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SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF PERFLUOROALKYL AND TRIFLUOROMETHYLSULPHONYL SUBSTITUTED INDOLINE SPIROCHROMENES

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SUMMARY

A number of new perfluoroalkyl and trifluoromethylsulphonyl substituted indoline spirochromenes have been synthesized. It was shown that the introduction of trifluoromethylsulphonyl or heptafluoropropyl groups into the chromene moiety of the indoline spirochromene molecule results in their ability to undergo photochromic conversions. The dyes were examined by spectrophotometry and the rate constants were determined for the fading reaction. Some correlations of the rate constants with the electron withdrawing properties of the substituents were observed

1 INTRODUCTION

Indoline spirochromenes with fluorine containing substituents are not known At the present time only dyes with fluorine atoms directly substituted in positions 5 and 8′ are described.[1] The greatest influence on the properties of indoline spirochromenes is exerted by substituents in the 6′ position.[2] It was considered interesting to ascertain the effect of the introduction of strong electron withdrawing substituents, such as perfluoroalkyl and trifluoromethylsulphonyl groups, on the spectral characteristics of these dyes The corresponding 5-substituted salicylaldehydes had to be obtained as starting materials for synthesis of indoline spirochromenes of that type

2. RESULTS AND DISCUSSION

When we tried to introduce a heptafluoropropyl group into the molecule of salicylaldehyde by heating its 5-iodo substituted derivatives with perfluoropropyl

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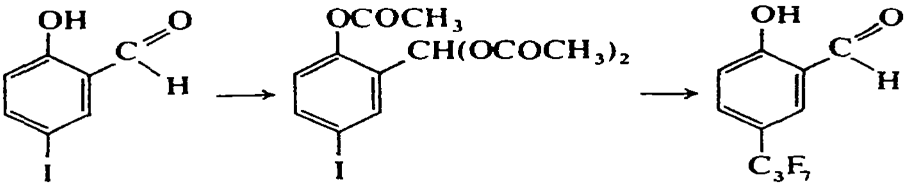
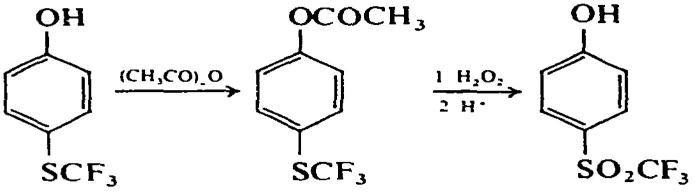
copper in hexamethylphosphoric triamide, only tar was obtained. On the other hand, the diacetate of 5-iodosalicylaldehyde[3] (**I**) reacted smoothly with *n*-perfluoropropyl copper, and 5-perfluoropropylsalicylaldehyde (**II**) was obtained after hydrolysis



I **II**

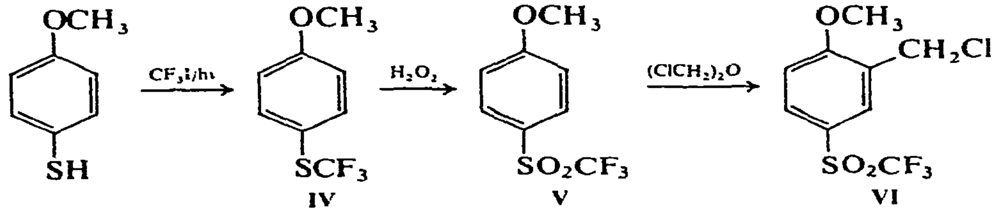
The simplest method of synthesis of trifluoromethylsulphonyl substituted salicylaldehyde would be via the formylation of 4-trifluoromethylsulphonylphenol (**III**) The latter was obtained earlier as a product of a multistep synthesis[4] Application of the ion-radical perfluoroalkylation reaction[5] made the phenol (**III**) more accessible, and it was obtained by oxidation of 4-(trifluoromethylthio)phenol acetate with hydrogen peroxide, followed by hydrolysis However, all attempts to formylate or chloromethylate (**III**) were unsuccessful



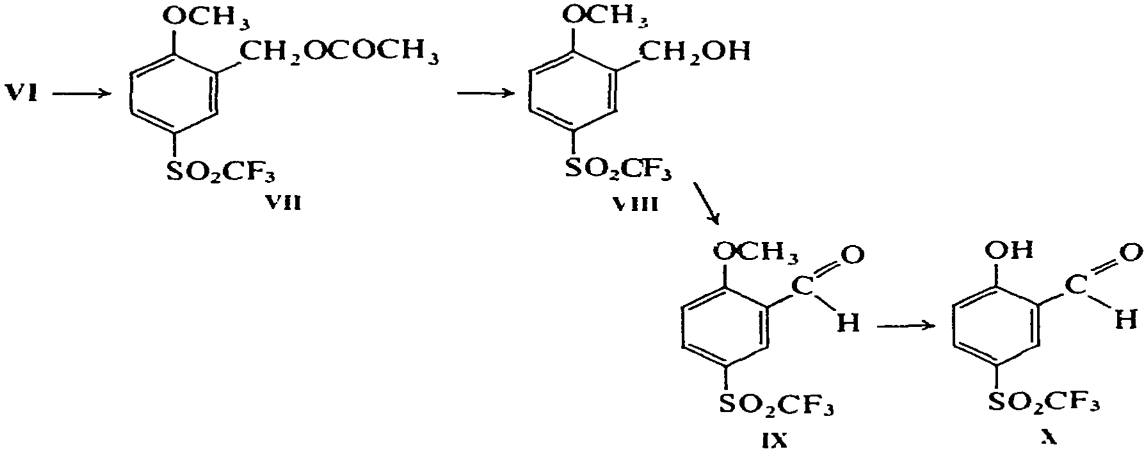
III

The possibility of chloromethylation of 4-trifluoromethylsulphonylanisole was investigated The literature describes a somewhat tedious procedure for its preparation[6] but we have found a simple method for the preparation of this substance by the ion-radical perfluoroalkylation reaction Trifluoromethylation of methoxythiophenol[7] with trifluoroiodomethane in liquid ammonia solution under u v irradiation leads to 4-(trifluoromethylthio)anisole (**IV**), which is easily oxidized to 4-trifluoromethylsulphonylanisole (**V**) by hydrogen peroxide in acetic acid. The latter is chloromethylated with 1,1′-dichlorodimethyl ether in concentrated sulphuric acid solution even at 0 °C to yield 2-chloromethyl-4-trifluoromethylsulphonylanisole (**VI**).

The chlorine atom in (**VI**) can be substituted by an acetoxy group after refluxing for only 2 h with silver acetate The use of potassium acetate for this purpose requires 100 h refluxing The application of catalytic amounts of 16-*crown*-6-ether in the latter case affords a high yield of 2-acetoxymethyl-4-trifluoromethylsulphonylanisole (**VII**) after 5 h refluxing Hydrolysis of the acetoxy group of (**VII**) with the



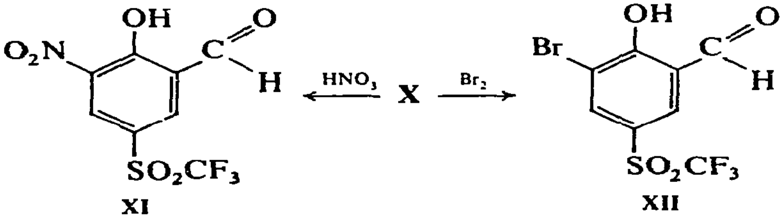
calculated amount of a 4 % solution of potassium hydroxide leads to 2-methoxy-5-trifluoromethylsulphonylbenzyl alcohol (VIII) The latter is easily oxidized to the corresponding aldehyde (IX) by pyridinium chlorochromate [8] Heating the mixture of (IX) and pyridinium chloride yields 5-trifluoromethylsulphonylsalicylaldehyde (X) which is required for the synthesis of indoline spirochromenes



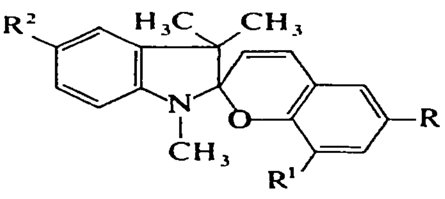
The corresponding 3-nitro (XI) and 3-bromo- 5-trifluoromethylsulphonylsalicylaldehyde (XII) were obtained from (X)

Heating II, X or XI with Fischer's base or its 5-trifluoromethyl derivative in ethanol leads to the indoline spirochromenes (XIII–XVIII) The earlier known nitro substituted spirochromenes (XIX, XX) were obtained for comparison.

The spirochromenes (XIII–XVIII) show photochromic conversions Under u.v



irradiation, solutions of compounds (**XIII–XV**, **XVII** and **XVIII**) in weakly polar or nonpolar solvents yield intense dark-blue or blue–violet colours, caused by conversion to their coloured merocyanine form In polar solvents they give red solutions, which slowly fade in visible light When the irradiation is terminated, the colour of the solution returns gradually to the original state



XIII $R = C_3F_7$ $R^1 = R^2 = H$
XIV $R = CF_3SO_2$, $R^1 = R^2 = H$
XV $R = CF_3SO_2$, $R^1 = H$, $R^2 = CF_3$
XVI $R = CF_3SO_2$, $R^1 = NO_2$, $R^2 = H$
XVII $R = NO_2$, $R^1 = H$, $R^2 = CF_3$
XVIII $R = CF_3SO_2$, $R^1 = NO_2$, $R^2 = CF_3$
XIX $R = NO_2$ $R^1 = R^2 = H$
XX $R = R^2 = H$, $R^1 = NO_2$

Thus, the introduction of trifluoromethylsulphonyl and heptafluoropropyl groups into the chromene moiety of the indoline spirochromene molecule results in their ready photochromic conversion activated by sources of irradiation of low intensity even at ambient temperatures This effect is comparable with that of introduction of the nitro or acyl group

The absorption spectra of (**XIII–XVIII**) in ethanol (Fig. 1) show an essential difference between the compounds (**XIII–XV**), which do not contain the nitro group in the chromene moiety of the molecule, and compounds (**XVI–XVIII**), which contain it The spectra of the spiro form of (**XIII–XV**) do not show absorption bands at wavelengths longer than 320 nm This supports the idea that the long-wave absorption band in the spectra of the spiro form is caused by the chromene moiety of

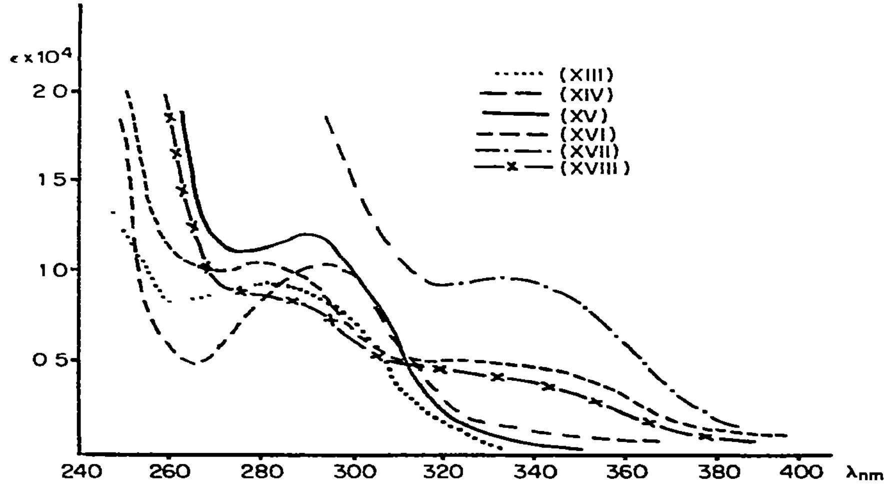


Fig 1 Absorption spectra of indoline spirochromenes **XIII–XVIII** in ethanol solution

the molecule[9] Our investigation has also shown that, though spirochromenes (**XIII–XV**, **XVII** and **XVIII**) give colourless solutions when dissolved in toluene, toluene solutions of chromene (**XVI**), on the other hand, absorb intensely in the visible range of the spectrum (λ_{max} 555 nm) This gives evidence for a pronounced shift of the equilibrium between the spiro and merocyanine forms in favour of the latter, even in the weakly polar medium, when two strong electron withdrawing substituents are present in the chromene moiety of the molecule

The introduction of the electron withdrawing trifluoromethyl group into the indoline moiety of the molecule (**XVI** and **XVIII**) results in the stabilization of the spiro form. This phenomenon may be explained by the increased positive charge on the carbon atom of the indoline ring at position 2, and the increased negative charge on the oxygen atom bonded to the aromatic ring. Any factor causing a decrease of these charges increases the stability of the merocyanine form.[10]

The long-wave absorption maxima of the photomerocyanine forms of spirochromenes (**XIII–XX**) are given in Table 1 All of the studied compounds reveal a negative solvatochromism[14] which is characteristic of the photomerocyanine forms of indoline spirochromenes with a nitro group in the chromene moiety of the molecule. The replacement of toluene by ethanol causes a hypsochromic shift of the long-wave absorption band of about 40–70 nm. It is known[15] that the ionic structure (A_1) prevails in the merocyanine form of the indoline spirochromenes. This fact is in good agreement with their negative solvatochromism.

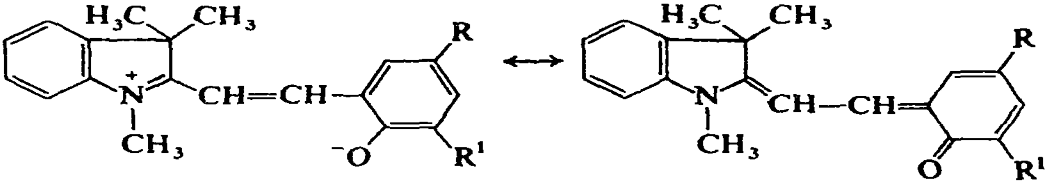
TABLE 1

SPECTROGRAPHIC AND KINETIC CHARACTERISTICS OF PHOTOCHROMIC TRANSITIONS OF INDOLINE SPIROCHROMENES

Indoline spirochromene NN	*Absorption maximum of merocyanine form (nm)*		*Rate constant of the fading reaction in the dark ($s^{-1} \times 10^2$, at 20°C)*	
	Toluene	*Ethanol*	*Toluene*	*Dioxane*
XIII	578	540	4 50	2 00
XIV	565	508	2 00	0 30
XV	575	535	4 80	2 80
XVI	555	493	—[a]	—[a]
XVII	600	552	6 00	2 60
XVIII	570	500	1 30	1 00
XIX	595[12]	532[12]	3 09[12]	2 97[12]
XX	598[13]	542[13]	3 89[12]	3 49[12]

[a] The merocyanine form is stable

Introduction of the electron acceptor groups R = C_3F_7(**XIII**), NO_2(**XIV**), CF_3SO_2(**XV**) into position 6′ (i.e. *para* to the oxygen atom) increases the contribution of the ionic structure (A_1) and produces a hypsochromic shift of the absorption band (λ_{max} values were measured in ethanol solution) corresponding to



A_1 A_2

the electronegativity of the substituents ($\sigma_p^{C_3F_7} = 0$ 52, $\sigma_p^{NO_2} = 0{\cdot}77$, $\sigma_p^{CF_3SO_2} = 1{\cdot}03$) [16] The trifluoromethylsulphonyl group at position 6′ causes therefore an essentially greater hypsochromic shift than the nitro group (cf **XIV** and **XIX**, **XV** and **XVII**)

Electron withdrawing substituents at position 6′ of the chromene moiety of the dye decelerate the dark fading reaction[10,17] in accordance with their increasing electron withdrawing ability $C_3F_7 < NO_2 < CF_3SO_2$ (cf **XIII**, **XIV**, and **XIX**, Table 1) The trifluoromethylsulphonyl group at position 6′ is slightly more effective in decreasing the rate of this process than the nitro group (cf **XIV** and **XIX**, **XV** and **XVII**) Two electron withdrawing substituents at positions 6′ and 8′ decelerate the reaction to a greater degree than one substituent (cf compounds **XVI** and **XX**, **XVIII** and **XV**). In contrast, the electron withdrawing substituent (trifluoromethyl group) in the indoline moiety accelerates the reaction of the dark fading reaction (**XV**, **XVII** and **XVIII** in comparison with **XIV**, **XIX** and **XVIII**, respectively) Comparison of the data for the dyes (**XVII** and **XIX**, **XV** and **XIV**, **XVIII** and **XX**), leads to the conclusion that the deceleration of the dark fading reaction affected by the presence of the CF_3SO_2 group in the chromene moiety prevails over the acceleration of this reaction caused by the influence of the trifluoromethyl group in the indoline moiety

3 EXPERIMENTAL

Electronic absorption spectra and data of the kinetics of the fading reaction in the dark were obtained as described elsewhere [17] Electronic absorption spectra were recorded on a VSU-2P spectrometer

3 1 *Materials*

All metal salts and organic reagents were reagent grade and used without further purification, unless otherwise stated Solvents were purified by the ordinary methods

5-Iodoacetylsalicylaldehyde diacetate (**I**) A mixture of 5-iodosalicylaldehyde (16·5g, 0 066 mol) and acetic anhydride (15 ml) was heated for 4h at 125°C After removal of acetic anhydride in vacuum, **I** was obtained in 87% yield, m p. 90–91 °C (benzene–hexane). Analysis found (%). I, 32 72 Calculated for $C_{13}H_{13}IO_6$: I, 32 31

5-Perfluoropropylsalicylaldehyde (**II**). **I** (4 g, 0·01 mol), 1-iodoperfluoropropane (9 g, 0·03 mol) and copper powder (3·3 g, 0·05 mol) in hexamethylphosphoric triamide (20 ml) were stirred for 10 h at 120 °C under argon in a flame-dried three-necked flask, equipped with a thermometer, a mechanical stirrer and a reflux condenser. The reaction was cooled and diluted with ether (100 ml). The ether layer was separated and the residue was washed with water. After removal of the solvent, 20 % hydrochloric acid (15 ml) was added to the resultant oil and the aldehyde (**II**) was extracted with ether. Yield: 0·88 g (30 %), b.p. 100–110 °C/10 Torr; m.p. 42–43° (pentane). Analysis: found (%): C 41·80, H 1·69. Calculated for $C_{10}H_5F_7O_2$: C, 41·37; H, 1·72.

4-Trifluoromethylsulphonylphenol (**III**). A solution of 4-(trifluoromethylthio)phenol (12 g, 0·06 mol) in acetic anhydride (12 ml) was heated for 30 min at 100 °C. A solution of 30 % hydrogen peroxide (25 ml) in acetic acid (12 ml) was then added and the reaction mixture was heated for 8 h at 100 °C. The reaction mixture was then diluted with water (50 ml), boiled for 30 min, cooled, extracted with ether and dried with magnesium sulphate. The removal of the solvent gave 10·4 g (74 %) of phenol (**IV**), m.p. 121–122 °C (hexane). Lit.[4] m.p. 122 °C.

4-(Trifluoromethylthio)anisole (**IV**). Trifluoroiodomethane (28·4 g, 0·15 mol) was condensed into a stirred suspension of 4-methoxythiophenol (14 g, 0·10 mol) in anhydrous liquid ammonia (100 ml) under a nitrogen atmosphere. The stirred reaction mixture was irradiated with a mercury lamp for 40 min at −30 °C. The ammonia was evaporated (water bath) with subsequent addition to the reaction mixture of 5 % sodium hydroxide solution (100 ml). The resulting product was extracted with ether, the ether solution was washed with water and dried with magnesium sulphate. Removal of the solvent and vacuum distillation gave the anisole (**IV**), yield 17·2 g (83 %), b.p. 85–87/16 Torr. Analysis: found (%): F, 27·60. Calculated for $C_8H_7F_3OS$, F, 27·40.

4-Trifluoromethylsulphonylanisole (**V**). A mixture of 4-(trifluoromethylthio)anisole (**IV**) (20·8 g, 0·1 mol) and 30 % hydrogen peroxide (35 ml) in acetic acid (60 ml) was stirred under reflux for 8 h. The resultant solution was poured slowly on ice and the crude anisole (**V**) was extracted with ether. The extract was washed with water and dried with magnesium sulphate. Removal of the solvent and vacuum distillation gave the product: yield 17·6 g (85 %), b.p. 168–170 °C/30 Torr. Lit.[6] b.p. 114 °C/4 Torr.

2-Chloromethyl-4-trifluoromethylsulphonylanisole (**VI**). 4-Trifluoromethylsulphonylanisole (24 g, 0·1 mol) was added dropwise to a solution of 1,1′-dichlorodimethyl ether (34 g, 0·3 mol) in concentrated sulphuric acid (80 ml, *d* 1·84) at −3 to −2 °C. The reaction was stirred for 3 h at 0 °C and poured on to crushed ice (250 g). The resultant oil solidified quickly and was collected under suction, washed with water, dried and recrystallized. Yield 23 g (83 %), m.p. 54–55 °C (pentane). Analysis: found (%): Cl, 12·50. Calculated for $C_9H_8F_3ClO_3S$: Cl, 12·30.

2-Methoxy-5-trifluoromethylsulphonylbenzyl acetate (**VII**). A mixture of (**VI**)

(29 g, 0·1 mol), anhydrous potassium acetate (21 g, 0·1 mol) and 18-*crown*-6-ether (0 2 g, 0 001 mol) in anhydrous acetonitrile (100 ml), was stirred for 5 h at 80 °C. The reaction mixture was cooled, diluted with water (400 ml) and extracted with ether to yield 25 g (81 %) of (**VII**); b.p 120–121 °C/0·5 Torr; m.p. 42 °C (hexane). Analysis: found (%) C, 42 22; H, 3 64 Calculated for $C_{11}H_{11}F_3O_5S$: C, 42·30; H, 3·55

2-Methoxy-5-trifluoromethylsulphonylbenzyl alcohol (**VIII**). **VII** (31·2 g, 0·1 mol) was suspended in 4 % potassium hydroxide solution (210 ml) and the mixture was stirred for 4 h at 100 °C. The reaction mixture was poured into water and the precipitated solid product was filtered off, washed with water and dried Yield: 22 g (82 %), m p 72–73 °C (hexane) Analysis· found (%)· F, 21 12 Calculated for $C_9H_9F_3O_4S$ F, 21 11

2-Methoxy-5-trifluoromethylsulphonylbenzylaldehyde (**IX**) **VIII** (2 7 g, 0 01 mol) and pyridinium chlorochromate (3·23 g, 0 015 mol) were suspended in anhydrous dichloromethane (20 ml) and the mixture was stirred for 10 h at 20 °C The reaction mixture was diluted with hydrochloric acid (10 %, 50 ml) and the aldehyde (**IX**) was extracted with ether Yield 19 g (70 %), m p 92–93 °C (hexane). Analysis. found (%) F, 21 01 Calculated for $C_9H_7F_3O_4S$ F, 21·26

5-Trifluoromethylsulphonylsalicylaldehyde (**X**) A mixture of **IX** (2·68 g, 0 01 mol) and pyridinium hydrochloride (3 45 g, 0 03 mol) was heated for 20 min at 200 °C The reaction mixture was cooled and diluted with 20 % hydrochloric acid (40 ml). The crude product was extracted with ether to give 18 2 g (71 %) of **X**, m p 120 °C (hexane) Analysis found (%) F, 22 59 Calculated for $C_8H_5F_3O_4S$· F, 22 44.

3-Nitro-5-trifluoromethylsulphonylsalicylaldehyde (**XI**) Aldehyde (**X**) (0 25 g, 0 01 mol) was added to a mixture of nitric acid (0 25 ml, *d* 1 52) and sulphuric acid (0 35 ml, *d* 1 84) at 0 °C The reaction mixture was stirred for 50 min at 5 °C and poured on to ice The solid product was filtered off, washed with water and dried to yield 0 21 g (73 %) of aldehyde (**XI**), m p 78–79 °C (hexane) Analysis found (%)· N, 4 79 Calculated for $C_8H_4F_3NO_6S$ N, 4 68

TABLE 2
INDOLINE SPIROCHROMENES

Compound NN	*Yield (%)*	*m p (°C) solvent*	*Found (%)*	*Formula*	*Required (%)*
XIII	35	93–94 ethanol	F 29 74	$C_{22}H_{18}F_7NO$	F 29 88
XIV	50	175–176 ethanol	C 59 01 H 4 42	$C_{20}H_{18}F_3NO_3S$	C 58 67 H 4 40
XV	54	73–74, hexane	F 23 68	$C_{21}H_{18}F_3NO_3S$	F 23 84
XVI	73	264–265 ethanol	N 6 40	$C_{20}H_{17}F_3N_2O_3S$	N 6 16
XVII	33	182–183, ethanol	C 61 66	$C_{20}H_{18}F_3N_2O_3S$	C 61 38
XVIII	58	265–267, ethanol	F 21 72	$C_{21}H_{17}F_6N_2O_5S$	F 21 79

3-Bromo-5-trifluoromethylsulphonylsalicylaldehyde (**XII**). A solution of bromine (0·16 g, 0·001 mol) in acetic acid (4 ml) was added dropwise to a solution of **X** (0·15 g, 0·001 mol) in acetic acid (4 ml). The reaction mixture was stirred for 2 h at 50 °C and poured on to ice. **XII** was filtered off and dried. Yield. 0·23 g (68 %); m.p. 122–123 °C (hexane). Analysis: found (%): Br, 23·68. Calculated for $C_8H_4BrF_3O_4S$: Br, 24·02.

Indoline spirochromenes (**XIII–XVIII**). A solution of the corresponding aldehyde (0·001 mol) and Fischer's base (0·0015 mol) in anhydrous ethanol (5 ml) was refluxed for 1 h and cooled. The precipitated dyes were filtered off and recrystallized. Yields, physical properties and results of microanalyses of dyes **XIII–XVIII** are given in Table 2.

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