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## Merocyanine Isomers of *Spiro*[indolino-indolopyrans]: <sup>1</sup>H and <sup>13</sup>C NMR and X-ray Crystal Structure Study

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The synthesis of stable merocyanine isomers **4** and **5** of the corresponding *spiro*[indolino-indolopyrans] is described. The structure of **4** and **5** was deduced on the basis of their <sup>1</sup>H and <sup>13</sup>C NMR spectra. Geometrical data from X-ray structure analysis show that indolo and indolino rings in **4** are coplanar with the central diene bridge. The bond length shortening of the central single bond and the heterocyclic moieties indicate an electron delocalization over the whole molecule.

### INTRODUCTION

A number of X-ray crystallographic studies of *spiro* indolopyrans,<sup>1–7</sup> and the corresponding merocyanines<sup>1,2,5</sup> are available. Most of the results on opened merocyanines in the *spirooxazine* series refer to the spectroscopic

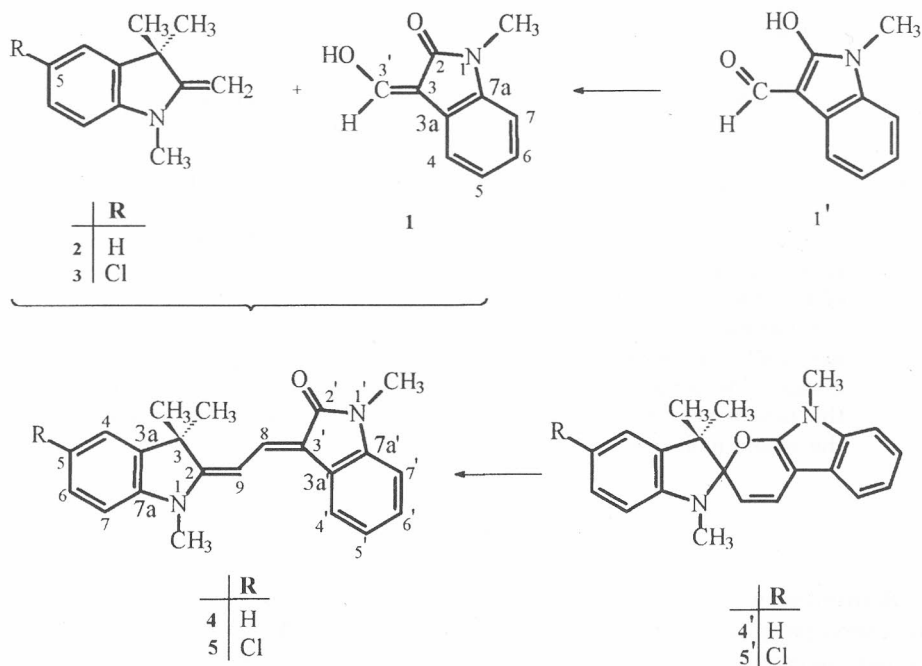
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studies in solution,<sup>8-11</sup> low temperature NMR experiments,<sup>12</sup> flash photolysis and theoretical calculation.<sup>13</sup> In this paper, we report for the first time the synthesis the stable merocyanine isomers **4** and **5** of the corresponding *spiro*[indolino-indolopyrans] **4'** and **5'**, respectively (Scheme).

## RESULTS

### Synthesis

3-Hydroxymethylene-1-methyl-2-indolinone (**1**) was obtained<sup>14</sup> by condensation of 1-methyl-2-indolinone<sup>15</sup> with ethyl formate. Contrary to the structure **1'** reported in the literature,<sup>14</sup> the <sup>1</sup>H and <sup>13</sup>C NMR (Tables II and III) as well as IR spectroscopic data in KBr clearly indicate that the product contains the enol tautomer **1** (Scheme).



Scheme

Two new merocyanine isomers **4** and **5** of the *spiro*[indolino-indolopyrans] **4'** and **5'** were prepared<sup>16</sup> by condensation of equimolar amounts of **1** with 1,3,3-trimethyl-2-methylene indolines (Fischer's bases) **2** and **3**, respectively.

#### *Attempted photochemical and thermal isomerization*

In order to induce photochemical conversion of **4** to **4'** (*c.f.* Scheme), an orange solution of **4** ( $6 \times 10^{-4}$  M) in *n*-hexane was irradiated under nitrogen flush at 0–5 °C through a Pyrex with a high pressure mercury immersion lamp for 28 hrs. The colour of the solution remained unchanged during irradiation. The absorption band at 452 nm of the visible spectrum showed no loss of intensity after irradiation. <sup>1</sup>H NMR and IR spectra of the solidified orange product that remained after evaporation of the solvent were in accord with those of **4**. Furthermore, a diglyme solution of **4** was heated for 12 hrs at 160 °C. The UV and visible spectra of the heated solution showed no change with respect to that of **4**. In addition, the red oily product obtained after evaporation of the solvent showed no presence of the IR absorption band in the range 930–990  $\text{cm}^{-1}$  characteristic of the N-C<sub>spiro</sub>-O group of *spiro* compounds.<sup>17</sup> This means that neither photochemical nor thermal isomerization of **4** to **4'** has taken place, indicating a high stability of the open merocyanine form **4'**.

#### *X-ray Crystal Structure Study*

A perspective view with atom numbering and a packing diagram in the unit cell of **4** are shown in Figures 1 and 2, respectively. Bond lengths and

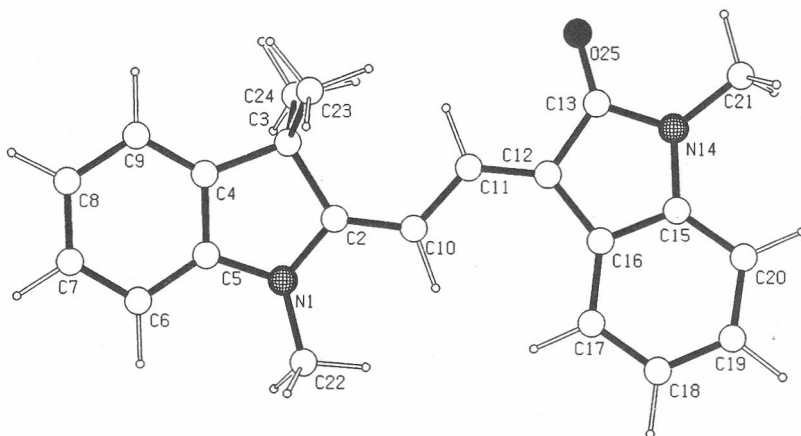


Figure 1. Perspective view with atom numbering for **4**.

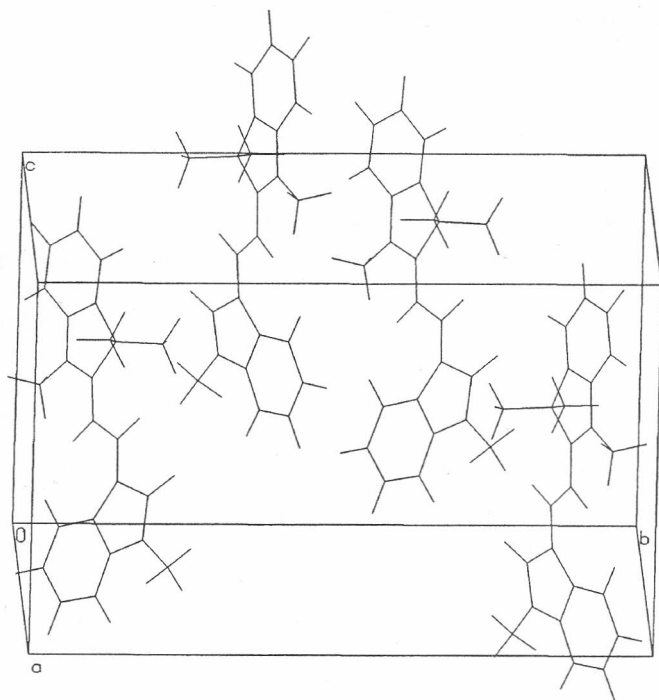


Figure 2. Packing diagram in the unit cell of **4**.

angles of **4** are summarized in Table I. The skeleton of **4** contains two planar indolino and indolo heteroaromatic rings linked by a C=C-C bridge. Both heterocyclic rings are coplanar with the central diene bridge. The double bond lengths C(12)-C(11) and C(10)-C(2) are almost identical, amounting to 1.368(8) and 1.366(9) Å, respectively. The central C(11)-C(10) single bond is 1.406(8) Å, *i.e.* significantly shorter than the standard value for the C-C single bond. These values closely agree with those found in a structurally similar conjugated system,<sup>18,19</sup> indicating electron delocalization over the whole molecule. Conjugation is also reflected in the shortening of the C(12)-C(13) and C(21)-N(14) bonds (Table I) of the indolo part of the molecule relative to the standard values in such heterocyclic systems. The bond lengths C(2)-N(1) and C(22)-N(1) of the indolino fragment are consistently shortened with respect to the corresponding values found in the unconjugated related *spirooxazine*<sup>20</sup> and *benzoxazine*<sup>4</sup> derivatives containing the same indoline fragment. The observed values for the bond lengths C(2)-C(10), C(10)-C(11) and C(11)-C(12) of the diene chain as well as for C(22)-N(1), N(1)-C(2) of the indoline part, are in good agreement with the corresponding ones of the related conjugated molecules.<sup>18,19</sup>

TABLE I

Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses in the structure of 4.

N1 - C2	1.376(6)	C10 - C11	1.406(8)
N1 - C5	1.401(8)	C11 - C12	1.368(8)
N1 - C22	1.433(6)	C12 - C13	1.468(7)
C2 - C3	1.531(7)	C12 - C16	1.455(5)
C2 - C10	1.366(9)	C13 - N14	1.375(8)
C3 - C4	1.527(8)	C13 - O25	1.226(6)
C3 - C23	1.531(7)	N14 - C15	1.393(6)
C3 - C24	1.544(6)	N14 - C21	1.449(8)
C4 - C5	1.389(6)	C15 - C16	1.399(6)
C4 - C9	1.367(9)	C15 - C20	1.393(8)
C5 - C6	1.400(8)	C16 - C17	1.403(5)
C6 - C7	1.36(1)	C17 - C18	1.388(8)
C7 - C8	1.383(8)	C18 - C19	1.381(9)
C8 - C9	1.407(9)	C19 - C20	1.388(7)
C2 N1 C5	111.2(4)	C2 C10 C11	125.2(5)
C2 N1 C22	125.5(4)	C10 C11 C12	127.4(5)
C5 N1 C22	123.1(4)	C11 C12 C13	119.6(4)
N1 C2 C3	108.1(4)	C11 C12 C16	133.9(4)
N1 C2 C10	123.0(5)	C13 C12 C16	106.4(4)
C3 C2 C10	128.9(5)	C12 C13 N14	107.0(4)
C2 C3 C4	101.8(4)	C12 C13 O25	129.6(5)
C2 C3 C23	113.9(4)	N14 C13 O25	123.4(5)
C2 C3 C24	108.9(4)	C13 N14 C15	110.3(4)
C4 C3 C23	110.7(4)	C13 N14 C21	124.2(5)
C4 C3 C24	109.3(4)	C15 N14 C21	125.5(5)
C23 C3 C24	111.7(4)	N14 C15 C16	109.6(4)
C3 C4 C5	108.5(4)	N14 C15 C20	127.5(5)
C3 C4 C9	130.7(5)	C16 C15 C20	122.9(4)
C5 C4 C9	120.8(5)	C12 C16 C15	106.7(3)
N1 C5 C4	109.9(4)	C12 C16 C17	135.1(3)
N1 C5 C6	128.4(5)	C15 C16 C17	118.3(3)
C4 C5 C6	121.7(5)	C16 C17 C18	119.2(4)
C5 C6 C7	116.9(5)	C17 C18 C19	121.1(5)
C6 C7 C8	122.4(6)	C18 C19 C20	121.4(5)
C7 C8 C9	120.2(6)	C15 C20 C19	117.1(5)
C4 C9 C8	118.0(5)		

## EXPERIMENTAL

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1**, **4** and **5** (Tables II and III) were recorded on a Varian GEM 300 (PFT mode, 300 MHz). The IR spectra were recorded on a Perkin Elmer 297 infracord spectrometer. Melting points were determined on a Kofler micro hot-stage (Reichert, Wien). UV spectra were recorded on a Hitachi Perkin-Elmer 124 spectrometer. The electron impact mass spectrum was recorded on the Extrel FT MS 2001. Exact mass measurements of the molecular ion of **5** were performed using the same instrument. Elemental analyses were performed by the Central Analytical Service, Ruđer Bošković Institute, Zagreb.

*3-Hydroxymethylene-1-methyl-2-indolinone* (**1**).<sup>14</sup> A mixture of ethyl formate (3.7 mL, 0.05 mol) and 1-methyl-2-indolinone (5.0 g, 0.04 mol) was poured into a hot solution of sodium (1.14 g) in absolute ethanol (30 mL). Almost immediately, the mass set solid. The content of the flask was taken up in water, and acidified with hydrochloric acid, whereupon the product separated as yellowish crystals, which were filtered and washed with a little alcohol and ether. Purification of the crude product by column chromatography on silica gel (0.063–0.2 mm) in acetone gave **1** (6.05 g, 59%), m.p. 187–190 °C, lit.<sup>14</sup> m.p. 192 °C, lit.<sup>22</sup> m.p. 186 °C, IR(KBr):  $\nu = 1680\text{ cm}^{-1}$  ( $\text{C}^2=\text{O}$ ).

*1-(1,3-Dihydro-1,3,3-trimethyl-2H-indole-2-yliden)-2-(1,3-dihydro-1-methyl-2H-indole-2-on-3-yliden)ethane* (**4**) was prepared by reacting **1** (0.80 g, 0.0053 mol) and freshly distilled 1,3,3-trimethyl-2-methyleneindoline (**2**) (0.94 mL, 0.0053 mol) in absolute ethanol (20 mL). After refluxing for 3.5 hrs, the resultant highly colored mixture was cooled. The solvent was removed under reduced pressure. The residue was recrystallized from ethanol to give orange crystals, 0.94 g (53.1%) of **4**, m.p. 194–7 °C, IR(KBr):  $\nu = 1670\text{ cm}^{-1}$  ( $\text{C}^2=\text{O}$ ), UV(abs. MeOH)  $\lambda_{\text{max}}(\log \epsilon)$  473 sh (6.81), 452 (6.79), 282 sh (6.59) and 262 broad (6.56).

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}$  (330.43): C 79.97, H 6.71, N 8.48; found: C 79.94, H 6.68, N 8.52%.

*1-(1,3-Dihydro-5-chloro-1,3,3-trimethyl-2H-indole-2-yliden)-2-(1,3-dihydro-1-methyl-2H-indole-2-on-3-yliden)ethane* (**5**) was obtained in the same way as described for **4**. The crude product was recrystallized from ethanol, yielding dark red crystals of **5** (0.70 g, 36,3%), m.p. 255–258 °C, IR(KBr):  $\nu = 1685\text{ cm}^{-1}$  ( $\text{C}^2=\text{O}$ ), MS (70 eV)  $m/z$  (rel. intensity) 366( $\text{M}^+$ , 22), 364(62), 351(32), 349(100), 314(22), 313(28), 299(14), 218(8), 206(10), 205(12); found  $\text{M}^+$  364.133692 calcd. for  $\text{C}_{22}\text{H}_{21}\text{N}_2\text{OCl}$  364.122888, UV(abs. MeOH)  $\lambda_{\text{max}}(\log \epsilon)$  475, sh (7.24), 454(7.22), 287 sh (7.02), 261(6.98).

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{21}\text{N}_2\text{OCl}$  (364.87): C 72.50, H 5.81, N 7.69; found: C 72.46, H 5.79, N 7.66%.

### Crystallography

A single crystal of **4**, suitable for X-ray structure analysis, was prepared by growth under slow evaporation at room temperature of a dilute solution of EtOH. An orange crystal, dimensions  $0.25 \times 0.30 \times 0.65$  mm, was mounted on a Philips PW 1100 diffractometer upgraded by Stoe; data were collected in the  $\theta - 2\theta$  scan mode ( $3 - \theta - 63.5^\circ$ ), graphite-monochromated Cu  $K\alpha$  radiation; lattice parameters from least-squares refinement of 17 reflections ( $35.05 - 2\theta - 59.53^\circ$ ); monitored reflections

TABLE II

<sup>1</sup>H NMR chemical shifts (δ/ppm)<sup>a</sup> and H-H coupling constants (J/Hz) for compounds **1**, **4** and **5** (c.f. Scheme).

	C(CH <sub>3</sub> ) <sub>2</sub>	N <sup>1</sup> -CH <sub>3</sub>	N <sup>1</sup> -CH <sub>3</sub>	OH <sup>b</sup>	H-3'	H-8	H-9	H-arom.
<b>1</b>	-	3.3(s,3H)	-	6.1(s,1H)	7.9(s,1H)	-	-	6.9-7.4(m)
<b>4</b>	1.7(s,6H)	3.4(s,3H)	3.3(s,3H)	-	-	8.1(d,1H) <sup>3</sup> J = 14	6.1(d,1H) <sup>3</sup> J = 14	6.8-7.6(m)
<b>5</b>	1.7(s,6H)	3.3(s,3H)	3.3(s,3H)	-	-	8.0(d,1H) <sup>3</sup> J = 14	6.1(d,1H) <sup>3</sup> J = 14	6.7-7.6(m)

<sup>a</sup> CDCl<sub>3</sub> solutions (0.05 M, 19 °C), chemical shifts refer to TMS. Multiplicities of coupling and the number of protons are given in brackets: s = singlet, d = doublet, t = triplet, q = quartet, m = complex multiplet.

<sup>b</sup> Confirmed after mixing the sample in the NMR tube with D<sub>2</sub>O.

TABLE III

<sup>13</sup>C NMR chemical shifts (δ/ppm)<sup>a</sup> for **1**, **4** and **5** (c.f. Scheme).

	N <sup>1</sup> -CH <sub>3</sub>	C <sup>3</sup> (CH <sub>3</sub> ) <sub>2</sub>	N <sup>1</sup> -CH <sub>3</sub>	C-2	C-3	C-3a	C-4	C-7	C-5	C-6	
<b>1</b>	26.2	-	-	170.0	106.4	122.3	127.2	108.7		122.6	
<b>4</b>	29.4	28.4	25.7	114.9*	46.9	123.7	107.3			121.4	
<b>5</b>	29.5	28.4	25.7	115.7*	46.9	123.5	108.0	107.5	126.8	121.5	
	C-7 <sup>a</sup>	C-2'	C-3'	C-3a	C-4'	C-5'	C-6'	C-7'	C-7a'	C-8	C-9
<b>1</b>	140.8	-	155.7	-	-	-	-	-	-	-	-
<b>4</b>	141.9	169.3	167.3*	139.8	121.7	125.7	127.9	121.1	143.9	134.0	93.2
<b>5</b>	142.0	169.2	166.5*	141.4	122.4	126.0	127.8	121.2	142.6	133.3	93.6

<sup>a</sup> The spectra of **1** (CDCl<sub>3</sub>) and **4** and **5** (d<sub>6</sub>-DMSO) were recorded at 19 °C. Sample concentrations were approximately 0.1 M. Chemical shifts refer to TMS. The assignments were confirmed by Attached Proton Test. The assignment of the 1-methyl-2-indolinone moiety in **4** and **5** was made in accord to that in the literature.<sup>21</sup>

\* The assignment may be interchanged.

TABLE IV

Non-hydrogen fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\times 10^4$ ) with e.s.d.'s in parentheses for **4**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{\AA}^2)^a$
N1	-1973(6)	4148(1)	8698(4)	578(6)
C2	-476(6)	3787(2)	8763(5)	505(7)
C3	133(6)	3439(2)	9968(4)	524(7)
C4	-1125(7)	3735(2)	10580(5)	575(8)
C5	-2339(6)	4138(2)	9777(5)	574(8)
C6	-3674(7)	4476(2)	10084(6)	731(11)
C7	-3695(8)	4408(3)	11219(6)	850(13)
C8	-2486(7)	4016(3)	12038(6)	799(12)
C9	-1164(7)	3671(2)	11716(5)	684(9)
C10	281(7)	3778(2)	7877(5)	578(8)
C11	1809(7)	3419(2)	7901(4)	562(7)
C12	2686(6)	3432(2)	7077(4)	540(7)
C13	4196(7)	2984(2)	7210(4)	581(7)
N14	4728(6)	3068(2)	6223(4)	595(7)
C15	3692(7)	3551(2)	5480(4)	524(7)
C16	2432(0)	3795(2)	5976(0)	516(7)
C17	1289(7)	4303(2)	5373(4)	602(8)
C18	1452(7)	4547(2)	4318(5)	676(9)
C19	2698(8)	4290(2)	3846(4)	686(10)
C20	3833(8)	3780(2)	4406(5)	640(9)
C21	6187(8)	2712(3)	6013(6)	771(11)
C22	-2974(8)	4533(2)	7700(5)	743(10)
C23	2048(7)	3587(3)	10677(5)	680(9)
C24	-208(7)	2677(2)	9790(5)	638(8)
O25	4911(7)	2596(2)	8014(4)	764(8)

$$^a U_{eq} = 1/3 \sum_{ij} U_{ij} a_i^* a_j^* a_i a_j$$

(2, 1, 3; -9, -23, -14 and 9, 23, 14) showed only statistical variation intensities; 1469 independent reflections were measured ( $h = -9, 9$ ;  $k = -23, 23$ ;  $l = -14, 13$ ),  $1335 \geq 2.5\sigma(I)$ ; Lorentz-polarization corrections were applied; the structure was solved by direct methods, full matrix least-squares refinement, H atoms were generated and allowed to ride at fixed distances from the attached atoms, isotropic thermal parameters were refined for two groupings of H atoms;  $R = 0.066$  and  $R_w = 0.074$  for 226 parameters and 1335 reflections,  $\omega = 1/[\sigma^2(F) + 0.05585(F)^2]$ ;  $(\delta/\sigma)_{max} = 0.001$ ; largest peaks in the final difference map: +0.46 and -0.42 eÅ<sup>-3</sup>. All calculations were performed with the SHELXS-86<sup>23</sup> and SHELXD<sup>24</sup> on an IBM PC/AT compatible microcomputer. Atomic coordinates with equivalent isotropic thermal parameters are given in Table IV. Crystal data for C<sub>22</sub>H<sub>22</sub>ON<sub>2</sub>:  $M_r = 330.43$  space group  $Ia$  with  $a = 7.981(1)$ ,  $b = 19.909(3)$ ,  $c = 11.894(2)$  Å,  $\beta = 107.83(1)^\circ$ ,  $V = 1799.1(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{calc} = 1.220$  gcm<sup>-3</sup> and  $\mu(\text{Cu K}\alpha) = 5.54$  cm<sup>-1</sup>. Additional X-ray crystallographic data,



*i.e.* full tables of bond distances and bond angles, tables of anisotropic thermal parameters, hydrogen atomic coordinates with isotropic thermal parameters, as well as the observed and calculated structure factors (3 pages) are given as deposit.

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## SAŽETAK

### **Merocijaninski izomeri *spiro*[indolino-indolopirana]: <sup>1</sup>H i <sup>13</sup>C NMR i rentgensko strukturno istraživanje**

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Opisana je sinteza stabilnih merocijaninskih izomera **4** i **5** *spiro*[indolino-indolopirana]. Strukture **4** i **5** su izvedene na temelju spektara <sup>1</sup>H i <sup>13</sup>C NMR. Geometrijski podaci iz rentgenske strukturne analize pokazuju da su indolo i indolinski prstenovi u spoju **4** koplanarni sa središnjim dienskim mostom. Skraćivanje srednje jednostruke veze i heterocikličkih jezgara ukazuje na delokalizaciju elektrona preko cijele molekule.