29. *Photochromism in Some Spiropyrans. Part III.*[1] *The Extent of Phototransformation.*

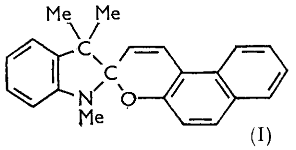
By Rahel Heiligman-Rim, (the late) Yehuda Hirshberg, and Ernst Fischer.

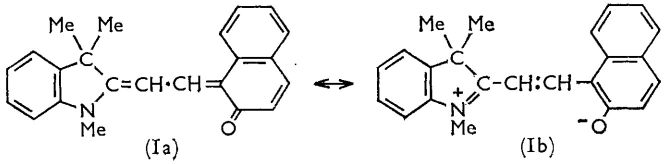
Photochromic spiropyrans were observed to have a narrow absorption band at about 245 mμ, characteristic for the colourless modification of these compounds. This band diminishes when the spiropyrans are converted by ultraviolet irradiation into the corresponding coloured dimethinmerocyanines, and reappears when the latter are reconverted into the spiropyrans. The attenuation of this band can therefore be used to estimate the extent of phototransformation, which was thus found to vary between 50% and 100%. Solutions of some compounds commonly thought to be dimethinmerocyanine dyes also show the above absorption band, and probably consist of equilibrium mixtures of the merocyanines and the corresponding spiropyrans.

Parts I and II of this series and related publications [1-5] gave a qualitative description of the phenomenon of photochromism in thermochromic and related spiropyrans. This phenomenon consists (*a*) of the transformation of these colourless compounds into coloured modifications when their solutions are irradiated with ultraviolet light at low temperatures and (*b*) of the reverse process which takes place when the temperature is raised and also, in some cases, at low temperature as a result of irradiation with visible light:

$$\text{Colourless modification} \underset{h\nu_2}{\overset{h\nu_1}{\rightleftharpoons}} \text{Coloured modification} \ (\nu_1 > \nu_2)$$

It should be recalled that the phototransformations all result in attainment of photo-equilibria and not thermodynamic equilibria. The latter are generally almost completely in favour of the spiropyran, and their establishment is prevented at sufficiently low temperatures only by the potential barrier of 15—20 kcal./mole which has to be passed when the merocyanine is converted into the spiropyran.[4] With the spiropyrans described in the present paper, thermodynamic equilibrium is established rapidly at temperatures above about —50°.


(I)



(Ia) (Ib)

When a (colourless) solution of, *e.g.*, the spiran (I) is irradiated with ultraviolet light, at temperatures below about —90°, it becomes intensely violet-red.[2] This was explained [2]

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[1] Part II, Hirshberg and Fischer, *J.*, 1954, 3129.
[2] Fischer and Hirshberg, *J.*, 1952, 4522.
[3] Hirshberg, Frei, and Fischer, *J.*, 1953, 2184.
[4] Hirshberg and Fischer, *J.*, 1954, 297 (Part I).
[5] Hirshberg, *J. Amer. Chem. Soc.*, 1956, **78**, 2304.

as being due to transformation into an isomeric dimethinmerocyanine-like modification which is actually a resonance hybrid of (Ia) and (Ib), in analogy with the structure suggested by several authors[9] for the thermochromic coloured modification of (I).

The colourless modification is re-formed from the coloured one either spontaneously,[2] when the solution is heated above about −50°, or by irradiation with visible light at the low temperature at which coloration took place.[3]

It was also shown that, whenever such a compound is convertible into both thermochromic and photochromic modifications, these two are identical and that, as observed in the bianthronyl series investigated earlier,[6,7] photochromism is also exhibited by some non-thermochromic spiropyrans.

Since then, greatly improved techniques,[8] including rigorous exclusion of air and hydroxylic contaminants from solutions in non-polar solvents, and information from related fields of research, have made possible more accurate and quantitative experimental work, and more insight can now be gained into the nature of the coloured isomers, the mechanism of the phototransformation, and the extent to which it takes place. These three aspects of the phenomenon form the subjects of the present and the two following parts of this series.*

Figs. 1a and 1c show the effect of progressive ultraviolet irradiation on solutions of the spiran (I) at two concentrations, namely, gradual appearance of the visible absorption bands, accompanied by pronounced changes in the ultraviolet region, the most marked being the gradual diminution of the sharp band at 244 mμ. Several well-defined isosbestic points are observed in the region in which both modifications absorb (Fig. 1c).

Ultraviolet irradiation of several other photochromic spiropyrans[1,4] (II)—(IX) resulted in somewhat similar spectral changes. Here too the most prominent change was diminution of a narrow band in the vicinity of 245 mμ, this band being common to the colourless modification of all the compounds. The results are summarized in Fig. 2, whereas details about the wavelength and the extinction coefficient of this absorption band are given in Table 1.

It is seen that for all naphthopyrans [(I)—(V)] the band in question is similar in shape and intensity and in the region of 244 ± 5 mμ. It probably corresponds to the ^1B_b transition, as defined by Platt.[10a] † For the benzopyran derivatives [(VI)—(IX)] the band is less intense and of a different shape and wavelength. It may correspond to the transition denoted by Platt as ^1L_a. The left-hand component (indoline, acridine, benzopyran) seems to have little effect on the band, which thus appears to characterize the closed, spiropyran structure given in the formulæ. The extent to which this band diminishes as a result of ultraviolet irradiation thus affords a means of estimating the degree of conversion of the spiropyrans into their coloured modifications analogous to (Ia) $\longleftrightarrow$ (Ib). In order to carry out such an estimation, an assumption must be made regarding the extinction coefficient of the coloured modification at the wavelength of the above band. There is no exact basis for any such assumption. However, the lower limit of the coefficient is obviously zero, giving a lower limit for the calculated degree of conversion into the coloured

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* For preliminary accounts see *Bull. Res. Council Israel*, 1958, **7**, *A*, 226; 1959, **8**, *A*, 151, 152.

† The ultraviolet spectra of the naphthopyrans closely resemble that of phenanthrene, which has absorption bands at 353, 303, and 252 mμ.[10b,c]

[6] Hirshberg, *Compt. rend.*, 1950, **231**, 903.

[7] Hirshberg and Fischer, *J.*, 1953, 629.

[8] Hirshberg and Fischer, *Rev. Sci. Instr.*, 1959, **30**, 197.

[9] (*a*) Dilthey and Wubken, *J. prakt. Chemie*, 1926, **114**, 179; (*b*) Dickinson and Heilbron, *J.*, 1927, 1699; (*c*) Wizinger and Wenning, *Helv. Chim. Acta*, 1940, **23**, 247; (*d*) Koelsch, *J. Org. Chem.*, 1951, **16**, 1362; (*e*) Knott, *J.*, 1951, 3038; (*f*) cf. also Chaudé's exhaustive study (Thèse, " Étude spectrophotometrique de l'isomerisation de divers spiranes thermochromes," edition de la Revue d'Optique, Paris, 1954).

[10] (*a*) Platt, *J. Chem. Phys.*, 1949, **17**, 484; (*b*) Klevens and Platt, *ibid.*, p. 470; (*c*) Klevens and Platt, " Survey of Vacuum Ultraviolet Spectra of Organic Compounds in Solution," Technical Report, Lab. of Molecular Structure and Spectra, University of Chicago, 1953—54.

form, whereas the upper limit of the degree of this conversion is of course unity (*i.e.*, complete conversion). As an example, for compound (I) in Fig. 1a, the optical density of the band at 244 mμ is reduced by irradiation from 0·94 to 0·37. This then corresponds to a content, after irradiation, of between (100 × 0·37/0·94 =) 39% and 0% of spiropyran, or a degree of photoconversion into the coloured form of between 61% and 100%. The

FIG. 1. *Spectra of solutions of spiran* (I) *before and after progressive irradiation with ultraviolet light at* 365 mμ. *Numbers on the curves denote time of irradiation, in minutes. In ethanol–methanol,* (a) 9 × 10^{-6}M, (c) 45 × 10^{-6}M. (b) *In methylcyclohexane–isopentane,* 5 × 10^{-6}M.

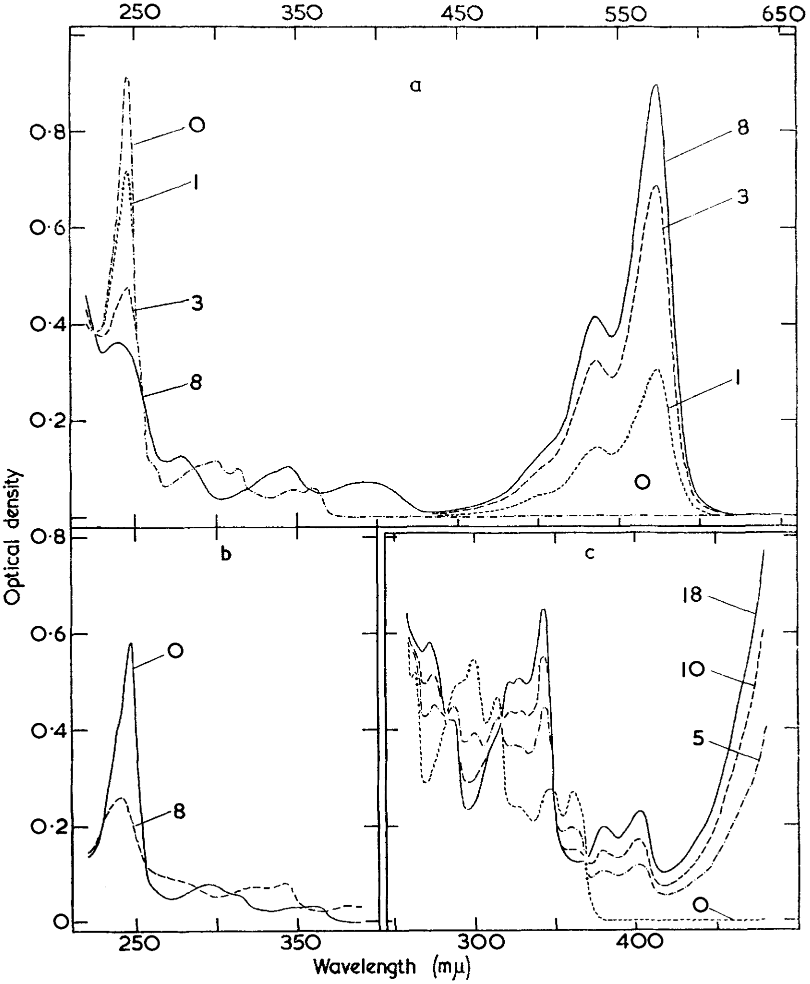
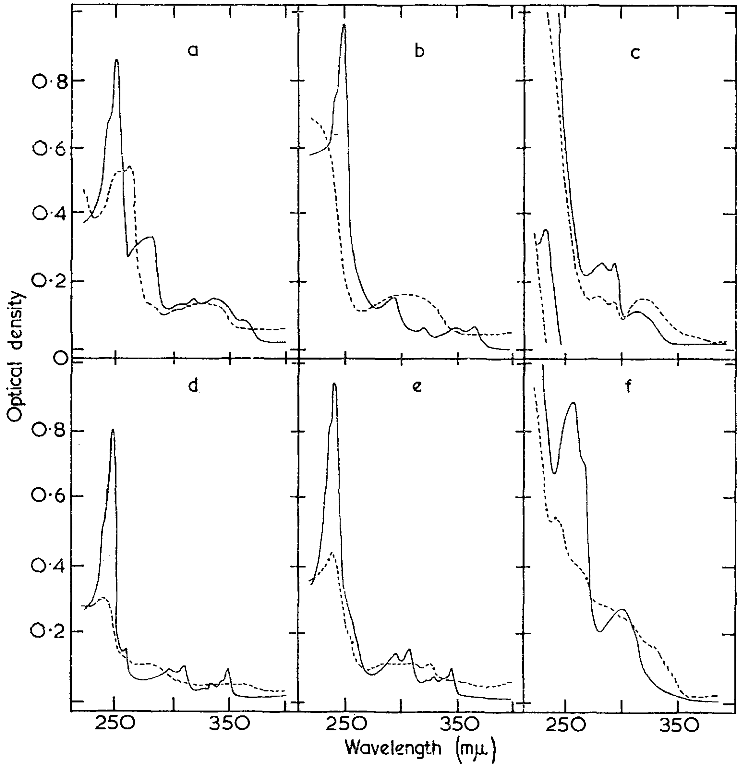


TABLE 1. *" Spiropyran " bands for various compounds in alcoholic solution.*

Compound	Peak wave-length (mμ)	Molar extinction coeff. (10^{-3} ε)	Compound	Peak wave-length (mμ)	Molar extinction coeff. (10^{-3} ε)	Compound	Peak wave-length (mμ)	Molar extinction coeff. (10^{-3} ε)
(I)	244	78	(IV)	248	73	(VII)	225	16
(II) *	244	140	(V)	249	63	(VIII)	245 (283)	15 †
(III)	239	74	(VI)	229 (291)	31 (7)	(IX)	226	25 †

* This compound contains two naphthopyran systems, and its " spiropyran " band is therefore about twice as high as those for the other naphthopyrans. † For technical reasons these values are only approximations.

FIG. 2. *Ultraviolet absorption spectra of some spiropyrans, before (full curves) and after (broken curves) irradiation with ultraviolet light. All solutions, except* d, *in ethanol–methanol.* (a) *Compound* (V) (1×10^{-5}M) *at* $-120°$, *irradn. at* 365 mμ; (b) *compound* (IV) (1×10^{-5}M) *at* $-120°$, *irradn. at* 365 mμ; (c) *compound* (VI) ($3{\cdot}5 \times 10^{-5}$M) *at* $-100°$, *irradn. at* 365 + 313 + 303 mμ; (d) *compound* (II) ($0{\cdot}6 \times 10^{-5}$M) *in methylcyclohexane, at* $-120°$, *irradn. at* 313 + 303 mμ; (e) *compound* (III) (1×10^{-5}M) *at* $-120°$, *irradn. at* 365 + 313 + 303 mμ; (f) *compound* (VII) (4×10^{-5}M) *at* $-80°$, *irradn. at* 365 + 313 + 303 mμ.



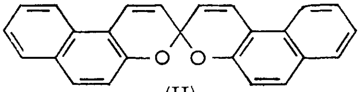
minimum values based on results of similar calculations, based on the data in Figs. 1 and 2, are summarized in the second column of Table 2.

TABLE 2. *Degrees of photoconversion of some spiropyrans into the coloured modifications, and molar extinction coefficients of these modifications.* (*Solutions in ethanol–methanol.*)

Compound	Conversion (%) into coloured modification		Main visible absorption band of coloured modification		
	Minimal	Probable	(mμ)	($10^{-3}\varepsilon$)	
				max.[b]	probable
(I)	62	88	573	120	85
(I)[a]	60	80	525	85	65
(II)	75	90	645	—	—
(II)[a]	65	90	600	32	25
(III)	55	70	568	62	47
(IV)	75	95	520	37	27
(V)	38	80	696	87	40
(VI)[c]	45	65	590	20	13
(VII)	55	90	622	18	10

[a] Solution in isopentane–methylcyclohexane. [b] Corresponding to minimal degree of conversion into the coloured modification. [c] From the absorption band at 291 mμ.

Inspection of Figs. 1 and 2 shows that the actual degrees of conversion are probably somewhere between the minimal percentages given and 100%. If in each case a " reasonable " assumption is made regarding the shape of the coloured modification's absorption curve, a " probable " degree of conversion can be calculated from such a curve and the two experimental curves. The results are given in the third column of Table 2. Both the minimal and the " probable " values for the degrees of conversion may serve to assess the molar extinction of the main absorption bands of the coloured forms in the visible region. Approximate values for these coefficients are given in the last two columns. The data collected in Table 2 appear to be the first direct experimental estimate of the degree of photoconversion of photochromic compounds into their coloured modification, and of the extinction coefficient of the latter.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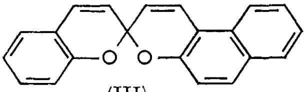
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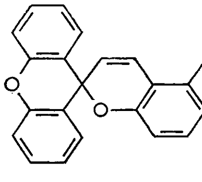
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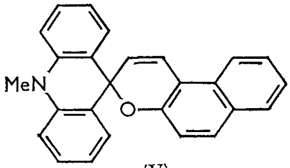

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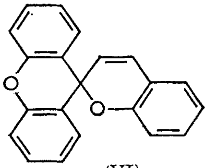
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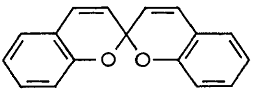
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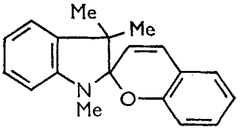

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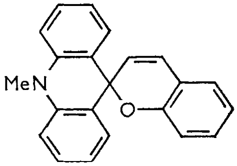

(IX)

An earlier paper from this Institute[11] pointed out the similarity between some dimethinmerocyanine dyes and the thermochromic coloured modification of some spiropyrans. It was suggested at that time that, *e.g.*, compound (X) might actually exist in solution as a mixture of the open merocyanine-like form (Xa) and the closed, spiropyran form (Xb).

This suggestion was challenged by Knott,[9e] but its correctness has now been proved by the method outlined in the present paper. The two dyes[12] (X) and (XI), whose structural formulæ in their (assumed) closed form (b) closely resemble that of spiropyran (I), were investigated. Fig. 3 shows the spectra of these two in decalin (full curves) and alcohol (broken curves), together with the spectra of spiropyrans (I) and (V) in their colourless (full curves) and coloured (broken curves) modifications. Comparison of Figs. 3a, 3b, and 3c shows a striking resemblance between the ultraviolet spectra of the colourless spiropyrans and those of the decalin solutions of compounds (X) and (XI), and also between the visible spectra of the alcoholic solutions of the dyes and those of the photochromic coloured modifications. The predominance of the spiropyran form is particularly striking in decalin solutions of dye (XI) (Fig. 3b), which are actually thermochromic. In alcoholic solutions of the same compound the open form is seen to predominate. This solvent effect on the thermal equilibrium between the two forms is similar to that observed with thermochromic spiropyrans.[4,5] Attempts to change the ratio between the two forms by irradiation at low temperatures have hitherto failed with both dyes.

If acid is added at room temperature to alcoholic solutions of those spiropyrans which

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[11] Bergmann, Weizmann, and Fischer, *J. Amer. Chem. Soc.*, 1950, **72**, 5009.
[12] Hirshberg, Knott, and Fischer, *J.*, 1955, 3313.

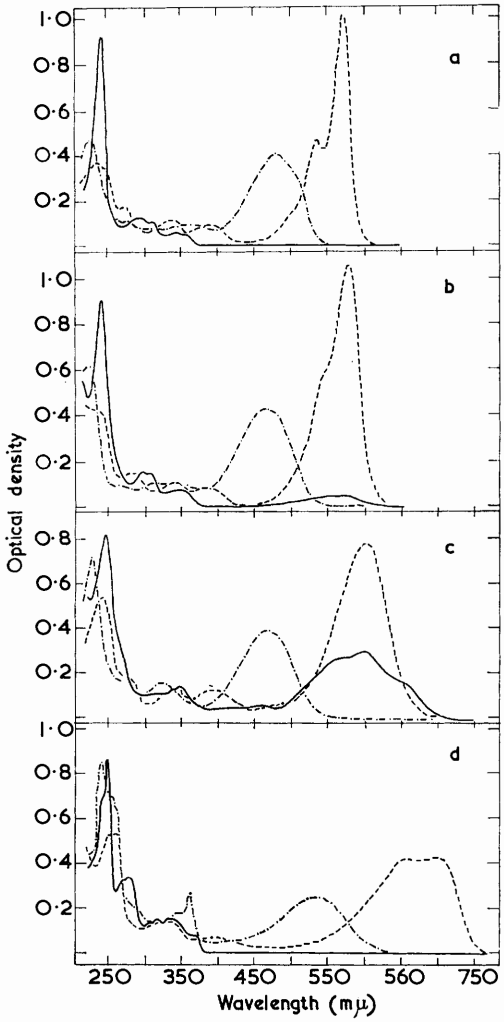
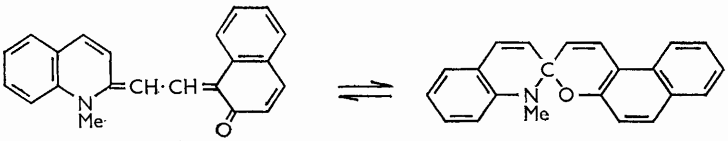


FIG. 3. *Absorption spectra of spiropyrans and merocyanines. Full curves, spiropyrans* (I) *and* (V) *in ethanol before irradiation, merocyanines* (X) *and* (XI) *in decalin; broken curves, same spiropyrans after ultraviolet irradiation, merocyanines in ethanol; dashed-dot curves, all compounds in ethanol at* 25° *after addition of excess of* HCl [600 *equiv. for* (I), 2 *equiv. for* (X), 10 *equiv. for* (XI), 60 *equiv. for* (V)]. (a) *Compound* (I), 0·9 × 10^{-5}M, −100°; (b) *compound* (XI), 1·5 × 10^{-5}M, +25°; (c) *compound* (X), *saturated solution in decalin,* 1·6 × 10^{-5}M *in propanol,* +25°; (d) *compound* (V), 1 × 10^{-5}M, −120°.

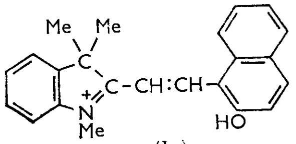
are derived from acridine or indoline [(I), (V), (VIII), (IX)], they are converted into salts of the open merocyanine-like form,[5,9f] presumably by way of the free merocyanine base which exists in thermal equilibrium with the spiropyran form in all thermochromic compounds at or beyond room temperature.[9] Thus, for example, compound (I) is transformed,



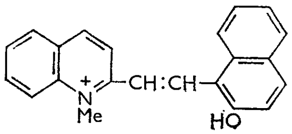
(Xa) (Xb)

(XIa) (XIb)

by way of (Ia) ⟷ (Ib), into (Ic). In the presence of excess of acid (about 600 equivalents of hydrogen chloride) the equilibrium is shifted completely in favour of form (Ic), thus



(Ic)



(Xc)

affording another path to the " open " structure, in addition to the photochromism described above. The dash-dot curves in Figs. 3a and 3d show the spectral changes involved. Here too the appearance of the salt band in the visible region is accompanied by disappearance of the spiropyran band at about 245 mμ, described above, and the appearance of a new band at about 230 mμ. No salt is formed if the acid is added at low temperatures, probably because in the sequence:

$$\text{Spiropyran} \overset{a}{\rightleftarrows} \text{" Merocyanine "} \overset{b}{\rightleftarrows} \text{Salt}$$

step (a) and its reverse do not take place any more under these conditions. However, if the solution is first cooled to about —100° and irradiated with ultraviolet light (broken curves) and then acid is added, the same salt is formed, indicating that step (b) is not appreciably slowed down by cooling. If an excess of acid is added at room temperature, the solution then cooled down to about —100°, and an excess of triethylamine added, step (b) above is reversed and the free merocyanine base formed, just as by irradiation of the original solution of the spiropyran. If it is assumed that the excess of acid added at room temperature shifts the equilibrium completely towards the salt, this would mean complete conversion of the spiropyran into the salt of the corresponding merocyanine. On the other hand, if an excess of acid is added at low temperature, after ultraviolet irradiation, then only that part of the spiropyran opened by irradiation will be converted into the salt. Comparison of the concentration of the salt obtained in these two ways affords another method of assessing the degree of radiative conversion of the spiropyran into the merocyanine. Compound (I) in Fig. 3a may again serve as an example. The height of the salt peak at 480 mμ, after addition of excess of acid at 25° and cooling to —100°, is 0·41 optical density unit, whereas if the acid is added at —100°, after ultraviolet irradiation, the height is only 0·36 optical density unit. The amount of conversion into the merocyanine is thus (100 × 0·36/0·41 =) 87%, in good agreement with the " probable " value of 88% given in Table 2.

The effect of addition of acid also serves to stress again the similarity between the merocyanine dyes (X) and (XI) and the coloured modification of the spiropyrans, such an addition resulting in the transformation of these dyes into salts such as (Xc). As shown by the dash-dot curves in Fig. 3, the spectra of the three salts are closely similar.

Experimental.—*Irradiations and spectrophotometric determinations.* These were carried out in special Dewar-type cells, in a Cary model 14 recording spectrophotometer.[8] The irradiation source was a 125 w Mazda type MB/U mercury lamp (with its envelope removed) housed in an elliptic reflector.[8] Combinations of Corning filters were used to isolate the 365 mμ line and the 365 + 313 + 303 mμ group, while an interference filter was used to isolate the 303 + 313 mμ group. The concentrations of the solutions given in the Figures refer to room temperature and are not corrected for contraction on cooling.

Solvents. The standard non-polar solvent was 2 : 1 methylcyclohexane–isopentane, freed from aromatic impurities by passage through a column of highly activated alumina. The mixture was distilled in a high vacuum from a potassium–sodium alloy directly into the cell, which was then sealed. Decalin was passed through an alumina column, as above. The standard polar solvent was 4 : 1 absolute ethanol–methanol, both freshly distilled from potassium hydroxide.

Compounds. These were prepared as described previously.[1,4,12]

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