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NEW FORMYL-SUBSTITUTED SPIROPYRANS OF THE INDOLINE SERIES

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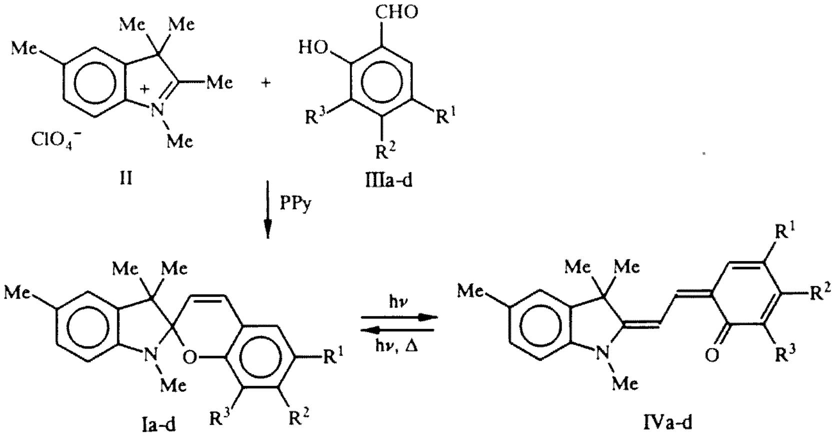
It was recently shown that an important structural factor influencing the photochromism of spiropyrans in solid amorphous films is the presence of the formyl group in the benzopyran fragment of the spiropyran molecule [1].

We synthesized new photochromic spiropyrans (I) containing the formyl group at the position 6 or 8 of the benzopyran fragment.



I, III, IV a R^1 – CHO, R^2 – H, R^3 – Me; b R^1 – CHO, R^2 – R^3 – Me; c R^1 – CHO, R^2 – H, R^3 – OMe; d R^1 – Me, R^2 – H, R^3 – CHO

Thus, the mixture of 0.29 g (1 mmole) of 1,2,3,3,5-pentamethyl-3H-indolium perchlorate (II), 1 mmole of the corresponding diformylphenol (III), and 0.09 g (1 mmole) of piperidine in 5 ml of propan-2-ol is boiled for 2 h. The mixture is concentrated, and the residue is chromatographed on a column with Al_2O_3 using chloroform as the eluent prior to the isolation of the spiropyrans (Ia-d).

The data of the elemental analysis for C, H, and N correspond with the calculated data.

1′,3′,3′,5′,8-Pentamethyl-6-formylspiro[2H-1-benzopyran-2,2′-indoline] (Ia). ($C_{22}H_{23}NO_2$). The yield is 62.5%. The mp is 144-145°C (from heptane). The PMR spectrum ($CDCl_3$) is as follows: 1.17 ppm (3H, s, 3′-CH_3), 1.24 ppm (3H, s, 3′-CH_3), 1.99 ppm (3H, s, 8-CH_3), 2.30 ppm (3H, s, 5′-CH_3), 2.64 ppm (3H, s, 1′-CH_3), 5.75 ppm (1H, d, J = 10.3 Hz, 3-H), 6.40 ppm (1H, d, J = 7.8 Hz, 7′-H), 6.86 ppm (1H, d, J = 0.9 Hz, 4′-H), 6.88 ppm (1H, d, J = 10.3 Hz, 4-H), 6.95 ppm (1H, dd, J = 7.8, J = 0.9 Hz, 6′-H), 7.44 ppm (1H, d, J = 2.1 Hz, 5-H), 7.50 ppm (1H, d, J = 2.1 Hz, 7-H), and 9.78 ppm (1H, s, 6-CHO).

1′,3′,3′,5′,7,8-Hexamethyl-6-formylspiro[2H-1-benzopyran-2,2′-indoline] (Ib). ($C_{23}H_{25}NO_2$). The yield is 60.2%. The mp is 170-171°C (from heptane). The PMR spectrum ($CDCl_3$) is as follows: 1.16 ppm (3H, s, 3′-CH_3), 1.23 ppm (3H, s, 3′-CH_3), 1.91 ppm (3H, s, 8-CH_3), 2.30 ppm (3H, s, 5′-CH_3), 2.51 ppm (3H, s, 7-CH_3), 2.63 ppm (3H, s, 1′-CH_3), 5.70

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ppm (1H, d, J = 10.3 Hz, 3-H), 6.40 ppm (1H, d, J = 7.8 Hz, 7'-H), 6.85 ppm (1H, d, J = 10.3 Hz, 4-H), 6.86 ppm (1H, d, J = 0.9 Hz, 4'-H), 6.95 ppm (1H, dd, J = 7.8, J = 0.9 Hz, 6'-H), 7.42 ppm (1H, s, 5-H), and 10.12 ppm (1H, s, 6-CHO).

8-Methoxy-1',3',3',5'-tetramethyl-6-formylspiro[2H-1-benzopyran-2,2'-indoline] (Ic). ($C_{22}H_{23}NO_3$). The yield is 58.4%. The mp is 186.5-188°C (from heptane). The PMR spectrum ($CDCl_3$) is as follows: 1.15 ppm (3H, s, 3'-CH_3), 1.26 ppm (3H, s, 3'-CH_3), 2.30 ppm (3H, s, 5'-CH_3), 2.70 ppm (3H, s, 1'-CH_3), 3.72 ppm (3H, s, 8-OCH_3), 5.73 ppm (1H, d, J = 10.3 Hz, 3-H), 6.41 ppm (1H, d, J = 7.8 Hz, 7'-H), 6.85 ppm (1H, d, J = 10.3 Hz, 4-H), 6.86 ppm (1H, d, J = 0.9 Hz, 4'-H), 6.95 ppm (1H, dd, J = 7.8, J = 0.9 Hz, 6'-H), 7.21 ppm (1H, d, J = 1.9 Hz, 5-H), 7.25 ppm (1H, d, J = 1.9 Hz, 7-H), and 9.77 ppm (1H, s, 6-CHO).

1',3',3',5',6-Pentamethyl-8-formylspiro[2H-1-benzopyran-2,2'-indoline] (Id). ($C_{22}H_{23}NO_2$). The yield is 56.7%. The mp is 118.5-119.5°C (from propan-2-ol). The PMR spectrum ($CDCl_3$) is as follows: 1.17 ppm (3H, s, 3'-CH_3), 1.29 ppm (3H, s, 3'-CH_3), 2.25 ppm (3H, s, 6-CH_3), 2.30 ppm (3H, s, 5'-CH_3), 2.69 ppm (3H, s, 1'-CH_3), 5.76 ppm (1H, d, J = 10.3 Hz, 3-H), 6.40 ppm (1H, d, J = 7.8 Hz, 7'-H), 6.83 ppm (1H, d, J = 10.3 Hz, 4-H), 6.85 ppm (1H, d, J = 0.9 Hz, 4'-H), 6.94 ppm (1H, dd, J = 7.8, J = 0.9 Hz, 6'-H), 7.07 ppm (1H, d, J = 2.1 Hz, 5-H), 7.41 ppm (1H, d, J = 2.1 Hz, 7-H), and 10.10 ppm (1H, s, 8-CHO).

We investigated photochromic conversions of the spiropyrans (I) in solid-phase amorphous films, obtained by the thermal vacuum deposition on glass or quartz supports using the VUP-4 and VUP-5 installations at the residual pressure of $5 \cdot 10^{-5}$ torr. The electronic absorption spectra of amorphous films of the spiropyrans (I) are most characterized by the long-wave absorption band with the maximum in the region of 300-360 nm. Such a band is typical of the cyclic structure (I) with the orthogonal hetarene and the 2H-chromene fragments.

The exposure of solid-phase amorphous films of the spiropyrans (I) (the DRSh-250 mercury lamp with the λ_{max} 313 nm) leads to their photocoloration as the result of the isomerization of the spirocyclic form (I) to the quinoid—betaine form (IV), absorbing in the visible spectral region.

The electronic absorption spectra of the photoinduced forms (IV) are characterized by the long-wave absorption band with maxima at 580 nm for (IVa), 577 nm for (IVb), 575 nm for (IVc), and 607 nm for (IVd). When the colored form (IVc) is exposed to light corresponding to the absorption band (the λ_{max} 550-560 nm), the photoinduced spirocyclization reaction proceeds with the formation of the spiropyrans (I).

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