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Imidocarbocyanines—Spectral Sensitizers of Photographic Silver Halide Emulsions

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SUMMARY

The review deals with the main results of several investigations of the relationship between the chemical structure of imidocarbocyanines and their basicity, redox potentials and photographic action in silver halide emulsions. A number of quantitative and qualitative relationships connecting pK_a *and* $E_{1,2}^{Ox(Red)}$ *of imidocarbocyanines and the Hammett* σ_p*-constants of different electronic substituents ranging from* CH_3O $(\sigma_p = -0{\cdot}27)$ *to* CF_3SO_2 $(\sigma_p = 0{\cdot}96)$ *and the Taft* σ^**-constants of groupings attached to the nitrogen atom (alkyl, aryl, ω-trifluoromethylalkyl or sulphoalkyl), are discussed. The main factors contributing to the total effect of spectral sensitization of silver halide emulsions by imidocarbocyanines are analyzed and a relationship between the degree of suppression of their sensitizing action by colour components and the tendency to aggregate on the surface of silver halide crystals is established.*

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1. INTRODUCTION

1,1',3,3'-Tetramethylimidocarbocyanine was described first in 1933[1] and at once drew specialists' attention. Its visible and UV spectra were studied[2] and the high basicity of the benzimidazole ring was revealed.[3] Subsequently it was shown that the compact structure of molecules of the dye causes its marked tendency to *J*-aggregation.[4]

Despite the fact that in 1949 a convenient method for the preparation of imidocarbocyanines (ICC) was introduced,[5] up to 1956 symmetrical dyes containing the benzimidazole moiety were mentioned in only a few patents together with the numerous asymmetrical compounds, e.g. imidooxacarbocyanines.[6]

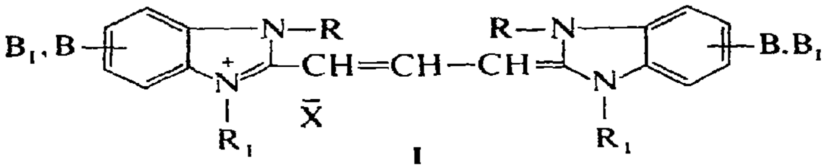
In 1956 at the International Conference on Scientific Photography in Cologne it was reported[7] that the introduction of electron-withdrawing substituents (Cl, CF_3) into the heterocyclic moiety of ICC results in considerable improvements in the photographic efficiency. An increasing number of patents and articles has followed. (In 1933–56 only ten articles concerning this problem appeared and in the years that followed (1957–82) there were more than 300 of them.) At the present time benzimidazole derivatives belong to one of the most intensely studied groups of polymethine dyes (PMD).[8]

Most of the publications deal with the preparation and application of ICC.[9-12] It is worth mentioning that ICC are recommended for sensitization of silver halide emulsions both individually and in mixtures with PMD of other types.[8] The numerous publications concerning the synthesis of ICC, their colour or solvatochromism[13,14] deserve a separate review.

A number of publications deal with information, mostly incomplete, concerning the properties of ICC—their basicity,[15,16] redox potentials,[17,18] ability to form charge-transfer complexes[15] and aggregate in different conditions,[19] photographic action,[20] luminescence and phosphorescence.[21]

Results of systematic studies of relationships between the physical, chemical and photographic properties of ICC and their structure have been published in different, sometimes unavailable journals. In this connection it was expedient to summarize the main results of these studies taking into consideration the tendencies which have been revealed in the literature in recent years.

Properties of ICC with different substituents in the benzene rings or linked to the nitrogen atoms (structure I) are discussed.[7,22–51]



I

(a) 5,5′-B; $R = R_1 = C_2H_5$
(b) 5,5′-B; $R = C_6H_5$; $R_1 = C_2H_5$
(c) 5,5′-B-6,6′-B_1; $R = R_1 = C_2H_5$
(d) 5,5′-B-6,6′-B_1; R and R_1 = different substituents B and R are specified in Tables 1–4.

2. BASICITY OF IMIDOCARBOCYANINES

The basicity of more than 300 imidocarbocyanines[22,26–30,32–40] was described in ref. 26. It was shown that the pK_a values of *p,p′*-disubstituted ICC **Ia** and **Ib**, analogously to indo-, thia-, quino-2- and 4-carbocyanines,[26–29,52] vary in proportion to the Hammett σ_p-constants of substituents ($r > 0{\cdot}97$). For example, for **Ia**:

$$pK_a = 5{\cdot}83 - 3{\cdot}23\,\sigma_p \qquad \text{(G)}$$

and for **Ib**:

$$pK_a = 4{\cdot}17 - 3{\cdot}16\,\sigma_p \qquad \text{(D)}$$

A notable feature of these relationships is the high value of ρ (> 3). This fact indicates a high 'sensitivity' of the basicity of these dyes to structural changes.[26–29,33]

Simultaneous introduction of substituents into the 5,5′- and 6,6′-positions of 1,1′,3,3′-tetraethyl-ICC (**Ic**) brings about almost in all cases the additive changes in the values of pK_a according to eqn. (1), that is $pK_{a(\text{exp})} = pK_{a(\text{calc.})}$ (e.g. dyes **1–3**, Table 1).[28,35]

$$pK_a = 5{\cdot}83 - 3{\cdot}23[(\sigma_I + \sigma_R)^B + (\sigma_I + \sigma_R)^{B_1}] \qquad (1)$$

In the case when B and B_1 are substituents which are able to interact with each other through direct polar resonance, for example OCH_3 and SO_2CF_3, OCH_3 and NO_2, F and SO_2CF_3 or F and $COOC_2H_5$ groups (e.g. dyes **4** and **5**, Table 1), the contribution of the σ_R component of the electron-donating (F, OCH_3) and electron-withdrawing ($COOC_2H_5$, NO_2, SO_2CF_3) substituents into conjugation with the benzimidazole rings is decreased. This results in a lower basicity of ICC compared with calculated values: $pK_{a(exp.)} < pK_{a(calc.)}$ (c.f. dyes **4** and **5**, Table 1).

$$pK_a = 5{\cdot}83 - 3{\cdot}23[(\sigma_I^B + \sigma_I^{B_1}) + n(\sigma_R^B + \sigma_R^{B_1})], \qquad n < 1 \qquad (2)$$

When B and B_1 are bulky electron-withdrawing substituents, disturbance of coplanarity by the substituents leads to a decrease in their conjugation with the chromophore and brings about an increase in the experimental pK_a value, i.e. $pK_{a(exp.)} > pK_{a(calc.)}$ (of dyes **6**–**9**, Table 1):

$$pK_a = 5{\cdot}83 - 3{\cdot}23[(\sigma_I + \sigma_R \cos^2 \theta)^B + (\sigma_I + \sigma_R)^{B_1}] \qquad (3)$$

(Values of θ are specified in Table 1.)

$$pK_a = 5{\cdot}83 - 3{\cdot}23 \times 2(\sigma_I + \sigma_R \cos^2 \theta)^B; \qquad B = B_1; \qquad \theta = 65° \quad (4)$$

As shown in Table 1, the basicity of ICC **5** and **4** is lower than expected

TABLE 1

Values of pK_a and λ_{max} of 5,5',6,6'-Tetrasubstituted ICC (Ic) in Ethanol[28,25]

Dye no.	*B*	B_1	pK_a *Exp.*	pK_a *Eqn.*	pK_a *Calc.*	ΔpK_a	λ_{max} *(nm)*	$\Delta\lambda_{max}$ *(nm)*
1	CN	Cl	3·00	1	3·06	−0·06	522	−1
2	F	F	5·45	1	5·44	+0·01	506	−2
3	CF_3	F	4·05	1	4·05	0·00	507	0
				1	2·53	−0·40		
4	SO_2CF_3	F	2·13	2(*n* = 0·5)	2·15	−0·02	527	+2
5	$COOC_2H_5$	F	3·92	1	4·18	−0·26		
				2(*n* = 0·75)	3·93	−0·01	519	0
6	$COOC_2H_5$	Cl	3·80	1	3·63	+0·17		
				3	3·78	+0·02	517	−6
7	$COOC_2H_5$	Br	3·83	1	3·63	+0·20	518	−7
				3	3·86	−0·03		
8	$COOC_2H_5$	I	4·00	1	3·80	+0·20		
				3	4·04	−0·04	518	−8
9	$COOC_2H_5$	$COOC_2H_5$	3·73	1	2·93	+0·80	516	
				4	3·71	+0·02		−14

In a series of 5,5'-dicarboethoxy-6,6'-B_1-ICC, the angle θ for different B_1 has values respectively of 0° (F), 33° (Cl), 44° (Br), 45° (I), 81° (CF_3).

according to the additivity principle (eqn. (1)): $\Delta pK_a = pK_{a(\text{exp.})} - pK_{a(\text{calc.})}$ and is respectively equal to $-0{\cdot}26$ and $-0{\cdot}40$. Taking into consideration the value of the σ_R components for $COOC_2H_5$ and SO_2CF_3 groups (0·15 and 0·31) it can be shown that the conjugation of the substituent with the chromophore is decreased by $\frac{1}{4}$ and $\frac{1}{2}$ respectively, i.e. at $n = 0{\cdot}75$ and 0·5 in eqn. (2) the experimental and calculated values of pK_a coincide.

On passing from 5,5'-dicarboethoxy-6,6'-difluoro-ICC (**5**) to the 5,5'-dicarboethoxy-6,6'-dichloro-bromo- or iodo- derivatives (dyes **6–8**) the use of eqn. (1) gives $\Delta pK_a = 0{\cdot}20–0{\cdot}80$.

Considering the fact that in a series of *o*-substituted *N*,*N*-dimethylanilines displacement of the substituent from the plane of the aromatic ring by an angle θ decreases the conjugation in proportion to $\cos^2 \theta$,[53] eqns (3) and (4) were proposed for the calculation of the pK_a values of 6,6'-disubstituted 5,5'-dicarboalkoxy-ICC. The pK_a values of 5,5'-dicarboalkoxy-6,6'-disubstituted and 5,5'6,6'-tetracarboalkoxy-ICC, calculated from these equations with due regard for the rotation of the carboalkoxy groups, coincide reasonably with the experimental data ($\Delta pK_a \leq 0{\cdot}05$, Table 1).

From Table 1 it also follows that in a series of 6,6'-disubstituted 5,5'-dicarboethoxy-ICC the values of ΔpK_a and $\Delta\lambda_{max}$ change in accordance with the rotation angle of the carboethoxy groups that allowed the rough separation of the influence of resonance (σ_R) and inductive (σ_I) components on the change in the colour of ICC. It was found that their contributions to the bathochromic shift of λ_{max} are almost equal.[35]

Properties of ICC with different substituents attached to the nitrogen atoms (**Id**) have also been investigated.[22,29,32,33,36–40]

Proceeding from the values of σ^* of *N*-alkyl groups one might expect that the basicity of ICC would increase with the number of carbon atoms ($R = C_nH_{2n+1}$). However, with the transition from 1,1'-diethyl- and 1,1'-diphenyl-3,3'-diethyl-ICC to higher 3,3'-di(*n*-alkyl) derivatives ($n = 3–10$) the pK_a values decrease (Table 2). This indicates a prevailing influence of the spatial arrangement of alkyl groups shielding the polymethine chain[54] which, thus, hinders protonation of the nitrogen atom.

This conclusion is confirmed by a comparison of the pK_a values of ICC containing *n*- and iso-octyl groups at positions 3 and 3' (cf. dyes **12**, **13** compared with **11**, $\Delta pK_a = 0{\cdot}56$ and 1·04) as well as by the lower basicity of 1,1'-di(*n*-butyl)-3,3'-(*n*-octyl)-5,5',6,6'-tetrachloro-ICC as compared with the corresponding 1,1'-diethyl-3,3'-di(*n*-decyl)-substituted compound (dyes **14** and **15**, $m + n = 12$, Table 2).

TABLE 2
Values of pK_a of 5,6,5′,6′-tetrachloro-ICC with Different N-substituents (**Id**)[29,32,33,38–40]

Dye no.	*R* C_nH_{2n+1}	R_1	pK_a
10	CH_3	C_2H_5	4·61
11	C_2H_5	C_2H_5	4·33
12	C_2H_5	n-C_8H_{17}	3·77
13	C_2H_5	i-C_8H_{17}	3·28
14	C_2H_5	n-$C_{10}H_{21}$	3·76
15	n-C_4H_9	n-C_8H_{17}	3·53
16	C_2H_5	$(CH_2)_3SO_3^-$	5·20
17	C_2H_5	$(CH_2)_3CH_3$	4·15
18	C_2H_5	$(CH_2)_3CF_3$	3·85
19	C_2H_5	CH_2CF_3	2·30

On passing from 1,1′-diethyl- and 1,1′-diphenyl-3,3′-diethyl-ICC to the corresponding dyes containing sulphopropyl groups at positions 3 or 3 and 3′, the basicity unexpectedly increases markedly (Table 2).[33,39]

Analysis of numerous data suggests the following explanation for the 'anomalous' increase in the basicity of these ICC. This can be explained by the formation of the internal betaine bond between the SO_3^- group and a positively charged nitrogen atom of the benzimidazole moiety in the molecule of highly basic imidocarbocyanines, thus increasing the electron density at the α-carbon atom of the polymethine chain.

In a series of 1,1′-diethyl-3,3′-di(ω-trifluoroalkyl)-5,5′-bis(trifluoromethylsulphonyl)-, -5,5′-bis(trifluoromethyl)- and 5,5′,6,6′-tetrachloro-ICC linear dependences between the values of pK_a and σ^*-constants of substituents at positions 3 and 3′ were found as follows in eqns (5)–(7) respectively; $r \geq 0{\cdot}98$:

$$\mathrm{p}K_a = 2{\cdot}20 - 1{\cdot}42\sigma^* \tag{5}$$

$$\mathrm{p}K_a = 3{\cdot}98 - 1{\cdot}84\sigma^* \tag{6}$$

$$\mathrm{p}K_a = 4{\cdot}08 - 1{\cdot}98\sigma^* \tag{7}$$

Determination of the redox potentials (in methanol) of p,p'-disubstituted (**Ia**, **Ib**) and some other (**Id**) ICC has shown that dependences $E_{1/2}^{\mathrm{Ox}} = f(\sigma_p)$ and $E_{1/2}^{\mathrm{Red}} = f(\sigma_p)$ are linear ($r \geq 0{\cdot}99$),[41] similar to those of indoline- and thia-carbocyanines.[55]

For ICC (**Ia**):

$$E_{1/2}^{\mathrm{Ox}} = 0{\cdot}512 + 0{\cdot}305\sigma_{\mathrm{p}}$$

$$E_{1/2}^{\mathrm{Red}} = 1{\cdot}805 + 0{\cdot}498\sigma_{\mathrm{p}}$$

For ICC (**Ib**):

$$E_{1/2}^{\mathrm{Ox}} = 0{\cdot}642 + 0{\cdot}220\sigma_{\mathrm{p}}$$

$$E_{1/2}^{\mathrm{Red}} = -1{\cdot}741 + 0{\cdot}461\sigma_{\mathrm{p}}$$

It should be noted that the $E_{1/2}^{\mathrm{Ox(Red)}}$ values of a number of ICC, notable for the hydrophobic–hydrophilic balance of substituents attached to the nitrogen atoms or for their spatial arrangement (see below), are quite close,[41,56] in contrast to the values of $\mathrm{p}K_{\mathrm{a}}$.

3. AGGREGATION CHARACTERISTICS OF IMIDOCARBOCYANINES

At present the ability of ICC to form *J*-aggregates on the surface of emulsion microcrystals is well known.[7,19,22,23] Their tendency to *H*-aggregation has been observed only in a few cases.[30,31,33,39] For the characterization of the absorption spectra of ICC in emulsion the following conventional designations for the correlation of the intensity of *J*- and *M*-bands are used: $J/M > 2 - J$; $2{\cdot}0 - 1{\cdot}5 - J > M$; $1{\cdot}4 - 1{\cdot}0 - J \geq M$; $1{\cdot}0 - J < M$.[23]

In 1956 it was found that the absorption spectra of 1,1′,3,3′-tetraethyl-ICC (**Ia**: B = H), in emulsion, showed in addition to the unresolved molecular absorption bands, J_1- and J_2-bands ($J_2 < J_1 > M$). The analogous 1,1′-diphenyl-substituted ICC (**Ib**) does not reveal a tendency to *J*-aggregation (*M* spectrum type,[7,22,23] Fig. 1b, curves 1 and 2).

All the substituents in the heterocyclic nuclei can be divided into three major groups according to their influence on the type of absorption spectra of ICC in emulsion:[23]

(i) Electron-donating: CH_3, CH_3O, CF_3O and CH_3CONH groups, which cause only a slight redistribution of *J*- and *M*-states in the adsorption layer; *J* spectrum type (Fig. 1a, curve 2).

(ii) Electron-withdrawing: Halogen, CN, $COOC_2H_5$ groups and such groupings as CF_3, $CF_3{-}CH{=}CH{-}$ and $CF_3{-}CF{=}CF{-}$ increase the ability for *J*-aggregation significantly;[42] *J* or $J > M$ spectrum type (Fig. 1a, curve 3).

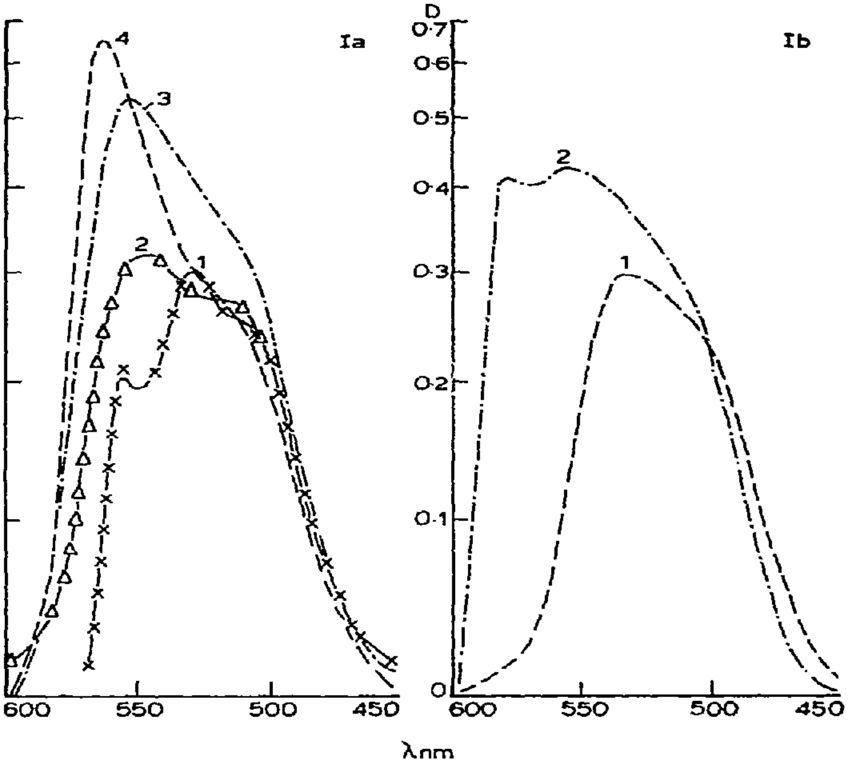


Fig. 1. Absorption curves in emulsion of ICC **Ia** and **Ib** ICC concentration = 192 × 10^{-6} wt/wt AgHal. **Ia**: 1, B = H; 2, B = OCH_3; 3, B = $COOC_2H_5$; 4, B = SO_2CF_3. **Ib**: 1, B = H; 2, B = $COOC_2H_5$.

(iii) Electron-withdrawing sulphur- and fluorine-containing groupings, such as CF_3S, CF_3SO, SO_2F, CF_3SO_2 and heteroaryl radicals suppress the tendency to *J*-aggregation almost completely; *M*-spectrum type (Fig. 1a, curve 4).

On passing from the 5,5′-disubstituted **Ia** ICC to the corresponding **Ib** dyes the ability to form *J*-aggregates is diminished (**Ib**, B = halogen, $COOC_nH_{2n+1}$, CN; Fig. 1b, curve 2).

5,5′6,6′-Tetrasubstituted ICC **Ic** with halogen atoms, CN, COOAlk or CF_3 groups, analogously to the disubstituted dyes, are adsorbed on the surface of emulsion microcystals preferably in J_2- or J_3-states. In the case when not only these substituents but also sulphur- and fluorine-containing groups (CF_3S, CF_3SO_2, etc.) are present, the ability of ICC to form *J*-aggregates disappears almost completely.[24,33,43]

The nature of sensitization and absorption spectra of ICC in emulsion is, to a lesser extent, affected by the influence of groupings attached to the heterocyclic nitrogen atoms, as has been observed in the case of thiacarbocyanines.[57] The increase in the number of carbon atoms in C_nH_{2n+1} groups at positions 3 and 3′ of 1,1′-diethyl-5,5′-di- and 5,5′,6,6′,tetra-substituted ICC decreases their tendency to *J*-aggregation markedly only after $n > 6$. The substitution of ethyl groups at 1,1′- and 3,3′ positions of ICC for *n*-alkyl with *n* and $m > 3$ (Table 2) decreases the absorbability of dyes on the surface of microcrystals (MC) and forms J_1- instead of J_2-states.[32,33,40]

Analogously to the tetraalkyl substituted dyes, *J*-bands also prevail in the absorption spectra of 1,1′-diethyl-3,3′-di(ω-trifluoroalkyl)-5,5′,6,6′-tetrachloro-ICC in emulsion, but the absorption maximum is shifted bathochromically by 35–37 nm in comparison with 40–45 nm for the 1,1′3,3′-tetrasubstituted dye.[39] The general shape of the sensitization and absorption spectra curves does not usually change with substitution of ethyl groups at positions 3 or 3 and 3′ in 5,5′-dicarboethoxy-, 5,5′,6,6′-tetrachloro- and other di- and tetra-substituted ICC for γ-sulphopropyl, γ-sulphoallyl or carboxyalkyl groups: a narrow intense *J* band with a shoulder on the shorter wavelength part of the curve in the region of the molecular absorption band prevails.[33,39,44–46] The lengthening of the alkyl radical of γ-sulphoalkyl groups at position 3 of 1,1,′3′-triethyl-5,5′,6,6′-tetrachloro- and especially of -5,5′-dicarboethoxy-ICC brings about a decrease in intensity of *J*-bands and sometimes even the appearance of *H*-band, that is a ‘heterogeneous’ structure of the adsorption layer is observed in this case (spectrum type $J \leq M \geq H$). The sodium salt of 1,1′-diethyl-3,3′-di(γ-sulphopropyl)-5,5′-bis(trifluoromethylsulphonyl)-ICC is absorbed on the surface of microcrystals mainly in the molecular state as is the 3,3′-diethyl substituted compound.[33,39]

4. SENSITIZING PROPERTIES OF IMIDOCARBOCYANINES

Systematic studies of relationships between the chemical structures of ICC and their photographic properties were carried out for a coarse-grained AgBr/J emulsion (CGE, $d = 1{\cdot}0\,\mu m$, $pBr = 2{\cdot}3 \pm 0{\cdot}1$, $pH = 7{\cdot}0$).

The sensitizing action was characterized by the value of the additional light sensitivity of the corresponding photolayers shielded with a yellow filter ($S_{0\cdot85}^{\mathrm{YCf}-18}$)† and data of the relative quantum yield of sensitization, ϕ_r^{420}.

It is known that the total effect of the spectral sensitization (SS) is determined by the change in the basicity of dyes and their tendency to *J*-aggregation according to the substituent present. Numerous experimental data have shown that a decrease in the basicity of the ICC dyes caused by the introduction of electron-withdrawing substituents into the heterocyclic ring usually increases both the sensitizing efficiency and the relative quantum yield of sensitization.[7,23,24,29,30,33,41] The increase in the basicity of ICC containing electron-withdrawing substituents brings about a decrease in the sensitizing and an increase in the hazing effects (dyes **20**, **21**, Table 3).

An increase in the efficiency of ICC on passing from dye **20** to the 5,5′-difluoro derivative, dye **22**, ($\mathrm{p}K_a = 5\cdot45$ and $6\cdot00$, respectively) is determined mainly by the formation in the absorption layer of photochemically active *J*-aggregates ($\phi_r^{420} = 0\cdot8$).

A decrease in the basicity of ICC (**Ia**) causes a high efficiency and corresponding values of ϕ_r^{420} of the molecular state of ICC (cf. dyes **20**, **26**, **27**). In the case of 5,5′-dichloro (CF_3, COOAlk, CN)-ICC (**Ia**) an increase in the sensitizing effect is a result of the increased ability for *J*-aggregation and of the increase in ϕ_r^{420} in *M*- and especially *J*-states with decreasing basicity (cf. dyes **20**, **23**, **24**).[23]

The particular importance of these factors for the SS total effect is confirmed by the following facts.

(i) In emulsions which differ from a coarse-grained emulsion in that surfactants are used for the precipitation of the solid phase, ICC dyes **20** and **22** do not show a tendency to *J*-aggregation and bring about the equal but lower level of light sensitivity of the photolayers.[33,56]

(ii) The equal efficiency of ICC dyes **20** and **25** ($\mathrm{p}K_a$ $5\cdot45$ and $4\cdot84$) and the rapid rise in efficiency on passing from **29** to **32** ($\mathrm{p}K_a$ $4\cdot45$ and $2\cdot78$).[23]

In a series of 5,5′-di($C_nF_{2n+1}SO_2$)-ICC (**Ia**) with $n = 1$–3, the properties of dyes are very close ($\Delta\mathrm{p}K_a < 0\cdot2$). At $n > 3$ and especially with branching

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† YCf, yellow colour filter.

TABLE 3
Properties of ICC **Ia** and **Ib**[23,33,41]

Dye no.	*B*	pK_a	$E^{Red}_{1/2}$	*Spectrum type*	$S^{YCf\text{-}18}_{0\cdot 85}$	D^8_0	ϕ_r^{420} *M*	ϕ_r^{420} *J*
				Ia $R = C_2H_5$				
20	H	5·45	−1·80	$J_2 < J_1 > M$	100	0·15	0·35	J_1 −0·44 J_2 −0·40
21	OCH_3	6·80	−1·94	$J > M$	25	0·44	—	—
22	F	6·00	−1·78	*J*	170	0·15	0·38– 0·58[a]	0·83
23	Cl	4·98	−1·69	*J*	200	0·15	0·50	0·65
24	$COOC_2H_5$	4·28	−1·55	*J*	300	0·17	0·57	0·73
25	Benzothiazol-2-yl	4·84	−1·60	*M*	100	0·40	—	—
26	$SOCF_3$	2·50	−1·46	*M*	230	0·12	0·70	—
27	SO_2CF_3	2·44	−1·34	*M*	320	0·14	0·75	—
				Ib $R = C_6H_5$				
28	H	4·45	−1·74	*M*	100	0·16	0·65	—
29	F	3·98	−1·71	$J < M$	120	0·20	0·67	0·43
30	Cl	3·40	−1·64	$J \ll M$	200	0·10	0·75	0·60
31	$COOC_2H_5$	2·62	−1·50	$J \leq M$	240	0·19	0·70	0·35
32	Benzothiazol-2-yl	2·78	−1·54	*M*	320	0·30	0·90	—
33	SO_2F	1·57	−1·34	*M*	170	0·12	0·58	—
34	SO_2CF_3	1·04	−1·31	*M*	170	0·15	0·35	—

[a] The value of ϕ_r of the *M*-state is overestimated by the superposition of a very intense *J*-band (λ_{max} 535 nm and 578 nm, respectively).

of the perfluoroalkyl radical chain the sensitizing action is drastically decreased: for example ten-fold on passing from the 5,5′-di(CF_3SO_2) derivative to the 5,5′-di($(CF_3)_3CSO_2$)-substituted dye. This is primarily caused by a decrease in the adsorption on the microcrystals.[47]

Most of the studied symmetrical tetra-substituted and asymmetrical di- and tri-substituted ICC do not differ from or improve on the corresponding disubstituted dyes in their sensitizing action. The sensitization and absorption spectra characteristics of these dyes in emulsion is determined by the combination of substituents.[24,33,43,48,49]

In a series of 1,1′-diethyl-5,5′-di- and 5,5′,6,6′-tetra-substituted ICC (**Id**) an increase in the number of carbon atoms in the C_nH_{2n+1} groups ($n = 2$–8) at positions 3 and 3′ does not affect the efficiency of the dyes,[32,33] but the efficiency is decreased in the case of 3,3′-di-$CF_3(CH_2)_n$-substituted dyes (n = 1–3).[38]

The sensitizing action and the value of ϕ_r^{420} of *J*- and *M*-states are markedly increased on passing from 1,1′,3,3′-tetraethyl-5,5′-dicarboethoxy-5,5′-dichloro- and -5,5′,6,6′-tetrachloro-ICC to the corresponding 3-ethyl-3′-(γ-sulphopropyl)- and 3,3′-di(γ-sulphopropyl)-substituted dyes.[33,39,44,45]

From Fig. 2[41] it is seen that the values of ϕ_r^{420} of *M*-states of ICC (**Ia**) rise with a decrease in pK_a and $E_{1/2}^{Red}$ and an increase in E^{Ox} (as used in the literature.[58,59] the designation $E_{1/2}^{Red}$ > or < implies the absolute value of $E_{1/2}^{Red}$).

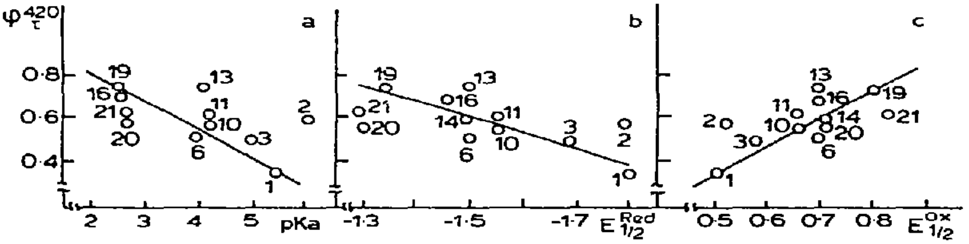


Fig. 2. Dependence of ϕ_r^{420} of *M*-states of ICC **Ia** in emulsion on the value of pK_a(a), $E_{1/2}^{Red}$ (b) and $E_{1/2}^{Ox}$ (c). Key for B: 1, H: 2, F: 3, Cl: 4, $CONHCH_3$; 5, thiazol-2-yl; 6, CN: 7, benzthiazol-2-yl; 8, $N{=}N{-}C_6H_5$; 9, $COOCH_3$; 10, $COOC_2H_5$; 11, CF_3; 12, SCF_3; 13, SO_2NHCH_3; 14, $SO_2N(CH_3)_2$; 15, $SO_2NHC_6H_5$; 16, $SOCF_3$; 17, $N{=}N{-}CF_3$; 18, SO_2F; 19, SO_2CF_3; 20, $SO_2CF_2CHF_2$; 21, $SO_2CF_2CHFCF_3$.

However, the relationships $\phi_r^{420} = f(pK_a)$, $\phi_r^{420} = f(E_{1/2}^{Red})$ and $\phi_r^{420} = f(E_{1/2}^{Ox})$ can be only roughly described by a linear equation with $r = 0{\cdot}60$–$0{\cdot}65$. A threefold increase in the efficiency of ICC (**Ia**) with a decrease in pK_a from 5·45 to 2·44 and in $E_{1/2}^{Red}$ from −1·80V to −1·34V was observed in emulsions with different sizes of microcrystals (d = 1·0–0·05 μm) and thus it is a general effect, although it is not consistent with the general idea that with an increase in the absolute value of $E_{1/2}^{Red}$ the efficiency of PMD rises or is not changed (when $E_{1/2}^{Red} \geq 1$–$1{\cdot}05$).[56–58]

From Fig. 3 it is seen that 1,1′-diphenyl-ICC (**Ib**) shows in a coarse-grained emulsion a marked ability to desensitize (S) which decreases with the basicity (from 4·45 to 1·04) and with $E_{1/2}^{Red}$ from −1·74V to −1·32V. At the same time $E_{1/2}^{Ox}$ increases from 0·64 to 0·85, and the relationships $S = f(pK_a)$ and $S = f(E_{1/2}^{Ox})$ approach linearity (r = 0·9 and 0·8). In a series

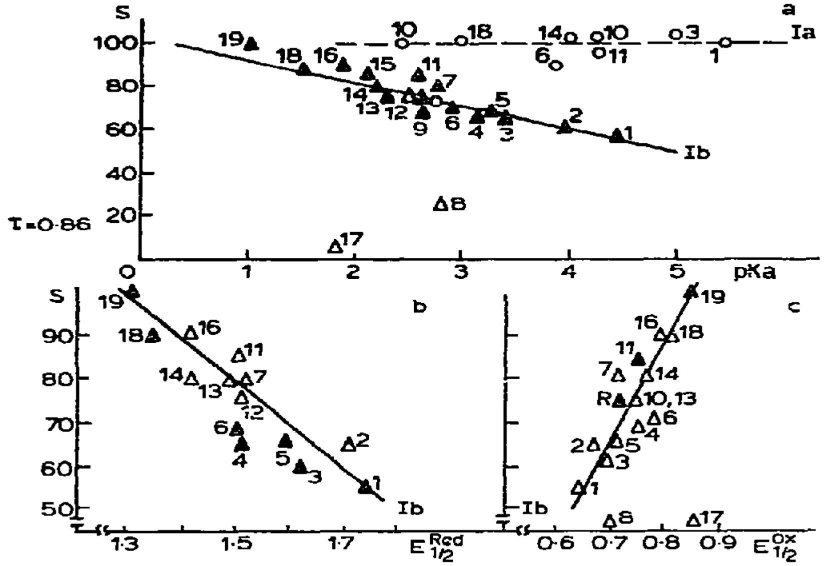


Fig. 3. Dependence of the sensitizing action of ICC **Ia** and **Ib** on the value of pK_a (a), $E^{Red}_{1/2}$ (b) and $E^{Ox}_{1/2}$ (c). B substituents are as in Fig. 2.

of 1,1′-dithyl-substituted ICC (**Ia**) the analogous changes in pK_a, $E^{Red}_{1/2}$ and $E^{Ox}_{1/2}$ do not cause desensitization. In this connection the ability of ICC for desensitization can be explained by twisting of the phenyl rings from planarity, causing a specific orientation of ICC on the surface of microcrystals.[33,50]

From the above, it follows that the properties of 1,1′-diethyl- and 1,1′-diphenyl-ICC (**Ia** and **Ib**) differ substantially. Data summarized in Table 4 characterize the changes in the basic parameters of these dyes caused by the introduction of substituents into the heterocyclic rings. It has been shown[50] that differences in the physicochemical and photographic properties can be logically explained by the assumption that the phenyl rings at positions 1 and 1′ of ICC, as in 1-phenylbenzimidazole, are rotated from the heterocycle plane, the deviation angle being equal to 52°[60] of 40°.[61]

A decrease of $\Delta\lambda_{max}$ and an increase of ΔpK_a observed on going from ICC **Ia** to **Ib** is apparently due to non-planarity of the phenyl rings. Comparison of pK_a values of ICC **Ia** and **Ib** after the introduction of substituents (ΔpK_a (**Ib**) > pK_a (**Ia**)) explains the earlier unclear[26] almost equal values of ρ (3·23 and 3·16) on equations (G) and (D). Thus taking

TABLE 4
Comparison of the Properties of ICC **Ia** and **Ib**

Parameter	*B*	*ICC*	
		Ia	**Ib**
$\Delta\lambda_{max}$ (nm)	$H \rightarrow Cl$	9	6
	$H \rightarrow SO_2CF_3$	22	15
$pK_a = f(\sigma_p)$	$SO_2CF_3 \cdots H \cdots OCH_3$		
ρ in equation		3·23	3·16
ΔpK_a	$H \rightarrow Cl$	0·47	1·05
	$H \rightarrow SO_2CF_3$	3·00	3·45
Absorption	H	$J_2 < J_1 > M$	M
spectrum type	5-Hal. $COOC_2H_5$	J	$J < M$
in a coarse-	CF_3. CN, $-CH{=}CH{-}CF_3$	J	$J \leq M$
grained emulsion	5, 6-Cl (F)	J or $J > M$	M: $M \gg J$
Component stability, $K_I(K_{ps})$ (see text)	5—Cl	100 (100)	60 (20)

into consideration only the values of pK_a 5·45 and 4·45 for ICC **Ia** and **Ib** (B = H) respectively, lower values of ρ should be expected in the second case. Differences in the steric configuration of ICC **Ia** and **Ib** which cause marked differences in the pK_a values do not markedly affect the values of $E^{Ox}_{1/2}$ and especially of $E^{Red}_{1/2}$ (for the dyes listed in Table 3, ΔpK_a = 2·02–0·6, $\Delta E^{Ox}_{1/2}$ = 0·13–0·04V and $\Delta E^{Red}_{1/2}$ = 0·06–0·036V).

Non-coplanarity of the phenyl rings in ICC (**Ib**) causes their weaker adsorption on the microcrystal surfaces in comparison with ICC (**Ia**). Thus, after introduction of 5,5′,6,6′-tetrachloro-ICC **Ia** and **Ib** into the coarse-grained emulsion at the optimal concentration (160×10^{-6} wt/wt AgHal) the first is adsorbed almost completely, whereas the second is partially retained in the gelatin phase.

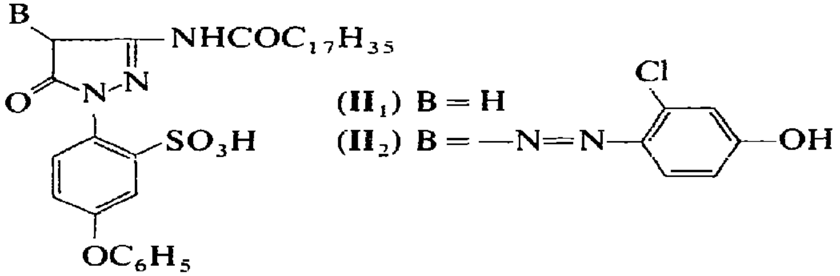
The steric configuration of ICC (**Ib**) is also clearly revealed in its ability to undergo *J*-aggregation on the surface of microcrystals. This effect either decreases in comparison with ICC **Ia** or disappears completely (Tables 2 and 4). Evidently, the deviation of the phenyl rings from planarity to a certain extent prevents the convergence of the molecules of ICC (**Ib**) on the surface of the microcrystals and diminishes the usual intermolecular interactions. It is well known that the introduction of phenyl rings into the polymethine chain or heterocyclic rings of thia-, oxa-, and thiazolo-carbocyanines increases their tendency for *J*-aggregation.[7]

5. COMPONENT STABILITY OF IMIDOCARBOCYANINES

The possibility of using suitable ICC for the spectral sensitization of coloured photographic materials has been mentioned in a number of patents[62] and in a review.[63] However, until 1968[25] there has been no systematic investigation of the component stability of ICC, i.e. the extent to which their sensitizing action is preserved in the presence of coloured non-diffusing components (CNC).

It was found that in this series of dyes, contrary to the findings with other carbocyanines and derivatives of benzothiazole the introduction of various substituents into the heterocyclic rings of ICC increases the component stability, *K*, from 5–10% up to 80–100% (Table 5).

$$K_{1.2} \text{ or PS} = \frac{S_{0\cdot85}^{\mathrm{YCf}-18} \text{ with component } \mathbf{II}_1, \mathbf{II}_2 \text{ or PS}}{S_{0\cdot85}^{\mathrm{YCf}-18} \text{ without component}} \times 100\%$$



II

PS dispersion of dibutyl phthalate and triphenyl-phosphate (2:1) in 10% gelatin solution ($\bar{d} = 0{\cdot}2\,\mu\mathrm{m}$).[51]

As can be seen from Table 5, the growth of K_1 is determined not by the electronic nature of substituents but mainly by their influence on the surface of the microcrystals. Thus introduction of chlorine, cyano or carboethoxy groups into positions 5 and 5′ of ICC **Ia** (B = H, spectrum type $J_2 < J_1 > M$), causes a sharp increase in the tendency to *J*-aggregation (spectrum type *J*) and leads to the increase of K_1 to 80–100%. In the case of ICC **Ib** with the same substituents spectra with

TABLE 5
Relationships Between the Component Stability of ICC **Ia**, and **Ib**, Their Structure and Their Ability to Aggregate[26,34]

B	**Ia**, $R = C_2H_5$		*Absorption spectrum type in emulsion*	**Ib**, $R = C_6H_5$		*Absorption spectrum type in emulsion*
	K_1 (%)	K_2 (%)		K_1 (%)	K_2 (%)	
H	5	1	$J_2 < J_1 > M$	5–10	< 1	M
Cl	100	15–20	J	60	10–15	$J < M$
$COOC_2H_5$	70–80	15–20	J	40	20	$J \leq M$
CN	100	15–20	J	50	20	$J \geq M$
SCF_3, $SOCF_3$	100	15–20	M	100	20	M
SO_2CF_3	100	15–20	M	100	15	M

several bands (spectrum type $J \geq M$) are exhibited and the value of K_1 is usually equal to 40–60 %. On the other hand, the sensitizing action of ICC **Ia** and **Ib** with sulphur-containing substituents which are adsorbed on the surface of the microcrystals mainly in the M-state is not reduced in the presence of component $\mathbf{II}_1$.

Thus the structure of the adsorption layer of ICC on the microcrystal surface as determined by the type of absorption spectrum (M- or J-band prevalent, or M- and J-bands similar in intensity) is the factor affecting the degree to which the sensitizing action of dyes is preserved when coloured components have been introduced into the emulsion. This is confirmed by a change in the component stability (K_1) of ICC when the emulsion parameters (composition, size of microcrystals, pBr, etc.) vary according to the absorption spectrum type of a dye in this system. This is exemplified by 1,1′,3,3′-tetraethyl-5,5′6,6′-tetrachloro-ICC, where in a coarse-grained emulsion $J > M$, $K_1 = 100\,\%$ and in a very fine-grained emulsion $J < M$, $K_1 = 60\,\%$.[33,46,56]

It is known that suppression of the light sensitivity of sensitized emulsions by the masking component $\mathbf{II}_2$ ($B = {-}N{=}N{-}Ar$) is due to the filter effect both of gelatin in the medium and also of the adsorbed component. It is also a result of the desensitizing action of the latter in displacing part of the dye from the microcrystal surface, and of its suppression of the value of ϕ_r^+.[20,64] The sensitizing action of ICC **Ia** and most of ICC **Ib** apart from some 5,5′-bisheteroaryl substituted derivatives[30,65] is sharply decreased after the introduction of masking components into the emulsion ($K_2 \leq 20\,\%$).

An increase in the component stability of di- and tetra-substituted ICC in relation to the masking components **II**$_2$ from 15–20% up to 60–70% can be achieved by an increase in the number of carbon atoms at the 3,3′-positions ($n \geq 6$) or in most cases by the substitution of ethyl groups for carboxy- or sulpho-alkyl groups.

The light sensitivity of photolayers containing ICC of this type in an emulsion together with a masking purple component as a rule decreases by not more than 30–40% largely due to the filter effect of the latter (Table 6).[32,33,39,44–46]

TABLE 6

The Relationship Between the Component Stability (K_2) of 1,1′-Diethyl-ICC **Id** and the Nature of Substituents at Positions 3 and 3′[32,33,38,39]

B	R_1	K_2 (%)
5,6-Cl	C_2H_5	20
5,6-Cl	n-C_8H_{17}	70
5,6-Cl	$(CH_2)_3CH_3$	45
5,6-Cl	$(CH_2)_3CF_3$	60
5,6-Cl	$(CH_2)_3SO_3^-$	70
5-$COOC_2H_5$	C_2H_5	20
5-$COOC_2H_5$	$(CH_2)_3SO_3^-$	70
5-SO_2CF_3	C_2H_5	20
5-SO_2CF_3	n-C_8H_{17}	70

It is also of interest to note that a significant increase in the component stability (K_1 and K_2) of ICC adsorbed on the microcrystals mainly in the *M*- and *J*-states can be obtained when oppositely charged polymethine dyes of different structure[33,46,66] or some quaternary salts of heterocyclic bases or organic sulphoacids[34,46] are introduced into the emulsion.

The depressing influence of the protected (hydrophobic) components and protecting solvents on the photographic properties of polymethine dyes is determined in the first place by the solubility of the dyes in the protecting solvents and their ability to aggregate on the microcrystal surface.[51]

For a series of 1,1′3,3′-tetraethyl-ICC (**Ia** and **Ib**), soluble in protecting solvents, the degree of suppression of their sensitizing action by protected components depends on the type of *J*-aggregates that are formed.[67]

As can be seen from Table 7, the parameters, K_1 and K_{ps}, for aggregating 5,5′-di- and 5,5′,6,6′-tetra-substituted ICC which characterize their resistance to desorption (K_1) and to dissolution by protecting solvent (K_{ps}) are in general changed to the same extent.

It has been shown that for a series of ICC the different degrees of extraction of *J*-aggregates adsorbed on the microcrystal surface into organic solvents can characterize the strength of these aggregates, i.e. the strength of the intermolecular interactions in the latter. On the basis of such data a correlation has been established between the compactness of the structure of J_1-, J_2- and J_3-aggregates of ICC and the strength of their adsorption on AgHal.[51,57]

TABLE 7

Relationship Between the Values of K_1 and K_{ps} of 1,1′-Diethyl-ICC (**Id**). Their Structure and Ability to Undergo *J*-aggregation[57]

B	R_1	*Adsorption spectrum type in emulsion*	K_1	K_{ps}
H	C_2H_5	$J_2 < J_1 > M$	5	≤ 1
5-SO_2CF_3	C_2H_5	*M*	100	20
5-SO_2CF_3	$(CH_2)_3SO_3^-$	*M*	15	95
5-CF_3	C_2H_5	J_1	60	30
5-$COOC_2H_5$	C_2H_5	J_2	80	30
5-$COOC_2H_5$	$(CH_2)_3SO_3^-$	J_2	100	100
5-Cl	C_2H_5	J_3	100	100
5,6-Cl	C_2H_5	J_3	100	100
5,6-Cl	$(CH_2)_3SO_3^-$	J_3	100	100

Specific structure–activity relationships shown by ICC dyes are connected with peculiarities of their structure, namely with the benzimidazole ring whose symmetry causes light absorption at shorter wavelengths than observed with their benzothiazole counterparts and is responsible for high basicity and the compactness of the molecule. These factors, in their turn, induce very high sensitivity of the molecule towards structural changes. For example in an appropriate series of ICC the dependence of the sensitizing action on the pK_a and $E_{1/2}^{Red}$ is revealed more clearly than in other groups of polymethine dyes. In general the values of ϕ_r^{+20} for the molecular state of ICC increase as the pK_a and the absolute value of $E_{1/2}^{Red}$ decrease and in certain series these are linearly related.

Another important parameter which determines the total effect of the spectral sensitization of ICC is their *J*-aggregation behaviour, the first factor prevailing in some cases (spectrum type *M*) and the second in others (*J* or $J > M$).

Relationships between the structure of ICC and their ability to undergo *J*-aggregation also have both general and specific characteristics. Introduction of bulky sulphur- and fluorine-containing groups or heteroatomic rings into a heterocyclic nucleus does not change the degree of compactness of the basic chromophore system but makes intermolecular interaction more difficult. This is analogous to the known 'negative' influence of the 'increase in the weight' of substituents on *J*-aggregation in the case of other polymethine dyes, e.g. 9-ethyl-5,5′-β-disubstituted thiacarbocyanines (B—$CH_3 \rightarrow C_2H_5$, $CH_3O \rightarrow C_2H_5O$).[7,68] On the other hand, in contrast to thiacarbocyanines an increase in the number of carbon atoms (up to $n = 6$) in a series of 1,1′-diethyl-3,3′-di(C_nH_{2n+1})-5,5′-di- or -5,5′6,6′-tetra-substituted ICC has no effect on the adsorption of dyes and their tendency to *J*-aggregation, which may be because of the possibility of orientation of ICC molecules at the surface of the microcrystals with the second adsorption centre, i.e. nitrogen atoms at positions 1 and 1′.

Coplanarity of the phenyl rings of ICC has specific effects for all studied physicochemical and photographic parameters (with the exception of $E^{\mathrm{Red}}_{1/2}$), including the degree of stability of the sensitizing action to the depressing action of colour components (K_1). It is necessary to mention that the established dependence of the structure of the ICC adsorption layer on the component stability (K) is specific. Thus in a series of dyes this is, generally, determined by their relative ability to undergo *J*-aggregation and also depends on the individual compound according to its change in different emulsions.

Comparison of the values of K_1 and K_{ps} in a series of ICC which are able to form J_1-, J_2- or J_3-aggregates on the microcrystal surface confirms the supposition that the structure of these aggregates differs according to the degree of overlap of the molecular planes which in turn causes differences in their properties.[57]

The peculiarities in the structure of imidocarbocyanines (the symmetry of benzimidazole rings and the high sensitivity of these dyes to structural changes) have permitted the establishment of relationships between the structure of these compounds and their various physicochemical and photographic properties.

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