REACTION OF γ-PYRONES WITH 1,3-BIS(DICYANOMETHYLENE)INDAN

B. P. Bespalov, A. G. Abolin,
and V. G. Rumyantsev

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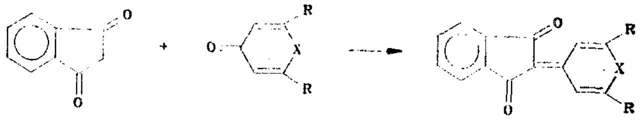
The condensation of γ-pyrones with 1,3-bis(dicyanomethylene)indan leads to the corresponding deeply colored 2-(pyran-4-ylidene)-1,3-bis(dicyanomethylene)indans. The reaction of the latter with primary aliphatic or aromatic amines leads to replacement of the pyran oxygen by an amino group. The resulting compounds are zwitterions and possesses dichroic properties. The IR and UV spectra, and also the dichroic spectra of the compounds obtained in a liquid crystal are given. A qualitative explanation of the nature of the absorption bands of these compounds in the visible region of the spectrum is presented.

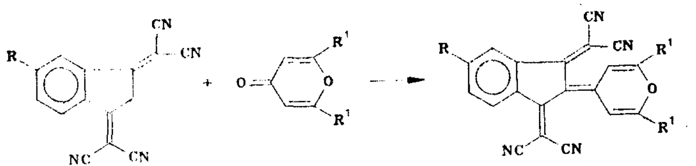
As is well known, the condensation of γ-pyrones with indan-1,3-dione leads to the formation of phthalone-like structures [1]:



X=O,NH; R=H,CH_3,Ph

The reaction takes place in spite of the fact that position 2 in indan-1,3-dione is fairly difficult to access because of steric factors. The introduction of more voluminous substituents such as dicyanomethylene groups into positions 1 and 3 of the indan molecule should passivate the condensation reaction in position 2 to an even greater degree. This is possibly one of the reasons why it has hitherto been impossible to introduce a third dicyanomethylene group into 1,3-bis(dicyanomethylene)indan.

We have succeeded in effecting the condensation of 2,6-disubstituted γ-pyrones with 1,3-bis(dicyanomethylene)indan with the formation of the corresponding products (II):



I a-c

II a-c

I, II a $R=R^1=H$; b $R=H$, $R^1=CH_3$; c $R=NO_2$, $R^1=CH_3$

The reaction of compounds (II) with primary amines might be expected to lead to the replacement both of the pyran oxygen and also of a nitrile group. The latter reaction is characteristic for polycyano derivatives of unsaturated compounds such as tetracyanoethylene and 7,7',8,8'-tetracyanoquinodimethane [2, 3]. According to the results of elementary analysis, only the replacement of the oxygen of the pyran ring took place, with the formation of the deep-blue-colored compounds (III) (Table 1).

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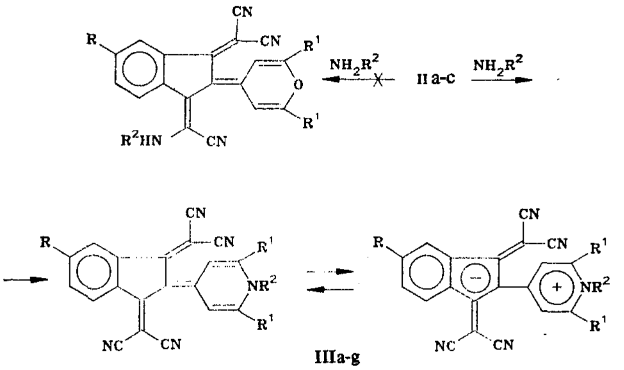
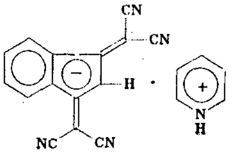


III a-f R=H, g $R=NO_2$; a—c, e—g $R^1=CH_3$, d $R^1=H$; a $R^2=H$, b $R^2=CH_3$, c, d, g $R^2=Ph$, e $R^2=(C_6H_4)_2—C_8H_{17}$-p, f $R^2=C_6H_4—N(C_2H_5)_2$-p

The electronic absorption spectrum of compound (IIb) in acetonitrile has a broad structureless band in the visible region which, on the basis of the structure of the molecule and a positive solvatochromic effect, can be assigned to an intramolecular charge transfer band. The spectra of compounds (III) in the visible region contain a structured band with λ_{max} 565 nm (Table 1 and Fig. 1, curve 3). It is assumed that this band is due to the absorption of the 1,3-bis(dicyanomethylene)indan anion. In actual fact, the spectra of compounds (III) almost completely repeat the spectrum of the pyridinium salt of 1,3-bis-(dicyanomethylene)indan (IV) (Fig. 1, a, curve 4). On this basis, we consider that under the conditions investigated the contribution of the zwitterionic resonance structure in compounds (III) predominates.



IV

The addition of triethylamine to a solution of compound (IIb) in acetonitrile led reversibly to the appearance of a band with λ_{max} 565 nm (Fig. 1, a, curve 2), but the nature of this effect has not been elucidated. Compound (IIc), which has a nitro group in the benzene ring of the indan moiety of the molecule, has only the intramolecular charge transfer band in its electronic spectrum (Fig. 1, b, curve 1), but this is at a longer wavelength (λ_{max} 570 nm) than for compound (IIb) and behaves similarly to compound (IIb) on the addition of triethylamine (Fig. 1, b, curve 2). In the electronic spectrum of the corresponding compound (IIIg) (Fig. 1, b, curve 3), the band of the anion had a longer wavelength and was close to the spectrum of the pyridinium salt of 1,3-bis(dicyanomethylene)-5-nitroindan (Fig. 1, b, curve 4).

The existence in the molecule of each of compounds (III) of two chromophoric systems with different directions of the charge oscillations has permitted the assumption of the existence of dichroic properties in these compounds. Compounds with dichroic properties are used in the creation of multicolored liquid-crystal indicators. If a solution of compound (III) is prepared in an oriented liquid crystal and is illuminated with polarized light, the color of the solution will depend on the direction of the plane of polarization of the incident light with respect to the axis of orientation of the liquid crystal. If the plane of polarization coincides with the direction of the long axis, i.e., with the axis of symmetry of the molecules of the compound (III), then the absorption of light is due to the pyridinium moiety of the molecule, while if the plane of polarization of the light is directed perpendicularly to the axis of symmetry of the molecule the absorption is due to the oscillations of the charge of the dicyanomethylene groups in the anion. If the oscillation of the charge takes place along the short axis of the molecule, as in this case, the dichroism is called negative. Only three classes of organic compounds with negative dichroism have been described: tetrazines [4], azoimidazoles [5], and bismerocyanines [6].

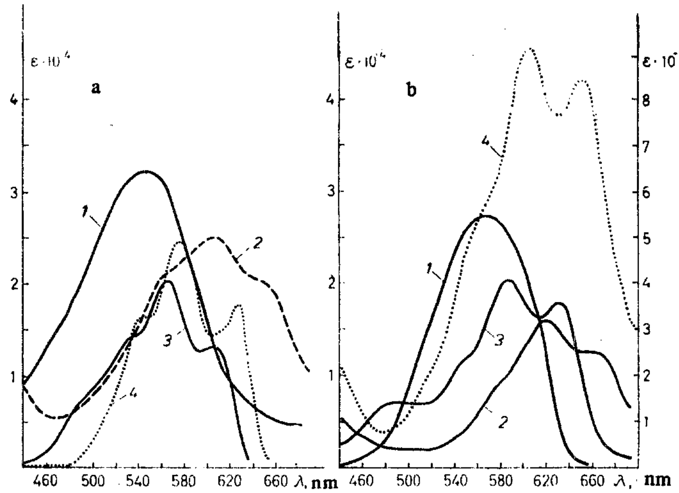


Fig. 1. Absorption spectra: a: 1) (IIb); 2) (IIb) after the addition of a drop of triethylamine; 3) (IIIc); 4) pyridinium salt of 1,3-bis(dicyanomethylene)indan (IV); b: 1) (IIc); 2) (IIc) after the addition of a drop of triethylamine; 3) (IIIg); 4) pyridinium salt of 1,3-bis(dicyanomethylene)-5-nitroindan (the values of ε are plotted on the right-hand axis).

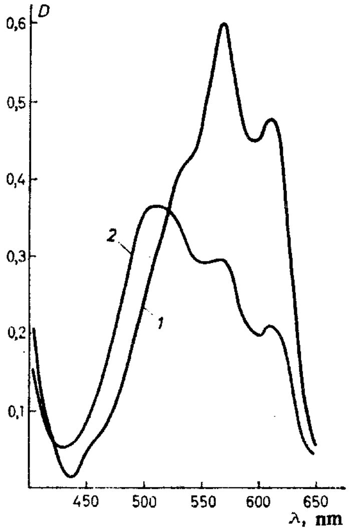


Fig. 2. Absorption spectra of compound (IIIe) in a liquid crystal: 1) polarization vector of the incident light perpendicular to the optical axis of the liquid crystal; 2) polarization vector parallel to the optical axis of the liquid crystal.

In order to study the dichroic properties of a compound (III), its molecule was elongated through the radical R^2 attached to the nitrogen atom (with the aim of increasing the degree of orientation of the molecule in the liquid crystal). Figure 2 shows the dichroism spectra for a solution of compound (IIIe). Information on the dichroic properties of some compounds, (II) and (III), is given in Table 1. The value of S characterizes the degree of orderliness of the oscillator of the given absorption band in the liquid crystal and is calculated from the formula [7]

$$S=\frac{D_{\parallel}-D_{\perp}}{D_{\parallel}+2D_{\perp}},$$

TABLE 1. Characteristics of the Compounds Synthesized (IIa-c), (IIIa-g)

Compound	mp,* °C	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm (ϵ)	Found, %			Empirical formula	Calculated, %			Yield, % (method)	Dichroism	
				C	H	N		C	H	N		λ, nm	S
II a	305(decomp.)	2207 (C≡N), 1617 (C=C), 940 (C—O—C)	550 (16 710, sh), 579 (20 830), 624 (14 260)	74,9	2,6	17,6	$C_{20}H_8N_4O$	75,0	2,5	17,5	92		
II b	240(decomp.)	2202 (C≡N), 1619 (C=C), 940 (C—O—C)	555 (32 125)	76,0	3,5	16,0	$C_{22}H_{12}N_4O$	75,9	3,5	16,1	96	565	−0,12
II c	274—275	2195 (C≡N), 1634 (C=C), 1337 (NO$_2$), 940 (C—O—C)	570 (27 500)	67,5	2,8	18,0	$C_{22}H_{11}N_5O_3$	67,2	2,8	17,8	83		
III a	>350	3279 (NH), 2195 (C≡N), 1640 (C=C), 1312 (C—N)	530 (22 230, sh), 568 (31 720), 605 (24 320)	76,0	3,8	20,2	$C_{22}H_{13}N_5$	76,1	3,8	20,1	93 (A)	515, 572, 616	+0,21; −0,11; −0,12
III b	344—345	2193 (C≡N), 1646 (C=C), 1316 (C—N)	530 (15 220, sh), 565 (20 630), 610 (16 840)	76,7	4,5	19,1	$C_{23}H_{15}N_5$	76,4	4,2	19,4	87 (A)		
III c	>350 (decomp.)	2195 (C≡N), 1631 (C=C), 1314 (C—N)	532 (14 125, sh), 565 (20 250), 610 (13 250)	79,4	4,0	16,4	$C_{28}H_{17}N_5$	79,4	4,1	16,5	91 (B)		
III d	329—330	2193 (C≡N), 1628 (C=C), 1313 (C—N)	530 (18 360, sh), 563 (21 890), 600 (16 820)	78,8	3,5	17,7	$C_{26}H_{13}N_5$	79,0	3,3	17,7	87 (B)		
III e	205,5—206,5	2195 (C≡N), 1631 (C=C), 1313 (C—N)	500 (15 780, sh), 540 (18 420, sh), 575 (22 100), 620 (17 890)	82,3	6,2	11,1	$C_{42}H_{37}N_5$	82,5	6,1	11,4	55 (C)	515, 575, 620	+0,10; −0,22; −0,23
III f	292,5—294	2189 (C≡N), 1626 (C=C), 1315 (C—N)	490 (15 700), 533 (18 460, sh), 566 (21 900), 610 (18 650)	77,7	5,0	17,3	$C_{32}H_{26}N_6$	77,7	5,3	17,0	78 (C)		
III g	>350	2194 (C≡N), 1632 (C=C), 1336 (NO$_2$), 1252 (C—N)	485 (7250), 550 (14 875, sh), 585 (20 250), 635 (17 750)	71,4	3,5	17,8	$C_{28}H_{16}N_6O_2$	71,8	3,4	17,9	86 (B)		

*Compounds (IIa, b, IIIa, b, d, g) from acetonitrile; (IIc) from acetonitrile—benzene (1:1); (IIIc, e) from methanol; (IIIf) from benzene—hexane (1:1).

where $D_\parallel$ and $D_\perp$ are the optical densities of the oriented solution of the dye for the polarization of light parallel and perpendicular to the optical axis, respectively. If the absorption oscillator is arranged along the long axis of the molecule or at a small angle to it, then $D_\parallel > D_\perp$ and $S > 0$, i.e., positive dichroism is observed. If, however, the oscillator is arranged at an angle close to 90° with respect to the long axis, then $D_\perp > D_\parallel$ and $S < 0$, and negative dichroism is observed.

EXPERIMENTAL

Solvents of "ch." ["pure"] grade were used for performing the reactions. The electronic absorption spectra were recorded on a Hitachi EPS spectrophotometer (in acetonitrile of "for chromatography" grade) and IR spectra on a Shimadzu IR 435 spectrometer (in KBr tablets). The procedure for preparing the oriented solutions of the dyes and recording their polarization absorption spectra (dichroism spectra) has been described previously [6]. As the liquid-crystalline material we used a mixture of alkyl- and alkoxycyanobiphenyls (ZhK-807). The concentration of the dyes was 0.5-2% by weight at a thickness of the measuring cells of 10-60 μm. The electronic absorption spectra were taken at a concentration of the solutions of all the compounds of 10^{-5} M.

The characteristics of the compounds (II) and (III) synthesized are given in Table 1.

1,3-Bis(dicyanomethylene)indan (Ia) was synthesized as described in [8]. The pyridinium salt of 1,3-bis(dicyanomethylene)indan (IV) was obtained similarly, but with the use of pyridine as solvent and the subsequent dilution of the reaction mixture with benzene; yield 92%, mp 274-275°C (from benzene—ethanol (1:1)). UV spectrum, λ_{max}, nm (ε): 546 (16,500); 578 (24,500); 626 (18,000). IR spectrum, cm^{-1}: 3197 (N—H); 3060 (C—H); 2215, 2197 (C≡N). Found: C 74.8; H 3.6; N 21.8%. $C_{15}H_6N_4 \cdot C_5H_5N$. Calculated: C 74.8; H 3.5; N 21.8%.

To obtain 1,3-bis(dicyanomethylene)-5-nitroindan (Ic) we used the pyridinium salt of 1,3-bis(dicyanomethylene)-2-ethoxycarbonyl-5-nitroindan. With heating, 8.33 g (43 mmole) of 4-nitrophthalic anhydride was dissolved in 66 ml of acetic anhydride; the solution was cooled to 50°C, and 5.6 ml (44 mole) of acetoacetic ester and 18.3 ml (130 mmole) of triethylamine were added. The solution was left at room temperature for one day and was then filtered, and the filtrate was poured into a mixture of 180 g of ice and 85 ml of concentrated HCl. The precipitate of 2-ethoxycarbonyl-5-nitroindan-1,3-dione was filtered off, washed with water, and dried. The yield of product was 8 g, and it was boiled in 80 ml of pyridine with 5 g (76 mmole) of malononitrile for 1 h. Then the solution was evaporated to a volume of 40 ml and cooled, after which 200 ml of benzene was added and the mixture was left for 1 h. The pyridinium salt of 1,3-bis(dicyanomethylene)-2-ethoxycarbonyl-5-nitroindan that deposited was filtered off and washed with benzene. Yield 8.1 g (42.8% calculated on the 4-nitrophthalic anhydride). For purification, the salt was reprecipitated from pyridine with benzene; mp 213-215°C. Found: C 62.9; H 2.9; N 18.8%. $C_{18}H_9N_5O_4 \cdot C_5H_5N$. Calculated: C 63.0; H 3.2; N 19.2%.

1-Bis(dicyanomethyl)-5-nitroindan (Ic) was obtained in the form of a pyridinium salt. A suspension of 2 g (4.6 mmole) of the pyridinium salt of 1,3-bis(dicyanomethylene)-2-ethoxycarbonyl-5-nitroindan in 5 ml of boiling ethanol was treated with 20 ml of concentrated HCl and stirred at 100°C for 30 min. Then the solution was cooled and filtered, the precipitate was dried on the filter and was dissolved in 10 ml (0.12 mole) of pyridine, and this solution was filtered and stirred while 100 ml of benzene was added. The precipitate of the pyridinium salt of 1,3-bis(dicyanomethylene)-5-nitroindan was filtered off, washed with benzene, and dried. Yield 1.38 g (82.6%); mp 153-155°C (from methanol—benzene (1:1)). UV spectrum, λ_{max}, nm (ε): 606 (9150); 652 (8450). IR spectrum, cm^{-1}: 3213 (N—H); 2194 (C≡N); 1338 (NO_2). Found: C 65.3; H 3.0; N 23.3%. $C_{15}H_5N_5O_2 \cdot C_5H_5N$. Calculated: C 65.6; H 2.8; N 22.9%.

1,3-Bis(dicyanomethylene)-2-(pyran-4-ylidene)indan (IIa). A mixture of 0.66 g (2.5 mmole) of the indan (Ia), 0.31 g (3.7 mmole) of γ-pyrone, and 5 ml (48.9 mmole) of acetic anhydride was boiled for 3 min and was then cooled. The precipitate was filtered off, washed with a small amount of acetic anhydride, and dried on the filter. Yield 0.76 g.

1,3-Bis(dicyanomethylene)-2-(2,6-dimethylpyran-4-ylidene)indan (IIb) was obtained similarly from 1.46 g (6 mmole) of 1,3-bis(dicyanomethylene)indan and 1 g (9 mmole) of 2,6-dimethyl-γ-pyrone in 10 ml of acetic anhydride. Yield 1.3 g. The mother liquor was diluted with water and was stirred for 2 h at room temperature, after which the precipitate was filtered off. This gave an additional 0.72 g of compound (IIb).

1,3-Bis(dicyanomethylene)-2-(2,6-dimethylpyran-4-ylidene)-5-nitroindan (IIc). The pyridinium salt of 1,3-bis(dicyanomethylene)-5-nitroindan (1 g; 2.7 mmole) was suspended in 5 ml of boiling ethanol and then the solution was cooled and, with continuous stirring, 20 ml of dilute (1:1) HCl was added to it. The mixture was cooled, and the precipitate was separated off and dried. This gave 0.71 g (90%) of the nitroindan (Ic). Compound (IIc) was obtained in a similar manner to the indan (IIa) from 0.7 g (2.4 mmole) of the nitroindan (Ic) and 0.45 g (3.6 mmole) of 2,6-dimethyl-γ-pyrone in 5 ml (48.9 mmole) of acetic anhydride. Yield 0.88 g.

The 1,3-Bis(dicyanomethylene)-2-(1-R^2-dihydropyridin-4-ylidene)indans (IIIa-g). A. A solution of 0.35 g (1 mmole) of compound (IIb) in 10 ml of acetonitrile and 1 ml of a 25% aqueous solution of an amine at 20°C was stirred for 1 h and was then poured into 100 ml of water and the precipitate was separated off and dried.

B. After 1 mmole of compound (IIa), (IIb), or (IIc) had been boiled in 3 ml (33 mmole) of aniline for 5 min, the mixture was cooled and was poured into 50 ml of 5% HCl, after which the precipitate was separated off, washed with water, and dried.

C. A solution containing 1 mmole of compound (IIb) or (IIc) in a 20-fold excess of the appropriate amine was stirred at 180°C for 5 min and was then cooled and chromatographed on silica gel (benzene—acetone (4:1)).

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