Tetrahedron. Vol 31, pp. 1957 to 1958. Pergamon Press 1975. Printed in Great Britain

NMR STUDY OF THE INVERSION AT CARBON 2 OF SOME 1'3'3'-TRIMETHYLINDOLINO DISUBSTITUTED SPIROBENZOPYRANES

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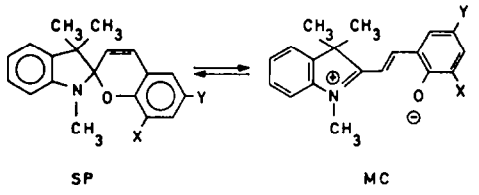
(*Received in UK 24 March 1975; Accepted for publication 3 April 1975*)

Abstract—The ^{1}H NMR spectra of some 1'3'3'-trimethylindolino-6,8-disubstituted-spirobenzopyranes in equilibrium with more than 5% of their merocyanine isomer were taken at different temperatures in dimethylsulfoxide d_6. This presents evidence of a fast inversion process at the asymmetric spiro carbon-2. It is shown that the intermediate responsible for the inversion process is certainly not the merocyanine but more likely the open ring *cis* isomer of the spiropyran.

Some indolinospiropyranes dissolved in chloroform or in dimethylsulfoxide are in equilibrium with a small amount of their colored open-ring merocyanine isomer. It is possible to shift the equilibrium in favour of the merocyanine isomer by adequate substitution at carbons 6 and 8[1,2] and in that case the merocyanine percentage can be measured with NMR spectroscopy.

This note reports an NMR study of five indolino spirobenzopyranes carried out at different temperatures in dimethylsulfoxide d_6.



SP MC

Table 1. Percentage of MC and coalescence temperature of geminal methyls in SP

Compound	X	Y	% MC†	T°	T_{coal}
1	Br	$COOCH_3$	5	R.T.	155°C
2	$COOCH_3$	NO_2	40	R.T.	90°C
			22	140°C	
3	NO_2	$COOCH_3$	70	R.T.	65°C
			62	120°C	
4	NO_2	COOH	75	R.T.	57°C
5*	COOH	NO_2	95	R.T.	

*The 8 COOH spirobenzopyrane is further stabilised by intramolecular proton transfer and hydrogen bonding (2).
†% MC are lower when the spectra are taken in $CDCl_3$.

Typical NMR parameters for both isomers are given in Table 2.

The *trans* structure of the MC isomer present in solution is evidenced by the 16 Hz value measured for the vicinal coupling between the vinyl protons H_3 and H_4.

In the SP isomer, which contains an asymmetric centre in C_2, the geminal Me at C_3' are not magnetically equivalent and display two singlet absorptions separated by 11 Hz for compounds **1** and **2** and by 13 Hz for compounds **3** and **4** in the 100 MHz spectrum.

In the NMR spectra, run at room temperature, the geminal Me signals of the SP isomer of compounds **3** and **4** (in equilibrium with more than 70% MC) are markedly broadened with respect to the corresponding Me absorptions in compounds **1** and **2**. This broadening can be explained by an exchange process between the two *gem* Me at C_3' due to a fast inversion of configuration at C_2. Indeed the formation of the MC isomer involves cleavage of the C_2–O bond, which leads also to the formation of the enantiomeric form of the initial SP. As a result, an exchange of the *gem* Me groups between two magnetic sites takes place and when this process becomes fast enough on the NMR time scale, a single peak will be observed.

Table 2. Characteristic chemical shifts and coupling constant for SP and MC isomers

Compound	δCH_3–C_3–CH_3		δCH_3–N_1	$\delta H_3/\delta H_4$		$^3J_{H_3-H_4}$
1. SP	1·12	1·23	2·64	5·9	7·12	10 (*cis*)
5. MC	1·8		4·04	8·38	8·50	16 (*trans*)

Solvent is $DMSOd_6$; δ are given in ppm vs TMS; J are given in Hz.

Thus, by raising the temperature, the two Me singlets will first broaden, then coalesce and finally give rise to an averaged Me signal.

To check this possibility, we have taken NMR spectra of compounds **1**, **2**, **3**, **4** at various temperatures and have found a coalescence for the geminal Me signals of the SP form. The more the percentage of MC at equilibrium, the lower is the temperature of coalescence (*cf.* Table 1).

For example: Compound **3** showed a coalescence temperature of 65°. At that temperature, the exchange rate constant of the *gem* Me is estimated[3] by the equation

$$k = \frac{\pi(\nu_A - \nu_B)}{\sqrt{2}}$$

where $(\nu_A - \nu_B)$ is the frequency difference of both singlets in absence of exchange (13 Hz). The rate constant for the inversion of configuration at C_2 is thus 29 sec^{-1} at 65°. At the same temperature, all other signals characteristic of the SP and MC isomers of **3** remain distinct; the close carbomethoxymethyls, for which $(\nu_A - \nu_B)$ is equal to 6·5 Hz, coalesce only at a temperature of 150°. From

that temperature and higher, other pairs of signals are gradually broadening.

Thus, for compound **3**, *the rate of isomerization SP⇄MC is much lower than the rate of inversion at carbon 2 in the SP form.* This is also true for compounds **2** and **4** for which a rate constant of 25–30 sec^{-1} for the inversion at the asymmetric carbon is reached at temperatures of 90° and 57° respectively.

For compound **1** (5% MC), the *gem* Me signals of the SP isomer coalesce only at about 155° with the consequence that the two exchange processes, namely between both enantiomers on one hand and between SP and MC on the other hand can no longer be separated.

CONCLUSION

Although the rate of inversion at the asymmetric carbon of the SP isomer is clearly related with the presence of a high percentage of MC in the equilibrium SP⇄MC, it is nevertheless evident, from the study of the various coalescence processes in function of the temperature, that the MC *trans* isomer cannot be the intermediate responsible for the inversion of configuration. To account for the experimental facts, we assume that the open-ring isomer (*cis* form) is the common intermediate both for the inversion process and for further formation of the merocyanine following the reaction scheme

$$\begin{matrix} SP_R \rightleftarrows \\ SP_S \rightleftarrows \end{matrix} \left[X = \begin{matrix} \text{open ring} \\ \textit{cis} \text{ isomer} \end{matrix} \right] \rightleftarrows MC\ \textit{trans}$$

This intermediate has not been detected by NMR and we suppose that it represents less than 1% of the merocyanine isomer.

EXPERIMENTAL

The NMR spectra were taken with a JEOL MH 100 in dimethylsulfoxide d_6 (CIS).

1',3',3' - trimethylindolino - 6,8 - disubstituted - spirobenzopyranes were prepared by reacting 1,3,3 - trimethyl - 2 - methylene - indolenine with the adequately disubstituted salicaldehyde in refluxing methylethylketone. More details on the synthesis are given elsewhere.[4]

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