Rev.*, **95** (1954) 1167.
4. Dyadyusha, G. G. & Ushomirsky, M. N., *Zh. Structur. Khimii* (in Russian), **28** (1987) 17.
5. Dyadyusha, G. G. & Ushomirsky, M. N., *Teoret. Experim. Khim.* (in Russian), **22** (1986) 137.
6. Dyadyusha, G. G. & Ushomirsky, M. N., *Teoret. Experim. Khim.* (in Russian), **21** (1985) 268.
7. Forster, Th., *Z. Phys. Chem., B*, **48** (1940) 12.
8. Knott, E. B., *J. Chem. Soc. (London)* (1951) 1020.
9. Dewar, M. J. S., *J. Chem. Soc. (London)* (1950) 2329.
10. Dyadyusha, G. G. & Kachkovskii, A. D., *Ukrain. Khim. Zh.* (in Russian), **41** (1975) 1176.
11. Kuhn, H., *J. Chem. Phys.*, **16** (1948) 840.
12. Streitweiser, A., *Molecular Orbital Theory for Organic Chemists*. Wiley, New York, London, 1965.
13. I'Haya, Y., *J. Amer. Chem. Soc.*, **80** (1958) 5543.
14. Ushomirsky, M. N., *Ukrain. Khim. Zh.* (in Russian), **50** (1984) 1096.
15. Kiprianov, A. I. & Pilyugin, G. T., *Uchen. Zap. Hark. Derzh. Univ.*, **10** (1937) 91.
16. Brooker, L. G. S., *Rev. Mod. Phys.*, **14** (1942) 275.
17. Il'chenko, A. Ya., *Ukrain. Khim. Zh.* (in Russian), **42** (1976) 162.
18. Yagupolskii, L. M., Trushanina, L. I. & Il'chenko, A. Ya., *Zh. Org. Khim.* (in Russian), **11** (1975) 2168.
19. Il'chenko, A. Ya., Kovalchuk, R. E. & Yagupolskii, L. M., *Zh. Org. Khim.* (in Russian), **11** (1975) 2163.
20. Platt, J. R., *J. Chem. Phys.*, **25** (1956) 80.
21. Dyadyusha, G. G. & Kachkovskii, A. D., *Ukrain. Khim. Zh.*, **44** (1978) 948.
22. Dyadyusha, G. G. & Ushomirsky, M. N., *Teoret. Experim. Khim.* (in Russian), **30** (1989) 266.
23. Ushomirsky, M. N., *Teoret. Experim. Khim.* (in Russian), in press.
24. Ushomirsky, M. N. & Lifshitz, E. B., *Teoret. Experim. Khim.* (in Russian), in press.
25. Heilbronner, E., *Helv. Chim. Acta*, **36** (1953) 170.
26. Lifshitz, E. B., Spasokukotskii, N. S., Yagupolskii, L. M. *et al.*, *Zh. Obshch. Khim.* (in Russian), **38** (1968) 2025.
27. Dyadyusha, G. G. & Kachkovskii, A. D., *Ukrain. Khim. Zh.* (in Russian), **44** (1978) 1069.

28. Kovalchuk, R. E. & Il'chenko, A. Ya., *Ukrain. Khim. Zh.* (in Russian), **42** (1976) 1174.
29. Nesterenko, Yu. A., Tolmachiov, A. I. & Kachkovskii, A. D., *Ukrain. Khim. Zh.* (in Russian), **54** (1988) 883.
30. Kiprianov, A. I., *Color and Structure of Cyanine Dyes*. Kiev, 1979 (translated from Russian).